When Smoothening Makes It Rough: Unhindered Step-Edge Diffusion and the Meandering Instability on Metal Surfaces

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The precise microscopic origin of step meandering is not known in many real situations. A detailed study of this instability has been made for copper, and none of the microscopic mechanisms proposed until now is able to describe all of the observed characteristic features of the instability, in particular, its dependence on the crystallographic orientations of steps. We propose a novel scenario, and using kinetic Monte Carlo simulations we show that essentially all features of step meandering of copper can be explained, if atoms diffuse along step edges and freely turn around the kinks they encounter along the ledge. Then, in a rather counterintuitive way, step meandering appears due to the very mechanism—step-edge diffusion—that may be expected to oppose it.

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Introduction. The step meandering instability.—Spontaneous patterning is a well known phenomenon in systems far from equilibrium [1,2]. Patterns may appear because of an external driving force, such as the ripples on the surface [3] of sand blown by the wind or the ripples at the surface of a silicon wafer heated by a direct current, or because of intrinsic effects, such as the ripples, ridges, and channels formed on vicinal crystal surfaces during deposition of atoms by a beam [4]. Spontaneous patterning of crystal surfaces appears to be one of the most promising ways of structuring a whole substrate at nanometric length scales. It is therefore of capital importance to gain a detailed understanding of the microscopic, atomistic mechanisms leading to spontaneous surface patterning. The present Letter addresses the self-structuring of vicinal crystal surfaces growing by step-flow. We show here that step-edge diffusion of atoms, instead of smoothing the step shape, as intuition suggests, induces a morphological instability that leads to a macroscopic patterning of the surface.

Growth instabilities of vicinal surfaces.—A vicinal crystal surface is made of atomic planes or terraces separated by steps of atomic height. The steps break the surface symmetry and may induce growth instability when the surface is brought out of equilibrium, e.g., during atom deposition and growth. Step-flow [5] is the growth mode in which adatoms are deposited by a beam on the surface and diffuse directly to the steps without nucleating islands on terraces. In several systems, either metals like Cu [4] or semiconductors like Si [6] and GaAs [7], it is observed that growth by step-flow proceeds in an unstable way. The steps that are straight and equidistant on average before starting the growth, upon deposition of atoms onto the surface do not keep their straight shape, but start wandering over the terraces. This growth instability is the precursor of the self-organization at long times of the step train into a structure made of ripples running along the direction of the surface slope [4,6,7].

Step meandering: The theoretical framework.—Bales and Zangwill (BZ) [8] assumed that diffusing adatoms experience an additional energy barrier, known as the (2D) Ehrlich-Schwoebel (ES) barrier [9–11], when jumping down a step. BZ showed that the existence of an ES barrier implies that the straight step shape is unstable during step-flow growth, and that the steps meander in phase. The competition between the ES barrier and smoothening effects (atom detachment from the step-edge, or step-edge diffusion) yields a pattern of meanders with a typical period λ_{BZ} scaling as the inverse square root of the deposition rate F, $\lambda_{\mathrm{BZ}} \sim F^{-1/2}$. The step shape instability due to an ES barrier is called here the BZ meandering. More recently, Ramana Murty and Cooper [12] have observed in kinetic Monte Carlo (KMC) simulations and Pierre-Louis and co-workers [13] have shown analytically that atom diffusion along step edges may also be responsible for step meandering, if a 1D ES barrier for turning around corners along the ledge is assumed. Indeed, for an atom diffusing along the step edge, turning around a corner is the analog of going over a step, and a (1D) ES barrier may be expected in that case also (Fig. 1). Such a barrier at kinks that is assumed to hinder corner rounding gives rise to what is called a kink ES effect, or KESE. We call the barrier E_{KESE}. The resulting step meandering is often called the KESE-induced meandering. The typical period of the meander pattern is set by the nucleation of 1D "islands" along the step edge [13]. This yields $\lambda_{\mathrm{KESE}} \sim F^{-1/4}$. The simultaneous presence and the competition of a 2D ES barrier and of 1D KESE has been investigated by Kallunki and co-workers [14], who found that the KESE meandering always overcomes the BZ meandering, unless the 2D ES barrier is very high. A very interesting feature of the KESE-induced meandering is its dependence on the crystallographic orientation of the steps [13]. Meandering is expected to occur for compact, closed-packed steps, but not for open ones. This expectation has been confirmed by

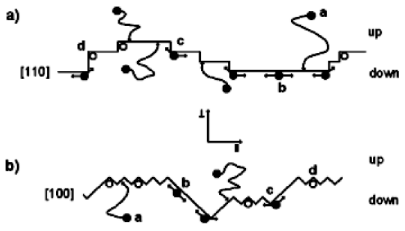

FIG. 1. Schematics of the atomistic moves in the USED model for closed-packed (top) and open (bottom) steps. Atoms diffuse on terraces (a) and along the step edge (b). Detachment from steps is forbidden. Corner rounding (c) occurs at the same rate as in (b). Atoms bound to kinks (d) are immobile.

