Dynamics of lines and grooves on vicinal crystals: Morphological instability and surface patterning

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The dynamics of lines and grooves made of two steps of opposite sign on vicinal surface has been theoretically investigated. A linear stability analysis has been performed and the development of in-phase and antiphase fluctuations of the structure profiles has been characterized. It has been found that during the growth regime, lines may undergo morphological instability, which may result in the formation of a pinched shape. In the case of grooves, pinchedlike morphology may also appear in the early beginning of the evaporation regime. The possibility of fabrication of nanostructures of various shapes has been finally discussed taking advantage of these morphological evolutions.

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The dynamics of atomic steps on vicinal surfaces has been intensively studied since it has been proven to be a key factor in the manufacturing of low-dimensional structures. It has been, for example, observed that semiconductor thin film growth on substrates by molecular beam epitaxy requires a step flow growth regime to achieve flat surfaces.[1] Another timely example is the fabrication using pulsed laser deposition techniques of $SrRuO_3$ flat thin films on $SrTiO_3$ substrates where step flow growth also plays a key role.[2] This regime of great technological interest may be altered since step bunching,[3–6] step meandering,[7,8] and step pairing[9] have been observed to appear for trains of identical steps during the crystal growth processes, thus modifying the final morphology of the micro- and nanostructures. Antibanding instability resulting from step crossing due to surface electromigration has been also observed on Si(111) leading to the formation of bands of steps of opposite sign.[10] Concerning surface patterning, the study of dot or line formation on Cu$\{110\}-(2\times 1)$O surfaces has shown, for example, that anisotropic islands may rearrange themselves into regularly spaced strips.[11] Likewise, direct fabrication of nanowires with lateral sizes smaller than 10 nm has been realized on the surface of thin carbon films[12] using electron-beam-induced deposition techniques. In this Brief Report, the dynamics of isolated lines and grooves made of two steps of opposite sign has been first investigated using the continuum description of steps. The patterning of vicinal surfaces has been then discussed taking advantage of the line and groove morphological evolutions.

A one-dimensional line consisting of two steps of opposite sign [see Fig. 1(a) for axes] and initially separated by a distance $2h_0$ has been first considered. It is assumed that the interaction between both steps occurs through the diffusion field only, other step-step interactions such as mechanical and/or entropic interactions, for example, being neglected. In the framework of the classical Burton–Cabrera–Frank model,[13] the concentration of adatoms, C_i, on the ith terrace (with $i=1,2,3$) satisfies, in the quasistatic limit, the following equation:

$$\nabla^2 C_i - \frac{C_i}{x_s^2} + F\frac{\tau}{x_s^2} = 0. \tag{1}$$

The incoming flux is labeled F, and the diffusion length x_s is defined by $x_s=\sqrt{D\tau}$, with D a diffusion constant and τ the evaporation time. The velocity of steps 1 and 2 initially located at $x=+h_0$ and $x=-h_0$, respectively, is determined from mass conservation. For example, step 1 normal velocity writes

$$v_1 = \Omega D \mathbf{n}_1 \cdot (\nabla C_1|_+ - \nabla C_2|_-), \tag{2}$$

where $+$ and $-$ refer to the lower and upper terraces, respectively, Ω is the atomic area of the crystal, and $\mathbf{n}_1$ is the normal to step 1 pointing to the lower terrace. The complete setting of the problem requires to consider at each step two kinetic boundary conditions. For step 1, these conditions read

$$\pm D\mathbf{n}_1 \cdot \nabla C_{i_\pm}|_\pm = k_\pm (C_{i_\pm} - C^1_{eq}), \tag{3}$$

with $i_+=1$, $i_-=2$, and $k_\pm$ the attachment-detachment kinetic coefficients.[14] The equilibrium concentration C^1_{eq} at step 1 is derived from the Gibbs–Thomson relation as follows: $C^1_{eq} = C^0_{eq}(1+\Gamma\kappa_1)$, where C^0_{eq} is the equilibrium concentration at the straight step and κ_1 the local curvature taken to be positive for a convex profile. The constant Γ is defined by $\Gamma = \Omega\gamma/k_B T$, with γ the step stiffness, k_B the Boltzmann constant, and T the temperature. A set of equivalent equations to Eqs. (2) and (3) is also considered for step 2. A linear stability analysis has been first performed in the growth regime, i.e., when the flux variation with respect to equilibrium $\Delta F = F - c^0_{eq}/\tau$ is positive. To do so, the position of step i, $\zeta_i(y,t)$ with $i=1,2$, is described in Fourier space. Taking a single Fourier mode, one can write $\zeta_1(y,t)=h(t)+e(t,\varphi)\exp(+iky+i\varphi)+\text{c.c.}$ for step 1 and $\zeta_2(y,t)=-h(t)+e(t,\varphi)\exp(+iky$

