Oscillatory Driving of Crystal Surfaces: a Route to Controlled Pattern Formation

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We show that the oscillatory driving of crystal surfaces can induce pattern formation or smoothening. The driving force can be of quite different origin such as a pulsed laser beam, an electric field, or elasticity. Depending on driving conditions, step bunching and meandering, mound formation, or surface smoothening may be seen in presence of a kinetic asymmetry at the steps or kinks (the Ehrlich-Schwoebel effect). We employ a step model to calculate the induced mass flux along misoriented surfaces, which accounts for surface dynamics and stability. Flux inversion is found when varying the driving frequency. Slope selection and metastability result from the cancellation of the mass flux along special orientations. Kinetic Monte Carlo simulations illustrate these points.

Sculpting surfaces at nanometer scale is of major technological interest. Besides lithography, spontaneous pattern formation during crystal growth has been proposed as a tool to create large scale nanostructured surfaces. In this letter we point out that oscillatory driving appears as an alternative route for pattern formation. We see two basic advantages in this method: first patterning and growth are separated, so that morphology is not a function of the growth process. Second it offers better control of the structure. An in situ and real-time control of the pattern becomes possible, opening a wide range of new applications.

On the side of fundamental physics, oscillatory forcing has been a long standing source of intriguing nonlinear phenomena, such as the inverted pendulum problem [1], and the Faraday instability [2] in fluid mechanics. Oscillatory forcing also induces pattern formation in granular media [3]. Moreover, parametric forcing of an ensemble of oscillators is known to lead, for example, to motion of domain walls [4]. In this letter, we show that oscillatory forcing of crystal surfaces induces macroscopic mass fluxes, leading to pattern formation or smoothening.

In the past 15 years, a large number of studies were devoted to surface roughening during crystal growth. We show that all the instabilities identified during growth (namely mound formation, step meandering, and step bunching) appear under oscillatory driving. The physical origin of this effect can be related to ratchets, in the sense that kinetic anisotropy of steps (Ehrlich-Schwoebel (ES) effect) is used to produce a mass flux along misoriented surfaces, as pointed out by Barabasi et al [5], who showed that AC electromigration should lead to directional smoothening of surfaces.

We first derive the mass flux along a misoriented (vicinal) surface in order to analyse the stability of the surface. The main results are illustrated by Kinetic Monte Carlo simulations. We also briefly mention some experimental situations where our analysis applies, such as pulsed laser-induced mound formation on metal-vacuum surfaces, ultra-sound driven pattern formation on thin films [6], and pattern formation at metal-electrolyte interfaces subject to an oscillating electrochemical potential.

We consider surfaces where adsorption, desorption, and defect creation (such as bulk vacancies) are not allowed. Mass transport then only occurs through surface diffusion. Since the mean height of the surface does not vary with time, we have

\[ \partial_t \langle h \rangle = -\nabla \cdot \langle j \rangle, \]  

where the brackets indicate that we have averaged over the timescales of oscillations, and \( \partial_t \equiv \partial / \partial t \). The mass flux \( \langle j \rangle \) is the key quantity for surface dynamics. Step properties are supposed to be isotropic and direct step interactions via elasticity, or electronic surface states, are neglected. Steps then only interact via mass exchange. The surface flux has two components \( \langle j \rangle = (J) n + (G) s \) where \( n = \nabla h / |\nabla h| \) and \( s = 0 \). From Eq. (1) it follows that a nominal surface is stable (unstable) if \( \langle J \rangle > 0 \) (\( < 0 \)). On a vicinal surface of mean slope \( m_0 \neq 0 \), an uphill flux \( \langle J \rangle > 0 \) also brings a destabilizing contribution to step meandering (i.e. undulations perpendicular to the mean slope direction). Nevertheless, in this case, the \( (G) \) component also intervenes in the stability criterion. A vicinal surface of mean slope \( m = |\nabla h| / a \), where \( a \) is the lattice spacing, is stable with respect to step bunching (i.e. undulation along the mean slope) if \( \partial_m \langle J \rangle > 0 \). Otherwise it is unstable.