KMC simulations of a ''realistic'' model for copper [15]. Indeed, a strong KESE is expected on copper surfaces, where E_{KESE} has been estimated to be $E_{\mathrm{KESE}} \approx 0.45$ eV, to be compared to a surface diffusion barrier $E_d \approx 0.4$ eV. KMC simulations based on such realistic parameters predict that compact steps should meander, but open steps should not. As we recall in the following, this is at variance with experiments.

The experiments.—The question naturally arises whether real systems fit in any of the theoretical expectations. The most detailed study of a meandering instability has been performed by Ernst and co-workers on vicinals of Cu(100) [4,16]. The main results of this study are the following: (i) Both compact ([110]) and open ([100]) steps undergo a meandering instability, with very similar quantitative features; in particular, (ii) The wavelength of the pattern varies as $\lambda_{\mathrm{Cu}} \sim F^{-0.16-0.2}$ in both cases. Result (i) does not fit in with the KESE scenario. Result (ii) does not fit in with the BZ scenario. We provide a novel scenario that agrees with experimental observations (i) and (ii). Surprisingly, the scenario we propose requires the absence of any ES barriers. Assuming *symmetric* attachment at steps, and *unhindered* diffusion of atoms along step edges, we prove with KMC simulations that step meandering appears, in much the same way as observed on copper.

Unhindered step-edge diffusion.—Preferential atomic diffusion along step edges is an essential ingredient of the description of step-flow growth of metal surfaces vicinal of the {100} orientations. The atoms attached to a compact [110] step edge are able to diffuse along the ledge without detachment even at very low temperatures. Because of the smoothing effect of step-edge diffusion, atomic islands on (100) terraces of metals are never fractal. However, during step-flow growth step-edge diffusion plays a different role. It makes the step smooth on short length scales, but it creates meandering on a larger scale. We present in this Letter strong evidence that step meandering on copper is a consequence of *essentially unhindered step-edge diffusion,* i.e., diffusion of atoms along the ledge with a vanishing or an extremely small KESE.

The physical origin of the destabilizing effect of step-edge diffusion is rather subtle. Consider, as sketched in Fig. 1(a), a nonstraight, compact step. Once attached to the step edge, atoms diffuse towards kinks. If atoms can easily ''turn around corners,'' that is, if a vanishingly small KES barrier is present, the atoms stick to kinks at the same rate from the front and from behind. The average diffusion current has by symmetry a vanishing component parallel to the average step direction, but sticking to kinks from behind, that is by turning around a corner, yields a nonvanishing, uphill component perpendicular to the average step direction (Fig. 1). An uphill current is the signature of a linear instability with respect to step meandering. We conclude that compact steps are unstable with respect to meandering if unhindered step-edge diffusion is active. Consider now Fig. 1(b). Along an open step edge, kinks are separated by portions of compact steps, along which atoms diffuse. In the absence of KESE, diffusion to kinks along these compact parts, which form an angle of 45° with respect to the step direction, yields a net nonvanishing uphill current that leads to the instability. When KESE is active, it tends to equalize the distance between kinks [10,11], and thus to make the step straight.

In conclusion, we claim that step-flow with unhindered step-edge atomic diffusion is able to lead to a step meandering instability, independently of the orientation of the steps. To check the expectation, we have performed KMC simulations of a simple model of step-flow growth with unhindered step-edge diffusion, which we call the USED model in the following.

Unhindered step-edge diffusion and step meandering.—A schematic representation of the key microscopic processes defining the USED model is shown in Fig. 1. In short, the USED model works as follows: atoms diffuse on the terraces between steps with a diffusion barrier coefficient $D = D_0 \exp(-E_d/k_B T)$, where E_d is the diffusion barrier. When adatoms stick to a step, they do not detach any more. We call them *stepatoms.* The stepatoms diffuse along the straight step edge with a diffusion coefficient $D_{\mathrm{step}} = D_0 \exp(-E_{\mathrm{step}}/k_B T)$, where the barrier $E_{\mathrm{step}} = E_d + E_a$. E_a may be either positive or negative. If a stepatom binds to a kink, it stops moving. If a diffusing stepatom comes to a corner, it can cross it by making a next-nearest neighbor hop, with the same diffusion barrier E_{step} as for nearest-neighbor hops along the ledge. The same prefactor D_0 is assumed for diffusion on terraces and along step edges, for simplicity. The model clearly violates detailed balance, and is therefore meaningful only at low enough temperature. The same model has been investigated by Ramana Murty and Cooper, who have shown that it possesses, indeed, an uphill current and that layer-by-layer growth is superseded by mounded growth on singular, high-symmetry surfaces. We simulate vicinal surfaces on a SC lattice of size 400×400 lattice spacings for compact [100] steps, and 840×841 for open [110] steps. We have chosen $E_d = 0.4$ eV, a value close to that expected for copper, the additional edge diffusion energy