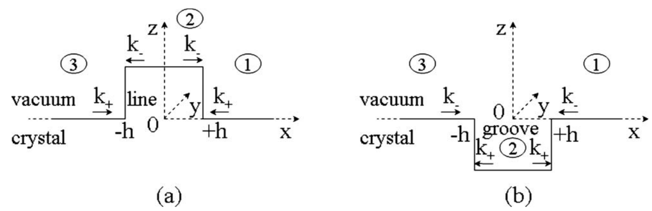

FIG. 1. (a) An initially straight line on a vicinal surface made of two steps of opposite sign separated by an unperturbed distance $2h(t)$. (b) A groove of unperturbed width $2h(t)$ composed of two steps of opposite sign.

$-i\varphi)+\text{c.c.}$ for step 2, where t is the time, $2h(t)$ the linewidth in the straight configuration, e the perturbation amplitude, k the wave number along the step direction, and φ the phase factor. For symmetry reason, only in-phase and antiphase fluctuations are considered in the linear regime; one thus takes $\varphi=0,\ \pi/2$. The general solution of Eq. (1) is $c_i(x,y)=C_i(x,y)-\tau F=c_i^{(0)}(x)+c_i^{(1)}(x,y)$, with $c_i^{(0)}(x)=A_i^{(0)}\exp(+x/x_s)+B_i^{(0)}\exp(-x/x_s)$ the concentration on terrace i in the straight configuration and

$$c_i^{(1)}(x,y)=\exp(+iky)\{A_i^{(1)}\cosh(\tilde{\lambda}x/x_s)+B_i^{(1)}\sinh(\tilde{\lambda}x/x_s)\}+\text{c.c.}$$

the first order correction in perturbation amplitude e to concentration on terrace i with $\tilde{\lambda}=\sqrt{1+x_s^2k^2}$ and $i=1,2,3$. For both configurations $(\varphi=0,\pi/2)$, the constants $A_i^{(0)},B_i^{(0)},A_i^{(1)},B_i^{(1)}$ have been determined by expanding Eqs. (1) and (3) up to order 1 in perturbation amplitude e and matching zero and first order terms, respectively. The heavy but straightforward calculation of these constants is not detailed in this Brief Report. Using Eq. (2), the time evolution equations of $\tilde{h}$ and $\tilde{e}$ have been finally found to be

$$\frac{d\tilde{h}(\tilde{t})}{d\tilde{t}}=\frac{1}{1+\tilde{d}_+}+\frac{\sinh[\tilde{h}(\tilde{t})]}{\cosh[\tilde{h}(\tilde{t})]+\tilde{d}_-\sinh[\tilde{h}(\tilde{t})]}, \tag{4}$$

$$\frac{1}{\tilde{e}(\tilde{t},\varphi)}\frac{d\tilde{e}(\tilde{t},\varphi)}{d\tilde{t}}=\frac{1-\xi\tilde{k}^2}{\frac{1}{\tilde{\lambda}}+\tilde{d}_+}-\frac{1}{1+\tilde{d}_+}+\frac{\cosh[\tilde{h}(\tilde{t})]}{\cosh[\tilde{h}(\tilde{t})]+\tilde{d}_-\sinh[\tilde{h}(\tilde{t})]}-\frac{\tilde{\lambda}\tilde{d}_-}{2}\frac{\left(1+\frac{\xi}{\tilde{d}_-}\tilde{k}^2\right)\cosh[\tilde{h}(\tilde{t})]+\left(\frac{1}{\tilde{d}_-}+\xi\tilde{k}^2\right)\sinh[\tilde{h}(\tilde{t})]}{\cosh[\tilde{h}(\tilde{t})]+\tilde{d}_-\sinh[\tilde{h}(\tilde{t})]}$$
$$\times\left\{\frac{(1+\cos 2\varphi)\cosh[\tilde{\lambda}\tilde{h}(\tilde{t})]}{\tilde{\lambda}\tilde{d}_-\cosh[\tilde{\lambda}\tilde{h}(\tilde{t})]+\sinh[\tilde{\lambda}\tilde{h}(\tilde{t})]}+\frac{(1-\cos 2\varphi)\sinh[\tilde{\lambda}\tilde{h}(\tilde{t})]}{\cosh[\tilde{\lambda}\tilde{h}(\tilde{t})]+\tilde{\lambda}\tilde{d}_-\sinh[\tilde{\lambda}\tilde{h}(\tilde{t})]}\right\}, \tag{5}$$