As a first qualitative example of a mass flux induced by oscillatory driving, let us consider a vicinal surface for which the temperature oscillates alternatively and abruptly between two values. In the high temperature regime, the equilibrium concentration on terraces is high, and the ES effect is repressed. In the low temperature regime, the equilibrium concentration is low, and the ES effect is strong (i.e. adatoms cannot attach going down-step). We start from a regular vicinal surface (Fig. 1 (a)) in the low temperature regime. We first switch to the
high temperature regime: atoms detach from the steps and go on terraces (Fig. 1 (b)). Steps slightly retract to the left. Switching back to low temperature, adatoms go back to the steps but only attach from ahead (Fig. 1 (c)). The step goes back to its initial position. A net uphill flux results from the last part of the cycle (This could be interpreted as a many-particle "ratchet effect").

Let us first consider a sinusoidal perturbation:

$$J = -\frac{D}{2} (\partial_x c_+ + \partial_x c_-)$$

(6)

To zeroth order in the perturbation the solution of Eq. 2 with the boundary condition 4 is $$c = c^{eq}$$ yielding zero contribution to 〈J〉. The oscillatory nature of the perturbation yields zero first-order contribution. From the second order solution of Eqs. 2-4 we obtain the mean flux:

$$\langle J_2 \rangle = \frac{\Omega}{2} \frac{D_0 c^{eq} m}{1 + m(d_{0+} + d_{0-})} \times \Re e \left[ \frac{\lambda d_{1+}(ch - 1 + \lambda d_{0-} - sh) - d_{1-}(ch - 1 + \lambda d_{0+} - sh)}{(1 + d_{0+}d_{0-} - \lambda^2)sh + \lambda(d_{0-} + d_{0+})ch} \right]$$

(7)

where ch = cosh(λ/m) and sh = sinh(λ/m), and λ² = ω₀/D. The mean flux 〈J₂〉 results from a combination of oscillations of the equilibrium concentration and step kinetics. The frequency and slope dependence of 〈J₂〉 is in general complicated. We do not wish to be exhaustive here, but rather to highlight some important features.

In the following we calculate the mass flux 〈J〉 along a misoriented (vicinal) surface, where steps are regularly spaced (with a distance ℓ = 1/m). Dynamics of a vicinal surface are described by the 1D step model of Burton Cabrera and Frank 8, modified by Schwoebel 9 in order to account for step kinetics. On terraces between steps, the adatom concentration only evolves via diffusion:

$$\partial_t c = D \partial_x^2 c$$

(2)

where D is the adatom diffusion constant and \( \partial_t \) denotes a time derivative. At the steps, mass conservation reads:

$$\frac{\partial_t z}{\Omega} = D \partial_x c_+ - D \partial_x c_-$$

(3)

where Ω is the atomic area, z denotes the step position, and the index + and − indicates the low and high sides of the step respectively. Relation 3 is valid when Ωc⁺ ≪ 1, i.e. when the adatom concentration is much smaller than that of the solid. In order to describe attachment and detachment kinetics at the steps, the incoming diffusion flux is related to departure from equilibrium 3:

$$D \partial_x c_\pm = \pm \nu_\pm (c_\pm - c^{eq})$$

(4)

where ν⁺ are kinetic attachment coefficients. We define the kinetic attachment lengths $$d_\pm = D/\nu_\pm$$, that are small for fast kinetics and large for slow kinetics.

Let us first consider a sinusoidal perturbation:

$$D = D_0 + D_1 \cos(\omega_0 t)$$

$$d_\pm = d_{0\pm} \pm d_{1\pm} \cos(\omega_0 t)$$

$$c^{eq} = c_{0^{eq}} + c_{1^{eq}} \cos(\omega_0 t)$$

(5)

where quantities with index 1 are small and not necessarily positive. The mean flux going through a step is
the perturbation: a steady mass flux along the surface is present. Since we considered a "tracer" model on a frozen surface, an additional condition is necessary to determine this flux, because the amount of matter on terraces is not fixed yet. We choose the coverage at the step site to be \( \theta_0 = 1 \) (i.e. there is always an atom at the edge of a step). We then find the following steady flux:

\[
J_{\text{steady}} = \frac{D_0 \Omega c_{\text{eq}} m}{2(1 + m(d_0 + d_0 - d_0))} \left( \frac{d_{1+}}{a + d_0} - \frac{d_{1-}}{a + d_0} \right)
\]

Taking the limit \( \omega_0 \to \infty \) in Eq. (6) leads to the same result, except that the \( a \)'s in the denominator are absent. This suggests that the step model is valid in the high frequency limit as long as step kinetics are not too fast i.e. \( d_{0 \pm} > a \).

