From Meandering to Faceting, Is Step Flow Growth Ever Stable?

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(Received 24 April 2003; published 25 November 2003)

Based on helium atom beam diffraction and scanning tunneling microscopy data, the coexistence of a meandering and a bunching instability during homoepitaxial step flow growth is established in a class of nonreconstructed, metallic vicinal surfaces, Cu $(1, 1, n)$, $n = 5, 9, 17$. Specifically, the meandering instability is shown to act as a precursor to the bunching instability, indicating that a one-dimensional treatment of bunching in step flow growth is not sufficient. Our findings might be generic to step flow growth in kinetically restricted systems.

DOI: 10.1103/PhysRevLett.91.226103 PACS numbers: 68.55.–a, 68.35.Ct, 68.49.Bc, 81.15.Hi

The use of morphological instabilities [1] in thin film growth [2] is currently actively explored as a promising pathway for planar nanostructuring of surfaces. In many cases, the key ingredient for spatial pattern formation through self-organization during growth is traced back to the presence of an excess energy barrier for adatom motion at and in the vicinity of surface steps, the Ehrlich-Schwöbel (ES) barrier [3,4], associated with diffusion across steps [two-dimensional (2D) ES barrier], or along curved, kinked steps [one-dimensional (1D) ES barrier] [5]. Thus, any attempt of a controlled nanostructuring of surfaces in this way demands a detailed understanding of pertinent kinetic mechanisms at the atomic scale.

A first quantitative step is the investigation of homoepitaxial growth in a nonreconstructed metallic system, since the number of kinetic pathways is reduced to the minimum. The preponderant role of steps in thin film growth has early been recognized [2]. On vicinal surfaces, ideally made up of a regular arrangement of straight steps delimiting terraces whose extension is imposed by a chosen miscut angle with respect to a high symmetry direction, growth proceeds without nucleation on terraces by direct incorporation of atoms to preexisting steps. Atoms attach to ascending and descending steps, which thereby advance along the step train direction with a velocity proportional to the widths of the adjacent terraces. Originally, this growth mode has been thought to produce perfect layer by layer growth, but unstable step flow has often been encountered: Initially straight steps develop a modulated structure (meandering), or the initially equally spaced steps group together (bunching). It has been shown both theoretically [5,6] and experimentally [7,8] that the presence of ES barriers is the source of the step *meandering* instability. It has long been established wisdom [1,3] that the presence of the 2D ES barrier stabilizes a vicinal surface against step *bunching*. Indeed, in this case, atoms attach preferentially to ascending steps, so that step velocities are mostly determined by the width of their *preceding* terraces. Consequently, step advancement is controlled by negative feedback, so that any fluctuation in the terrace widths during growth gets suppressed. Oppositely, bunching occurs, when atoms attach preferentially to descending steps. Thus, meandering and bunching instabilities are *a priori* mutually exclusive.

In this Letter, we report that for the growth of Cu on vicinal Cu surfaces, meandering and bunching instabilities do coexist in the same system for a wide range of incident flux simply by tuning the deposition temperature. The bunching instability is shown to supersede the meandering instability smoothly upon increasing the growth temperature, indicating that the latter acts as a precursor to the former. Thus, in the whole temperature range covered by our experiments (170 to 660 K), stable step flow is never encountered. Given the fact that these instabilities are observed in model metallic systems with a minimum set of kinetic pathways at hand, the reported behavior may be generic to step flow growth on vicinal surfaces.

Morphological information on step flow in ultrahigh vacuum has been obtained by using helium atom beam scattering (HAS) and variable temperature scanning tunneling microscopy (STM) as atomic scale structural probes. Earlier studies [7,8] of step flow on Cu (1, 1, 5) and (1, 1, 17) have been refined, complemented, and extended. We report here mainly the results of our investigation of step flow growth on Cu (1, 1, 9) and refer to the results obtained for growth on the other surfaces when systematic conclusions for this class of vicinals are drawn. The $(1, 1, n)$ vicinals exhibit (001) terraces delimited by steps running along the close packed $[1\bar{1}0]$ direction. Terrace widths are 6.4 Å, 11.5 Å, and 21.7 Å for Cu (1, 1, 5), (1, 1, 9), and (1, 1, 17), respectively. All single crystals have been prepared according to established procedures [7,8]. Cu has been evaporated at normal incidence at a typical rate of 10^{-2} monolayer/s (ML/s).