where $\varphi=0,\ \pi/2$, $\tilde{t}$ is the dimensionless time defined as $\tilde{t}=t/t_0$ with $t_0=x_s^2/(\Omega D\tau\Delta F)$, $\tilde{e}(\tilde{t},\varphi)=e(\tilde{t},\varphi)/e_0(0,\varphi)$, and $\tilde{h}(\tilde{t})=h(\tilde{t})/x_s$. The other nondimensional parameters are defined as follows: $\tilde{d}_+=D/(x_sk_+)$, $\tilde{d}_-=D/(x_sk_-)$, $\xi=c_{eq}^0\Gamma/(\tau\Delta F x_s)$, and $\tilde{k}=x_sk$. It can be first observed that Eqs. (4) and (5) can be analytically integrated when $h/x_s\rightarrow+\infty$. In that case, both Eqs. (4) and (5) are no longer h dependent. The steps evolve separately and one gets the classical results obtained by Bales and Zangwill[8] and others[15] for an isolated step. In the general case of interacting steps, using Eq. (5) and assuming that $e(0,0)=e(0,\pi/2)=e_0$, the amplitude ratio for antiphase and in-phase perturbations can be written as

$$\frac{\tilde{e}\left(\tilde{t},\frac{\pi}{2}\right)}{\tilde{e}(\tilde{t},0)}=\exp\left(\int_0^{\tilde{t}}f\{\tilde{h}(t')\}dt'\right), \tag{6}$$

with f the functional defined by

$$f\{\tilde{h}(\tilde{t})\}=\frac{2\left(1+\xi\frac{\tilde{k}^2}{\tilde{d}_-}\right)\cosh[\tilde{h}(\tilde{t})]+2\left(\frac{1}{\tilde{d}_-}+\xi\tilde{k}^2\right)\sinh[\tilde{h}(\tilde{t})]}{\{\cosh[\tilde{h}(\tilde{t})]+\tilde{d}_-\sinh[\tilde{h}(\tilde{t})]\}\left\{2\cosh[2\tilde{\lambda}\tilde{h}(\tilde{t})]+\left(\frac{1}{\tilde{\lambda}\tilde{d}_-}+\tilde{d}_-\tilde{\lambda}\right)\sinh[2\tilde{\lambda}\tilde{h}(\tilde{t})]\right\}}. \tag{7}$$

It can be deduced from Eqs. (6) and (7) that since $f\{\tilde{h}(\tilde{t})\}$ is always positive at any time $\tilde{t}\geqslant 0$ and for any set of $\tilde{d}_+,\tilde{d}_-,\xi$ parameters and $\tilde{k}$ values, the antiphase configuration would grow faster than the in-phase one provided that during the growth regime, the development of each morphological change is favorable, that is, $\tilde{e}(\tilde{t},\pi/2)$ and $\tilde{e}(\tilde{t},0)$ are increasing functions with respect to time. To determine in which conditions the development of these fluctuations is favorable or not, the time evolution Eqs. (4) and (5) of $\tilde{h}$ and $\tilde{e}$ have

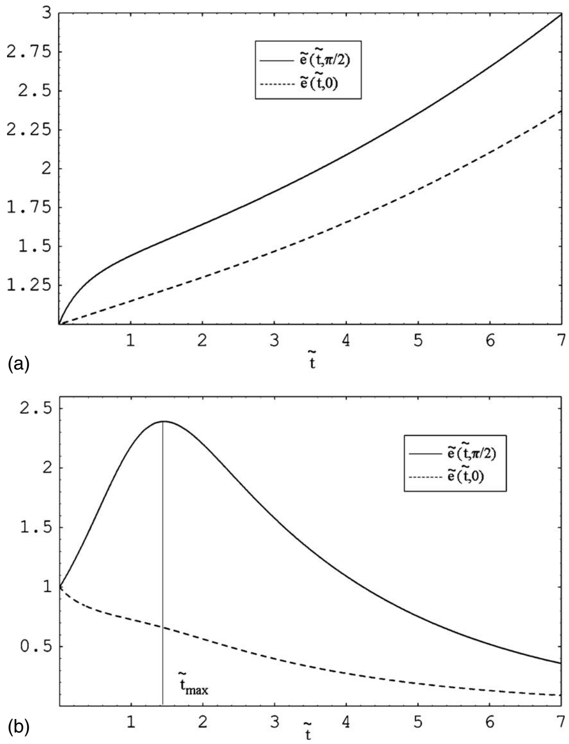

FIG. 2. $\tilde{e}(\tilde{t},\varphi)$ versus $\tilde{t}$ for $\tilde{k}=0.9$, $\tilde{h}_0=0.01$, $\tilde{d}_+=0.1$, $\tilde{d}_-=2.0$, $\xi=0.1$, and $\varphi=0$, $\pi/2$. (a) Case of a growing line: $\Delta F>0$. (b) Case of a widening groove: $\Delta F<0$.

