Kinetic Step Pairing

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We report on the theoretical and experimental discovery of pairing of identical crystal steps. We first show that step bunching always occurs at long wavelength in the vicinity of an instability threshold when step dynamics is local. But an instability towards a stable train of pairs can be obtained when steps dynamics is nonlocal. This instability is shown to occur for transparent steps under electromigration. Observations on Si(111) under electromigration around 1230 °C show stable trains of pairs. By controlling both supersaturation and electromigration, we establish an experimental morphology diagram, from which we conclude that the transparency kinetic coefficient is negative.

The dynamics of atomic steps on crystal surfaces has proved to be a key ingredient for a quantitative description of the formation of micro and nanostructures. Not only equilibrium morphologies, but also nonequilibrium spontaneous pattern formation can be understood from step dynamics. For example the understanding of kinetic instabilities at nanometer scale during Molecular Beam Epitaxy, or under electromigration, is based on step models [1–7].

Up to now, two instabilities were known for vicinal surfaces with identical steps: step meandering and step bunching. We present here a novel type of instability: the pairing of steps. This instability is discovered both in theory and in experiments.

We show that the pairing instability occurs only when the dynamics of a step is coupled to the velocity of its neighbors, or more generally when step dynamics is nonlocal. We find that such a coupling is present when steps are transparent. From a nonlinear analysis for transparent steps under adatom migration, we then find that a train of identical steps may undergo a subcritical transition to a stable train of pairs.

Many scenarios are known to lead to bunching, such as diffusion in a 3D phase, or the presence of impurities [8]. Here we analyze clean surfaces in contact with the vacuum, so that both scenarios can be ruled out. In 1989, Latyshev et al. [2] showed that step bunching on Si(111) surfaces at high temperatures may occur as a consequence of electromigration. Controlling both electromigration and supersaturation, we observe the pairing instability. Furthermore, the observed morphology diagram proves that the kinetic coefficient which accounts for step transparency is negative.

We start with a presentation of the step model. We account not only for adsorption and desorption of adatoms on terraces, but also for adatom electromigration with a velocity \(v\) along the electric current. On the surface of metals, adatoms are expected to drift in the direction opposite to that of the current, due to the so-called wind force caused by conduction electrons [9]. But for semiconductor surfaces, the direction of the drift is not known \textit{a priori} [10,11]. For the sake of simplicity, we consider a one dimensional vicinal surface (i.e., all steps are straight), and migration perpendicular to the steps. The concentration \(c\) of adatoms on each terrace obeys the following quasistatic equation [3]:

\[
D \frac{\partial c}{\partial x} - \frac{D}{\xi} \frac{\partial c}{\partial z} + \frac{F - ce}{\tau} = 0, \tag{1}
\]

where \(D\) is the adatom diffusion constant, \(F\) the incoming flux, \(\tau\) the desorption time, and \(\xi = D/\nu\) (we choose \(\nu > 0\) for a downhill drift). Kinetic boundary conditions at the steps read [3,12]

\[
D \frac{\partial c}{\partial x} - \frac{D}{\xi} c = \pm \nu \left( c_z - c_\pm \right) + \nu_0 (c_+ - c_-). \tag{2}
\]

\(\nu_+, \nu_-\) are attachment-detachment kinetic coefficients for the lower and the upper sides of the step, respectively. \(\nu_0\) is the kinetic coefficient describing direct exchange between terraces; this exchange is called step transparency. The kinetic coefficients can be positive or negative, depending on the underlying microscopic physics. Some example of negative kinetic coefficients can be found in Ref. [13]. Kinetic lengths are defined as \(d_+ = D/\nu_+, d_- = D/\nu_-,\) and \(d_0 = D/\nu_0\). Since steps are defects at the surface, they are subject to elastic interactions. The interaction energy is \(-1/\ell^2\) per unit length, where \(\ell\) is the distance between steps. The local equilibrium concentration is then obtained via a linearized Gibbs-Thomson relation:

\[
c^0_\pm = \frac{c^0_\pm \left[ 1 + \frac{A}{3} \left( \frac{1}{\ell_n} - \frac{1}{\ell_{n+1}} \right) \right]}{1 + \frac{A}{3} \left( \frac{1}{\ell_n} - \frac{1}{\ell_{n+1}} \right)} \tag{3}
\]

where \(\ell_n\) is the distance between the \(n\)th and the \((n + 1)\)th steps. Finally, mass conservation at the step reads

\[
\frac{V}{\Omega} = \left[ D \frac{\partial c}{\partial x} - \frac{D}{\xi} c \right]_+ - \left[ D \frac{\partial c}{\partial x} - \frac{D}{\xi} c \right]_. \tag{4}
\]