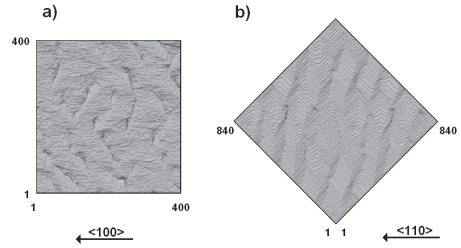

FIG. 2. Snapshots of the simulated surfaces for compact (a) and open (b) steps with $E_{\mathrm{KESE}} = 0$, showing the surface instability after depositing 500 MLs. Deposition parameters are $T = 340$ K, $F = 10^{-3}$ ML/s.

$E_a = 0.12$ eV, and the prefactor $D_0 = 10^{11}$ s^{-1}. The resulting energy barrier for step-edge diffusion, $E_{\mathrm{step}} = 0.52$ eV, is not far from the value experimentally deduced for straight compact steps on copper. We have then varied the terrace width d between 5 and 20 lattice spacings, the deposition rate between 10^{-4} and 1 monolayer/s (ML/s), and the temperature between 300 and 340 K. A sample of the results of the simulations is shown in Fig. 2(a) for compact steps ($d = 5$) and in Fig. 2(b) for open steps ($d = 15.5$). The temperature and deposition rate are $T = 340$ K and $F = 10^{-3}$ ML/s, respectively, and 500 MLs have been deposited. At this deposition rate and temperature, both compact and open steps are clearly unstable, even though only open steps [Fig. 2(b)] self-organize at late times in fingerlike structures, as observed experimentally. Moreover, open steps have a zigzag shape that resembles strongly that of the steps on a Cu(0 1 12) surface. The instability of the vicinal surface with compact steps is enhanced for higher deposition rates, leading to a more moundlike structure. The unstable behavior is less pronounced the larger the terraces. The instability of open steps survives very tiny KES barriers [$E_{\mathrm{KESE}} = E_d/40$ in Fig. 3(a)], but it disappears when E_{KESE} becomes of the order of a tenth of E_d [Fig. 3(b)]. Thus, the USED model clearly shows that in the absence of any ES barrier, or at most for very small barriers, both types of steps exhibit a meandering instability, as we claimed. This is the main result of our work: unhindered step-edge diffusion does not smoothen a step, but makes it unstable, irrespective of the

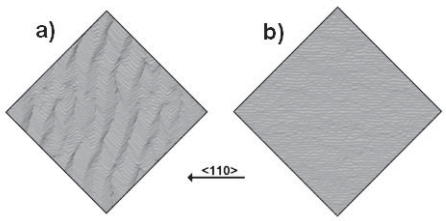

FIG. 3. Snapshots of the simulated surfaces with open steps, for the same parameters as in Fig. 2. The instability is well pronounced when $E_{\mathrm{KESE}} = 0.01$ eV (a), but it disappears altogether for $E_{\mathrm{KESE}} = 0.04$ eV (b).

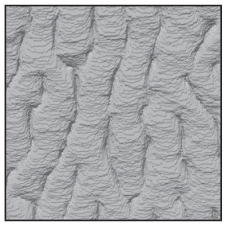

FIG. 4. Snapshot of the simulated surface with compact steps, for the same parameters as in Figs. 2 and 3, and $E_{\mathrm{KESE}} = 0.01$ eV. Self-organization in fingerlike structures is clearly observed.

crystallographic orientation of the step. ES barriers are not needed for the appearance of a meandering instability. As expected, a large kink rounding barrier enhances the instability for compact steps, but kills it for open steps.

A detailed understanding of the step morphology would require a continuum description of the evolution of the instability. We can try to guess the main terms that should appear in a continuum equation for the step evolution, on the basis of phenomenological arguments. For both compact and open steps, the instability appears only if the local step slope is nonvanishing. At first order, we can guess that the nonequilibrium current will be proportional to the local step slope itself. As is known from the work of Politi and Villain [2], nucleation noise and diffusion noise yield smoothing currents of Mullins-like form [17], i.e., proportional to the Laplacian of the local interface slope. Overall, we can conjecture that the step shape evolution will be described by a linear equation of the form $\partial h/\partial t = -\nu\nabla^2 h + K\nabla^4 h$, whose first term on the right side comes from the uphill current, and is responsible for unstable growth ($\nu > 0$), while the second is a smoothing contribution from random nucleation and/or diffusion. Krug and Rost [18] have discussed the scaling behavior of a linear, unstable equation of this form. They found that the interface width has an unusual scaling behavior, with an exponential asymptotic increase at long times.