Our main observations, taking advantage of a combined reciprocal and real space investigation, are summarized in Figs. 1 and 2 for the Cu (1, 1, 9) surface in the meandering [Figs. 1(a), 1(b), and 2(a)] and bunching [Figs. 1(c), 1(d), and 2(b)] regimes. As on Cu (1, 1, 5) [7] and Cu (1, 1, 17) [7,8], during step flow at around 200 K

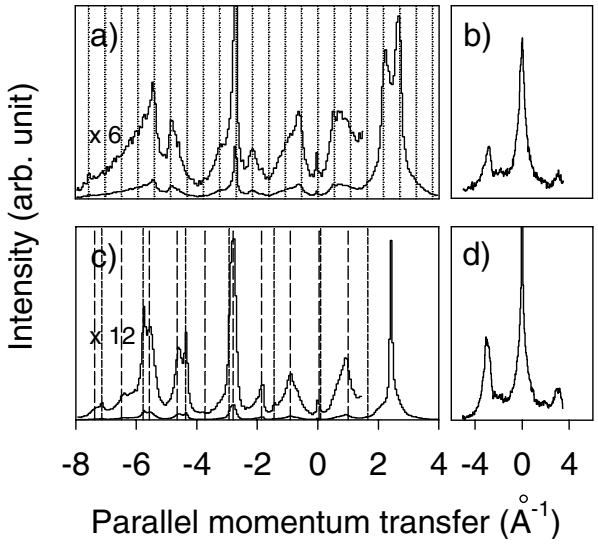

FIG. 1. HAS angular distributions of the Cu (1, 1, 9) surface after step flow growth in the meandering (upper panel), and in the bunching (lower panel) regimes for diffraction perpendicular (a),(c), and parallel (b),(d) to the average step direction $[1\bar{1}0]$. (a),(c) are sensitive to the interstep spacing, (b),(d) to meandering. In both cases $F = 10^{-2}$ ML/s, with deposition of 15 ML at $T = 190$ K (a),(b) and 20 ML at $T = 400$ K (c),(d). The incident wave vector is $k_i = 11.2$ Å^{-1}; the angle between source and detector is set to $\Theta_{SD} = 92°$ (a),(c) and $\Theta_{SD} = 104°$ (b),(d). In (a) not all diffraction peaks related to the (1, 1, 9) step grating (dotted lines) are visible because of strongly meandering steps and the chosen scattering conditions highlighting the "rainbow doublet" [9]. In (c) the peaks are no longer related to the (1, 1, 9) grating but correspond to patches of Cu (1, 1, 3) (short dashed lines), Cu (1, 1, 5) (long dashed lines), and (001) orientation (not labeled).

a meandering instability develops, which leads to a collective in-phase modulation of steps with characteristic wavelength. This formation of ripples or trenches is signaled through the appearance of satellite diffraction peaks [Fig. 1(b)] in the HAS diffraction spectrum recorded parallel to the average step direction $[1\bar{1}0]$, which are otherwise absent for (nearly) straight steps prior to deposition. The diffraction spectrum parallel to the step train direction, which is sensitive to the interstep spacing [Fig. 1(a)] shows (besides a decrease in overall intensity with respect to the signal from the pristine surface) exclusively peaks related to the (1, 1, 9) step grating, indicating that the terrace width is maintained during meandering. We note that this morphology persists for coverages as high as 250 ML; the predicted transition [10] to a moundlike morphology with increasing coverage has not been observed so far.

Unexpectedly, the very same system produces a step bunching instability simply by increasing the deposition temperature to $T = 400$ K. This is immediately witnessed by the HAS angular distribution recorded along the step train direction $[\bar{1}\,\bar{1}\,0]$ [Fig. 1(c)], which shows diffraction peaks not related to the (1, 1, 9) step grating. A detailed analysis reveals that the regular step train is decomposed upon growth into bunches of reduced interstep distance corresponding locally to Cu (1, 1, 5) and (1, 1, 3) grids, separated by large (001) terraces. The continuing presence of the satellite peaks along the average step direction $[1\bar{1}0]$, sensitive to step meandering [Fig. 1(d)], asserts that the morphology must have a "scaly" aspect. This is confirmed by inspecting the corresponding STM topograph [Fig. 2(b)]. A lateral modulation of the bunched steps is still visible, reminiscent of the meandering instability observed at low deposition temperatures; however, extended phase correlation is lost.

It is worth noting that annealing the surfaces to about 750 K restores the pristine morphology [11]. Therefore, the observed instabilities are purely kinetic in origin and out of equilibrium phenomena.

This unexpected growth scenario has been found in a whole class of Cu vicinal surfaces, Cu $(1, 1, n)$, $n = 5, 9, 17$. A detailed investigation of the transition between the meandering and bunching instabilities might hold the key to understand the origin of this finding.

One imagines that bunching during step advancement starts through the formation of an increasing number of

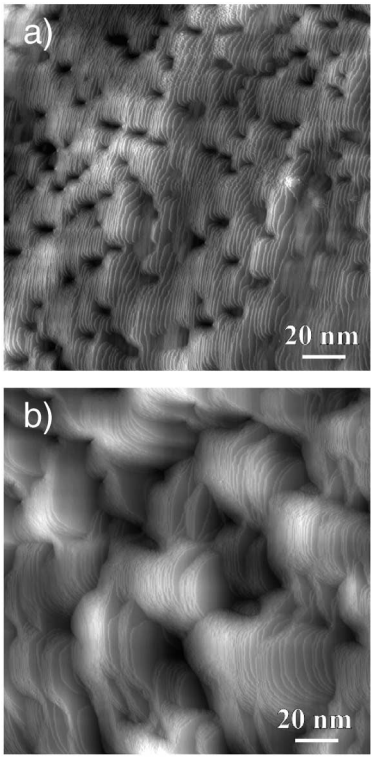

FIG. 2. $(170\ \text{nm})^2$ STM topographs of the Cu (1, 1, 9) surface after step flow growth in the meandering (a), and in the bunching (b) regimes corresponding to HAS spectra [Figs. 1(a) and 1(b)] and [1(c) and 1(d)], respectively. (a) 15 ML deposited at $T = 230$ K, $F = 10^{-2}$ ML/s, and (b) 30 ML deposited at $T = 400$ K, $F = 10^{-2}$ ML/s. Tunneling parameters are 1 nA current and -0.4 V sample bias.