been numerically integrated using standard techniques implemented in a calculus software[17] and the amplitude variations of in-phase and antiphase fluctuations have been then plotted in Fig. 2(a) as a function of time $\tilde{t}$ for $\tilde{k}=0.9$, $\tilde{h}(0)=\tilde{h}_0=0.01$, $\tilde{d}_+=0.1$, $\tilde{d}_-=2.0$, $\xi=0.1$. It is found that in the beginning of the growth regime of an initially $2h_0$ thick line with $h_0 \ll x_s$ such that both steps may interact, there exists a set of $\tilde{d}_+$, $\tilde{d}_-$, and ξ parameters and $\tilde{k}$ values for which the development of the fluctuations is favorable. It is assumed that the phase shift effect generated during the first stage of the growth regime of an initially thin line would last as the line is widening and the steps are separately evolving.[8,15] This result is different from that already obtained for trains of identical steps where the in-phase mode has been found to develop during the growth regime.[15,16] At this point, it thus appears from the linear stability analysis that even if the growth rate difference between both configurations may be small [see Fig. 2(a)], a pinchedlike morphology is suspected to preferentially emerge and develop during the growth regime rather than a pure serpentinelike shape provided that diffusion and attachment-detachment kinetics ($k_- \neq 0$) are considered on the surface of the line.[14] This result should be confirmed by nonlinear analysis where interactions between the different harmonics of the line profile development are considered. On the other hand, during the evaporation regime, i.e., $\Delta F<0$, a numerical study of $1/\tilde{e}(\tilde{t},\varphi)d\tilde{e}(\tilde{t},\varphi)/d\tilde{t}$ variations as a function of $\tilde{k}$ and $\tilde{h}$ has shown that for $d_+=0.1$, $d_-=2.0$, and $\xi=0.1$, $1/\tilde{e}(\tilde{t},\varphi)d\tilde{e}(\tilde{t},\varphi)/d\tilde{t}$ is always negative, the shrinking line thus being stable with respect to shape perturbation.

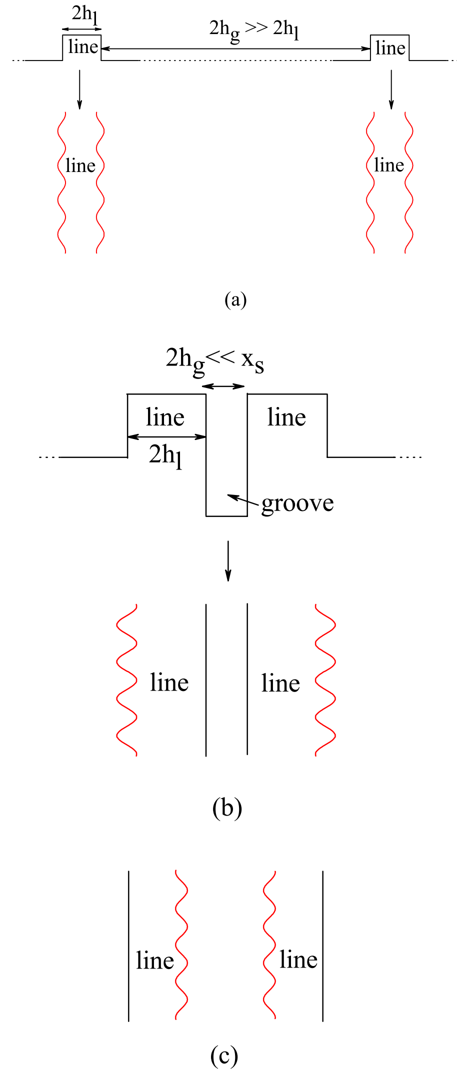

FIG. 3. (Color online) (a) Two isolated widening lines during the growth regime ($\Delta F>0$). (b) Two widening lines interacting through a shrinking groove during the growth regime. (c) Two shrinking lines interacting through a widening groove during the evaporation regime $\Delta F<0$.