To check the preceding guess, we have computed the height difference correlation function $G(x, t) = \langle [z(x, t) - z(0, t)]^2 \rangle$ along the direction parallel to the steps, x. The

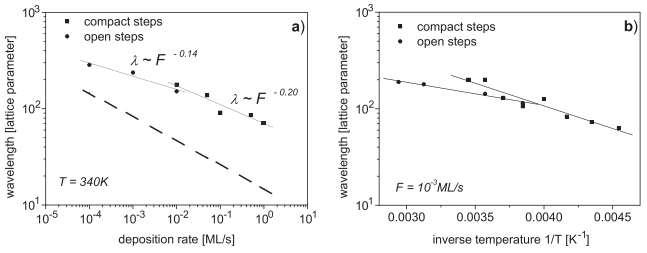

FIG. 5. Meander wavelength λ as a function of the deposition rate F (a) and the temperature dependence of the meandering wavelength (b), for compact (squares) and open (circles) steps, for $E_{\mathrm{KESE}} = 0$. Both lengths are in units of the square lattice spacing. Fixed parameter values are as in the previous figures.

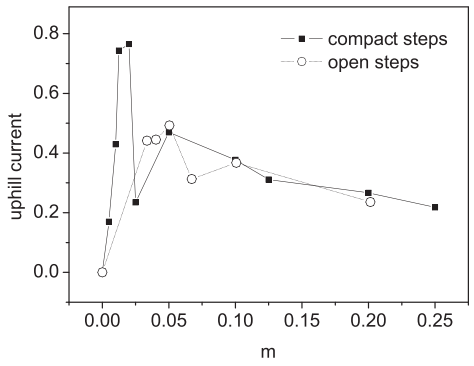

FIG. 6. Uphill diffusion current as a function of the surface slope $m = d^{-1}$ for compact (squares) and open (circles) steps. The uphill current was calculated up to total coverage $\theta = 0.1$ ML at 300 K for $E_{\mathrm{KESE}} = 0$.

definition implies averaging along y, perpendicular to the steps. The computed correlation function (not shown) exhibits, indeed, a scaling form $G(x, t) = t^{2\beta} \exp(2t/\tau) \times g(x/\xi)$, which appears to corroborate our guess. A more detailed study of correlations in the USED model will be published elsewhere.

The USED model and copper.—Comparison of our simulated surfaces with published pictures of open copper steps clearly shows that the USED model captures many fine details of the actual morphologies. Adding a very small KES barrier [Fig. 3(a)], the morphology is even more resemblant. The same $E_{\mathrm{KESE}} = 0.01$ eV makes the simulated compact steps look exactly like Cu(1 1 17) steps (Fig. 4). The level of description of unstable copper surfaces with the USED model is not only qualitative: we have investigated the dependence of the meander period λ with a varying deposition rate F. Experimentally, a power law of the form $\lambda \sim F^{\alpha}$ is found. As shown in Fig. 5(a), our results for the power α are in good quantitative agreement with experiments. The absolute values of the simulated wavelengths exceeds the experimental ones by a factor of 3 at most, but no effort has been made in our simulations of best fitting the experimental results. Figure 5(b) shows the behaviors of the period of the pattern as the growth temperature is varied. Note that the precise mechanism that fixes the unstable wavelength λ in the USED model is still unknown. Nucleation along the step ledge is definitely ruled out, as shown in Fig. 5. Work is in progress on this point and will be reported elsewhere.

The explanation of the origin of the meandering instability in the USED scenario is the same as for the KESE—an uphill current is induced, which makes the surface unstable towards meandering. We computed the uphill current for both open and closed-packed steps as the authors in Ref. [11] did. The results show clearly that even in the absence of any KESE, the uphill current is still there, and so the instability, as observed (Fig. 6).

The main objection to the adequacy of the USED model for copper is the rather large value of the KES barrier along Cu step edges indirectly estimated from measurements of step fluctuations [4], and previously used in studies of the meandering instability of copper [15]. We stress again that a large KESE is at variance with the observed instability of open steps. Step fluctuations in the framework of the USED model will be investigated.

Conclusion.—The USED model provides a novel scenario for understanding the onset and the development of the self-organized meandering on copper vicinal surfaces, for both open and compact steps. It is at present the only model that is able to describe both qualitatively and quantitatively the main experimental features observed on copper surfaces. The key mechanism responsible for the instability is identified with unhindered step-edge diffusion, even though this is very surprising at first sight, because diffusion along the step edge is just the physical process that is expected to make the steps smoother. The simulations show that KES barriers may play only a minor role in the instability, and we estimate that their actual value for copper must be extremely small (of the order of 10 meV).

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