In the low frequency limit \( \omega_0 \to 0 \), the flux vanishes: as \( \langle J \rangle_\infty \sim \omega_0^2 \). In this limit, a wide variety of slope dependances can be obtained. We shall first focus on the occurrence of flux inversion as frequency varies. When attachment-detachment is fast, i.e. when \( md_{0\pm} \ll 1 \), (and for \( \omega_0 \to 0 \)), an expansion of (6) provides:

\[
\langle J \rangle = \frac{\Omega c_{\text{eq}}}{8 D_0 m^2} \omega_0^2 (d_{1+} - d_{1-})
\]

By comparison to Eq. (6), it is seen that if \( (d_{1+}/d_{0-} - d_{1+}/d_{0+})(d_{1-} - d_{1+}) < 0 \), there must exist a frequency \( \omega^* \) for which \( \langle J \rangle \) changes sign. Hence, surface stability can be changed by tuning the frequency.

In the limit of slow step kinetics \( md_{0\pm} \gg 1 \) (and \( \omega_0 \to 0 \)), we find:

\[
\langle J \rangle = \frac{\Omega c_{\text{eq}}}{2 D_0 m^2} \omega_0^2 \left( \frac{d_{1+}}{d_{0+} - d_{0-}} - \frac{d_{1-}}{d_{0+} - d_{0-}} \right) \frac{d_{0+}^2 - d_{0-}^2}{(d_{0+} + d_{0-})^3}
\]

Comparing the sign of this expression to that of Eq. (6), we see that \( \langle J \rangle \) might change for a special slope \( m^* \). Two cases are possible: (i) If \( d_{1+} < d_{1-} \), and \( d_{1+} - d_{0-} > d_{1+} - d_{0+} \), then a nominal surface is unstable, but the flux changes sign for \( m = m^* \). In this situation, slope selection is expected. (ii) If \( d_{1+} > d_{1-} \), and \( d_{1+} - d_{0-} < d_{1+} - d_{0+} \), the surface is stable with respect to small fluctuations, but mounds of slopes larger than a special slope \( m^* \) are subject to an uphill mass flux. A surface of finite initial roughness may be destabilized although a flat one is linearly stable: it is metastable. An analogous metastable situation occurs for morphologically unstable steps in presence of kink Ehrlich-Schwoebel effect during growth (11).

Since mass fluxes are second order, they strongly depend on the temporal "shape" of the perturbation. As an example consider the low frequency square perturbation mentioned earlier (Cf. Fig. 1). Here \( \cos(\omega t) \) is replaced by \( \text{sign}[\cos(\omega t)] \) in Eq. (8), leading to the following flux, calculated for finite perturbation amplitudes (i.e. \( d_{1\pm} \) and \( c_{\text{eq}} \) are not small):

\[
\langle J \rangle \approx \frac{\Omega c_{\text{eq}}}{4\pi} \omega_0 (d_{1+} - d_{1-} + 2m(d_{1+} d_{0+} - d_{1-} d_{0-})) / [1 + m(d_{0+} + d_{1})[1 + m(d_{0-} - d_{1})]]
\]

where \( d_0 = d_{0+} + d_{0-} \) and \( d_1 = d_{1+} + d_{1-} \). The slope and frequency dependance of this flux are different from the sinusoidal case [Eq. (6)], leading to new conditions for surface stability. Taking \( d_{0+} = d_{1+} = 0, c_{\text{eq}} = c_{\text{eq}} \) and \( d_{1-} = d_{0-} \) (case A), which corresponds to the case depicted in Fig. 1, we obtain an uphill flux, leading to mound formation and step meandering. If instead \( d_{1-} = -d_{0-} \), a downhill flux is found (case B). Nominal surfaces should then be smoothed and step bunching is expected on vicinal surfaces.