The case of a widening isolated groove of initial width $2h_0$ has been also investigated in the evaporation regime [see Fig. 1(b)]. An equivalent procedure to that described in the first part of this Brief Report for a single line has been used and is not detailed. The ratio of perturbation amplitudes $\tilde{e}(\tilde{t},\pi/2)/\tilde{e}(\tilde{t},0)$ has been written in the form displayed in Eq. (6), where the functional equivalent to that given in Eq. (7) has been also found to be always positive as a function of d_+,d_-,ξ parameters and $\tilde{k}$ wave number. Time evolution equations of $\tilde{h}$ and $\tilde{e}$ have been determined and numerically integrated.[17] In Fig. 2(b), $\tilde{e}(\tilde{t},\varphi)$ has been plotted versus time $\tilde{t}$ taking $\tilde{k}=0.9$, $\tilde{h}_0=0.01$, $\tilde{d}_+=0.1$, $\tilde{d}_-=2.0$, and $\xi=0.1$. It is found that during the first stage of the evaporation regime, that is, for $\tilde{t}_{max} \leq 1.4$, which corresponds to a maximum width $\tilde{h}(\tilde{t}_{max}) \approx 2.4$ for groove, antiphase fluctuations may grow with time. During the later stage of the evaporation regime, for $\tilde{t} > \tilde{t}_{\max}$, the groove widens and the interaction between steps weakens until steps separately evolve, each fluctuation thus decreasing with time.[15] It is also observed in Fig. 2(b) that for the values of d_+, d_-, ξ parameters and $\tilde{k}$ wave number used in this Brief Report, the groove is stable with respect to the in-phase mode since $\tilde{e}(\tilde{t},0)$ decreases with time. Finally, it can be pointed out that during the growth regime and when the initial width of the groove is small enough such that both steps may interact, i.e., $\tilde{h}_0 \leqslant 0.1$, it has been numerically found that for the d_+, d_-, and ξ parameters used in this work, $1/\tilde{e}(\tilde{t},\varphi) d\tilde{e}(\tilde{t},\varphi)/d\tilde{t}$ is always negative as a function of $\tilde{k}$ and $\tilde{h}$, the shrinking groove thus being stable with respect to shape perturbation. Finally, it can be emphasized that these kinetic morphological instabilities which have been found to modify the shape of stripes (lines and grooves) should be perturbed when edge diffusion is considered. The competition between terrace and edge diffusions should be investigated as well as step-step interactions for narrow stripes to get a more complete description of the morphological evolution of these isolated structures and to determine, for example, whether or not circular islands may be formed from initially one-dimensional straight lines. Concerning step-step interaction effects, it has been, for example, demonstrated that in the case of trains of identical steps, elasticity leads to coarsening[19] while step-step repulsion has a smoothing effect on the step profile.[7] For striped domains, it has been found that in case of homoepitaxy, two-dimensional dipolar interactions have a stabilizing effect on the shape of the stripes.[20]

However, the present analysis is supposed to be relevant in understanding the evolution of lines and grooves composed of a limited number of pairs of monoatomic steps of opposite sign. Hence, the patterning of vicinal surfaces has been discussed taking advantage of these kinetic morphological instabilities of stripes. In the growth regime, if one considers two parallel thin lines of width $2h_l$ (with $h_l \ll x_s$) and spaced out from a distance $2h_g$ on the flat surface such that $h_g \gg h_l$, each line is supposed to evolve independently. Choosing d_+, d_-, ξ parameters such that both lines are unstable, a possible pattern on the crystal surface may be a distribution of pinched lines [Fig. 3(a)], as already experimentally observed during Pb deposition on Cu(111) surfaces.[18] This pinch-off effect would be specially observed for materials each time the evaporation time τ of adatoms is sufficiently high such that the linewidth is smaller than the diffusion length x_s.

If these two lines are now separated by a thin groove of thickness $2h_g$ with $h_g \ll x_s$, $h_l \ll x_s$, and taking values for d_+, d_-, ξ parameters such that the lines are unstable and the groove stable with respect to shape perturbations, the formation of the symmetric structure (with respect to the median plane perpendicular to the groove) depicted in Fig. 3(b) is expected. In the evaporation regime, considering two lines separated by a thin groove ($h_g \ll x_s$), the lines being stable and the groove unstable with respect to fluctuations, the morphological evolution may lead to the formation of the pattern described in Fig. 3(c) provided that the evaporation process is canceled before the decreasing regime of shape instability takes place. It is also believed that more complex patterns (symmetric or not) would be obtained on different areas of vicinal crystals by monitoring the flux variation on the surface and by alternating areas where isolated lines are present with areas where close lines separated by grooves are lying.

As a conclusion, it is believed that this analysis opens lines of inquiries in studying the morphological evolution of stripes. In particular, it would be relevant to investigate in the nonlinear regime and taking into account step-step interactions and edge diffusion, the long-time evolution of line and groove morphologies and the possibility of formation of dots, circular islands, or more complicated structures.

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