From the step model [(1)–(4)], step velocities can be calculated explicitly. The velocity of the \(n\)th step reads...
\[ V_n = f(\ell_n, \ell_{n-1}, c_{eq}^{*n-1}, c_{eq}^n, c_{eq}^{*n+1}) \]  
(5)

where \( c_{eq}^* = c_{eq} + \beta V_n/\Omega \), with \( \beta = (\nu_+ + \nu_- + \nu_+\nu_-/\nu_0)^{-1} \). The fact that step velocities can be recast into the form (5) comes from a possible rewriting of the boundary conditions as shown in Ref. [13]. The form of Eq. (5) implies that coupling to next nearest neighbors is present only via \( c_{eq}^* \), and it is due to elastic interactions.

In the absence of transparency (\( \beta = 0 \)), \( c_{eq}^* \) does not depend on step velocity. From this simple fact, one can conclude that an instability will occur at long wavelength close to any instability threshold. Indeed, linearizing Eq. (5) and choosing a small periodic perturbation proportional to \( \exp[i\omega + in\phi] \), one finds a dispersion relation, which provides \( i\omega \) as a function of \( \phi \). If \( \Re[i\omega] \) is positive for a given value of \( \phi \), then the perturbation, which has the wavelength \( 2\pi \ell / \phi \) is unstable. In general, we find

\[ \Re[i\omega] = 2[1 - \cos(\phi)]B_2 - 4[1 - \cos(\phi)]^2B_4 \]  
(6)

where the coefficients \( B_i \) depend on the derivatives of the function \( f \). The last term comes from the elastic interaction via the coupling to nearest neighbors. It is therefore stabilizing, i.e., \( B_4 > 0 \). An instability will occur if \( B_2 > 0 \). Close to the instability threshold, \( B_2 \sim \epsilon \), where \( \epsilon \) is a small dimensionless parameter. When one crosses the threshold, the instability first occurs at long wavelength (i.e., for small \( \phi \)).

The most unstable wavelength will be \( \sim \epsilon^{-1/2} \) and the typical time for appearance of the instability will be \( \sim \epsilon^{-2} \). Several studies have already focused on this situation. One can indeed expand Eq. (5) as a function of \( \epsilon \) and obtain a nonlinear partial differential equation which catches the relevant features of dynamics of step bunching [4].

In the presence of step transparency, the structure of the function \( f \) is changed. Indeed, the equation of motion now involves the velocity of neighboring steps. If we wanted to write the velocity of a step as a function of the position of the other steps only (not their velocity), one would have to eliminate the velocity in the right hand side of Eq. (5), and doing so, we would obtain a relation involving all steps. Therefore, dynamics is nonlocal. The dispersion relation (because of its lengthy expression, we do not write it here) cannot be reduced to Eq. (6) anymore. Therefore, one does not necessarily have instabilities at long wavelength close to the instability thresholds; they can occur at any wavelength. Even the shortest wavelength instability, which is step pairing, can be observed.

We are more specifically interested in the regime of nonlocal mass transport [14,15] where step transparency is strong and attachment-detachment kinetics is slow: \( |d_0| \ll \ell \ll d_\perp, d_- \). Here, nonlocality comes from the diffusion of adatoms on large scales, and through many steps before attaching at one step. Since the Schwoebel effect is irrelevant in this regime, we choose \( d_\perp \approx d_- \). We also consider the limit \( d_\perp \ll \xi, x_\perp = (D\tau)^{1/2} \), which is relevant for our experiments. From a linear stability analysis, a threshold is found for a downhill drift during sublimation, where steps initially form pairs. When elastic interactions are weak, one finds

\[ \tilde{F}_p = -d_0 \frac{6Dc_{eq}^0}{\xi^3}. \]  
(7)

The threshold of macroscopic step bunching, which limits the region where bunching occurs at long wavelength, is found to be

\[ F = -d_0 \frac{6Dc_{eq}^0}{\xi^2d_\perp}. \]  
(8)

These results are reported in Fig. 1. The linear analysis determines which are the unstable modes at the first stage of the instability. Nevertheless, it is not sufficient to determine the resulting morphology of the surface, which involves changes in the steps positions that are not small. A fully nonlinear analysis is then needed.