![FIG. 3. SOS simulations on a 256 x 256 lattice, greyscale represents surface height, \( \omega_0/2\pi = 0.1 \) MCSPS^{-1}. E_b = 1., E_{1\beta} = 0.3, E_s = 2, and T = 0.4. For (a) and (b) E_{1\beta} = 1.9; for (a) and (d) E_{1s} = -1.9. Starting from a flat nominal surface (a) is obtained after 5\times10^5 MCSPS. Mound formation is seen and r.m.s. roughness is \( w \approx 8 \). Starting from the patterned surface (a), we obtain (c) after 2 \times 10^5 MCSPS, with \( w \approx 0.25 \). In (b) and (d) we have plotted the height minus that of the initial regular vicinal surface. Steps are initially parallel to the \( y \) axis. Meandering (b) and bunching (d) of steps take the form of ripples along \( x \) or \( y \).](image-url)
\( d_+ = 0 \) (i.e. \( d_{0+} = d_{0-} = 0 \)), \( d_- = \exp[E_s/T] - 1 \). \( E_b \) and \( E_a \) oscillate in a square fashion, between \( E_{0b} - E_{1b} \) and \( E_{0b} + E_{1b} \) (and similarly for \( E_s \)) leading to case A or B depending on whether their oscillations are in-phase, or out-of-phase. We use the following parameters \( E_b = 1 \), \( E_{1b} = 0.3 \), \( E_s = 2 \), \( E_{1s} = \pm 1.9 \), \( T = 0.4 \), and \( \omega_0/2\pi = 0.1 \). The resulting patterning of the surface correspond to the expectations, as seen in Fig. 3.

We also studied the coarsening of these structures on a nominal surface. We have performed simulations for switching frequencies 1/10, 1/30, and 1/100. In all cases, surface roughness behaves as \( t^\beta \), with \( \beta \approx 0.44 \pm 0.02 \). The typical lateral length-scale on nominal surfaces also follows a scaling law \( t^\alpha \), with \( \alpha = 0.09 \pm 0.02 \). The up-down asymmetry of the mounds is smaller than during growth. This might be related to the non-zero mean step velocity during growth \[\text{(3)}\]. As expected, the surface can also be smoothed (see Fig. 3(c)).

Let us now turn to some applications of this phenomenon. A pulsed laser could induce the abrupt temperature change leading to the uphill flux presented in Fig. 1. Conditions similar to that of Ref. [12] would be needed. For our analysis to be valid, the surface should not melt, and no dislocation should be induced.

In recent experiments, high amplitude surface ultra sound waves were applied to an Al thin film \[\text{(4)}\], and pattern formation was observed. It is not clear whether this results from the oscillatory driving or from Grinfeld instability as pointed out in Ref. [6]. Moreover, further experiments would be needed in order to determine whether dislocations are present.

The oscillatory driving of the potential in an electrochemical cell can provide morphological changes. On the basis of the surface-embedded-atom-method (SEAM) \[\text{(5)}\] we have surveyed the dependence of the ES barrier and the adatom equilibrium concentration on Ag(111) as a function of the departure of the electrochemical potential from the potential of zero charge (pzc) \[\text{(6)}\]. We find that increasing the potential from 0 to +0.85 V (relative to the pzc) increases the adatom formation energy from 0.85eV to 0.92eV (which implies a decrease of the adatom equilibrium concentration), but also increases the ES barrier from 0.22eV to 1.16eV. This cycle thus should lead to case A. We also find that as the potential is cycled from 0 to negative voltages, \( c_{eq} \) still increases, but the ES barrier goes back up. Therefore cycling between 0V and negative voltages we should be in case B. Hence, it should be possible to create or smoothen mounds depending on the chosen cycle.

Note that oscillatory driving could also be applied during growth via the techniques described above, in order to smoothen or pattern the surface.

In conclusion, oscillatory driving is a promising tool for in situ and real time control of the surface morphology. We have shown that it allows one to create and smoothen patterns on nominal and vicinal surfaces. A wide variety of behavior among which step bunching and meandering, mound formation, slope selection, metastability, and mass flux inversion are found. Similar phenomena should result from a Kink-Schwoebel effect, as a consequence of non-equilibrium line diffusion, as shown for growth in Ref. [1].

In order to be more quantitative and to predict the typical wavelength of the instabilities, the next step of this study will be to consider stabilizing effects coming from line tension, step interactions, and nucleation. As in growth, initial stages of the instability on nominal surfaces, as well as the shape of mounds crucially depend on nucleation. Including this effect is the main challenge for a global understanding of pattern formation via oscillatory driving.

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