We therefore look for nonlinear steady states where steps form pairs, with terrace widths \( \ell_{2p} = \alpha \ell \), and \( \ell_{2p+1} = (1 - \alpha)\ell \). We also define two dimensionless numbers

\[ q = \frac{F - c_{eq}^*}{\tilde{F}_p} \]  
(9)

and

\[ r = \frac{32 c_{eq}^* \xi A}{3 c_{eq}^* d_0 \ell^3} \]  
(10)

which, respectively, account for supersaturation and for the balance between electromigration and elasticity. From Eq. (5), one then finds:

\[ q = -1/\gamma + (r/\gamma^4)(1 - \gamma/4) \]  
\[ 1 - b(r/\gamma^4)(1 - \gamma/4) \]  
(11)

where \( \gamma = 4\alpha(1 - \alpha) \) and \( b = \beta \tilde{F}_p/c_{eq}^* \). As shown in Fig. 2, Eq. (11) leads to a subcritical bifurcation when \( r \) is

![FIG. 1. Morphology diagrams for transparent steps (with \( d_0 > 0 \) and \( d_0 < 0 \)) as a function of supersaturation \( \sigma = F\tau/c_{eq} - 1 \), and adatom migration \( \sim 1/\xi \). The shaded regions indicate the results from the linear stability analysis. The numbers (1) to (4) refer to Fig. 2. In the C region, quasiperiodic or chaotic step bunching are observed, with a bunch size which does not grow in time.](image-url)
small. Therefore, the pairs are stable with respect to variations of the pairing parameter $\alpha$ in the upper branch of Fig. 2, where $4^{-1/3} \alpha_c < \alpha < \alpha_c$, with

$$\alpha_c = (r/16)^{1/3}. \quad (12)$$

Larger $r$ corresponds to stronger elastic repulsion between steps. When $r > 4/(13 + 10b)$, the bifurcation becomes supercritical, and when $r > 4/3$, the pairing region disappears (i.e. $|\tilde{F}| > |\tilde{F}_p|$).

One can then ask the question of the stability of the train of pairs with respect to bunching or pairing of pairs. A full stability analysis would be too long to be reported here. Nevertheless, a simple argument allows one to answer this question. Indeed, pairs of steps should behave as effective steps, with effective parameters. We use the substitution: $\ell \to 2\ell$, $d_0 \to 2d_0$ and $d_+ \to d_+/2$. Performing these changes in Eqs. (8) and (7), one finds that $\tilde{F}$ is unchanged, and $\tilde{F}_p \to \tilde{F}_p/4$. Hence, the train of pairs should be stable close to the threshold.

Solving the full dynamics (5) numerically, we check that the regular train of pairs is a stable steady state with a periodic train of 200 steps. We also check that our predictions of the value of $\alpha$ are quantitatively accurate, and that a hysteresis loop can be observed (see Fig. 2).

Once we get deeper in the unstable region, one finds quasiperiodic dynamics. The quasiperiodicity was checked by means of a Fourier analysis. As we go even deeper in the unstable region, chaos is observed. The important point is that bunches form, but their size does not increase in time. Once the threshold for macroscopic bunching is exceeded, bunches merge, and become larger and larger in time.

We now come to the experimental observations. We have performed in situ observation of Si(111) by means of a Reflection Electron Microscope (REM). An electric current passes through the silicon wafer. This current is used both for heating and for electromigration. Nevertheless, both phenomena can be decoupled using a biased ac current. The supersaturation is controlled by differential heating between the sample and another silicon crystal in the vacuum chamber [16].

From previous studies, there are three well identified temperature regimes at high temperature (where the surface is not reconstructed) [2, 16]. Our experiments were performed around 1230 °C, in the intermediate temperature regime. In this regime, previous studies [16] have shown that bunches are observed when the product of the electromigration drift $\nu$ with the supersaturation is positive. From this analysis, it was concluded that steps may be transparent (i.e., $d_0 \to 0$). Nevertheless, it was pointed out recently that fast steps attachment-detachment kinetics (i.e. $d_+ \to 0$) leads to the same stability condition [14]. We shall clarify this point in the following.

Our observed morphology diagram is that of Fig. 3. For a vicinal surface with $l = 1.1 \times 10^4$ Å, we have used an uphill current. We start with fast growth with an uphill current, where the train of steps is stable. Decreasing the incoming flux, the pairing threshold is found to be $\tilde{F}_p = 1/3$ ML s$^{-1}$, where ML means monolayer. The presence of pairs (see Fig. 4) readily shows that the steps must be transparent, and we must have $|d_0| \ll \ell \ll d_+$. The experimental morphology diagram clearly corresponds to the case $d_0 < 0$ in Fig. 1. Kinetic coefficients can become negative when diffusion in the step region is faster than on terraces. Using a thermodynamically consistent phase field model as in Ref. [13], and in the limit $|d_0| \ll d_+$, one indeed finds

$$d_0 = \int dx \left( \frac{D}{M} - 1 \right) \quad (13)$$

where the integral is taken along the step normal. $M$ is the diffusion constant of mobile atoms in the step region. Far from the step $M \to D$. Therefore, $d_0 < 0$ when $M > D$. A general analysis of the sign of the kinetic coefficients will be given elsewhere [17].

Another possible scenario would be that mass transport is due to migration of ad-vacancies, as proposed in

**FIG. 2.** Subcritical bifurcation of the pairing instability. The solid line is the analytical prediction Eq. (11). The symbols are the results of the numerical solution of Eq. (5). The triangles and circles are obtained by increasing or decreasing $q$ respectively. Between (1) and (2) one can see the hysteresis loop. Between (2) and (3), a stable train of pairs is found. Between (3) and (4), quasiperiodic dynamics and chaos are observed. (4) is the threshold for macroscopic bunching. We have used: $\ell / \ell_0 = 10^2$, $\tilde{A} / \ell^3 = 10^{-8}$, $c = \ell^2 = 10^3$, $d_0 / \ell = 10^{-2}$, and $d_+ / \ell = 10$.

**FIG. 3.** Morphology diagram observed in experiments. The regions $C$ correspond to the formation of bunches which do not grow in size, and which recombine permanently.
Ref. [18]. A simple way to consider ad-vacancies is to make the transformation $\Omega \to -\Omega, A \to -A, F \to -F, \tau \to -\tau$. This means that we account for sublimation as an effective “deposition” of ad-vacancies, and growth as a “desorption” of ad-vacancies. The morphology diagram of Fig. 1 with $d_0 > 0$ then transforms into the experimental one Fig. 3 if the ad-vacancies migrate along the direction of the current. But this latter result is in contradiction with that of Ref. [11], which stipulates that the mass flux due to electromigration is along the current. Hence, this scenario cannot be accepted.

The observed pair compression coefficient is $\alpha = 0.1$. Close to the threshold for pairing, no intermediate value of $\alpha$ (between 0.1 and 0.5) is observed. This jump in $\alpha$ proves that the transition is subcritical. Using Eqs. (7) and (12), and $A = 10^2 \text{Å}^3$ [19], we obtain $\xi Dc_{eq}^0 = 3 \times 10^{19} \text{Å}^{-1}$, and $d_0 Dc_{eq}^0 = -6 \times 10^{11} \text{Å}^{-1}$.

Going deeper in the unstable region, we first found step bunching with bunches that do not grow in size, but which recombine permanently. This is in concordance with the results of the step model. When one reaches equilibrium, the bunches grow indefinitely with time.

Using another train of steps, with $\ell = 5 \times 10^3 \text{Å}$, we looked for the macroscopic bunching threshold by changing the supersaturation with a downhill current. The threshold is very close to the equilibrium point where desorption exactly compensates adsorption. We could only define an upper bound: $\tilde{F} < F_p/240$. Using Eq. (8), we conclude that attachment-detachment is very slow: $d_+ = d_- > 80\ell = 4 \times 10^5 \text{Å}$.

Since we were nevertheless close to the instability threshold, we could observe long wavelength step bunching. We have measured the initial wavelength, and the typical time for the instability to appear. These observations are not quantitatively very accurate, but provide good orders of magnitude. From the linear stability analysis of Ref. [14], the most unstable wavelength is $\lambda_m = 2\pi (A \xi D \Omega c_{eq}/V)_{eq}^{1/2}$. Using this expression, we find $\xi Dc_{eq}^0 = 3 \times 10^{20}$, which is of the same order of magnitude as the result obtained from the pairing threshold. From the stability analysis, one can also calculate the time scale for appearance of the instability. By observing the bunching time (around $10^2$ s), we obtain $Dc_{eq}^0 = 4.5 \times 10^{12} \text{Å}^{-1}$, which in turn leads to $d_0 = -0.13 \text{Å}$ and $\xi = 10^7 \text{Å}$. This latter result can be reformulated in terms of an effective charge $q$ on the adatoms, which is defined via the expression of the drift force $f = k_B T/\xi = qeE$. We find $q = 0.6$ electron charge, whose order of magnitude is in agreement with the previous results in the literature [10,20,21], suggesting that $q$ is of the order of 0.1.

To conclude, we have discovered, both theoretically and experimentally, a novel kinetic instability of vicinal surfaces, namely, the pairing of identical steps. Furthermore, the kinetic coefficient for step transparency is negative on Si(111) at 1230 °C. This is, to our knowledge, the first time that a negative kinetic coefficient has been observed and quantitatively determined. This result is probably related to a faster diffusion in the step region.

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