narrow terraces compensating for a few larger ones. The resulting asymmetry in the terrace width distribution can be traced by HAS through a close inspection of diffraction peaks sensitive to destructive interferences between neighboring terraces ["out-of-phase condition" with respect to (001) terraces] [9,12]. Figure 3 shows the evolution of the rainbow doublet [9] with growth temperature. The peak positions inside the doublet shift towards each other and merge finally into the diffraction peak associated with (001) terraces. This continuous shift reflects the expected emerging asymmetry in the terrace width distribution [12] and allows one to locate the "onset temperature" of the bunching instability between 250 and 275 K. For the present purpose it is important to note that both HAS and STM data reveal the continuous presence of *meandering* steps over this whole temperature range, indicating that the presence of 2D step profiles is the key element for the bunching instability to develop [13].

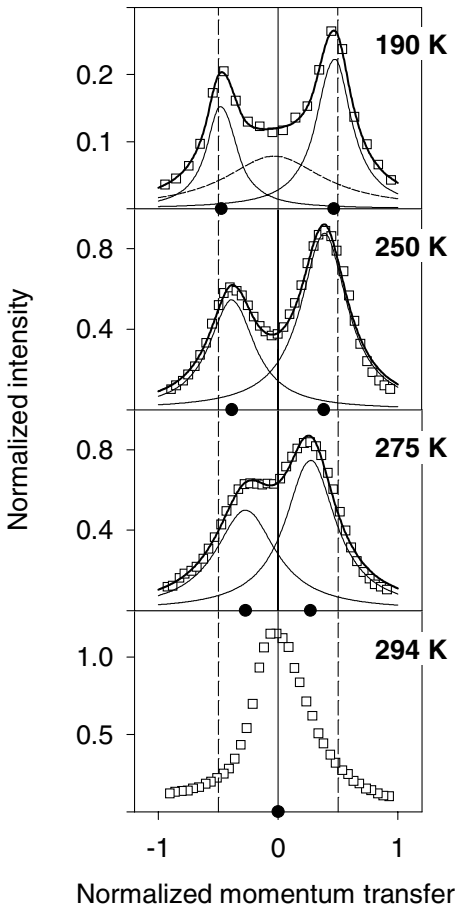

FIG. 3. HAS rainbow doublet [9] recorded after deposition of 35 ML at $F = 10^{-2}$ ML/s for temperatures in the range 190—294 K. (□) experimental data, (thin and thick lines) fitted Lorentzian peaks whose positions are reported as black dots. The shift of the rainbow peaks from their ideal positions at $K = \pm\frac{1}{2}$ (vertical dashed lines) towards the center of the (001) Brillouin zone (vertical full line) reflects a smooth transition from a stable step train in the meandering regime with narrow terrace width distribution (190 K) to an unstable step train in the bunching regime with asymmetric distribution and adjoining (001) facets (294 K). Note that, at $T = 190$ K, an additional peak (short dashed line) has to be introduced to account for the strong meandering of the steps off the $[1\bar{1}0]$ direction.

The meandering instability can be traced back to the competing influence of the 1D ES and 2D ES barriers [5,6]. Purely 1D theories, assuming straight step edges [1,3,14], exclude therefore the appearance of the bunching instability in the same system, unless, at high temperatures, an "inverse" 2D ES (IES) barrier appears; i.e., the attachment of adatoms to ascending steps becomes kinetically unfavorable or inhibited. This mechanism has originally been invoked for bunching observed in molecular beam epitaxy of GaAs [15]. So far, for nonreconstructed metallic systems, there is no indication that such a process exists. Possibly the "compensation effect" [16] could produce such a crossover with temperature even in simple metallic systems. In this case, within an Arrhenius-type description, diffusion across steps is characterized not only by an excess energy barrier but also by a larger preexponential factor as compared to diffusion on terraces. Thus, a higher attempt frequency could compensate for the excess energy barrier, leading to preferential attachment to descending steps at high temperatures. However, measurements of the surface phonon spectra that are related to the preexponential factor exhibit no extra signature [17]. More importantly, the IES barrier has been shown to stabilize against step meandering [18]. Therefore, the bunched morphology should exhibit *straight* step edges, contrary to the scaly aspect experimentally observed.

The "two particle" model of Pimpinelli and coworkers [19] considers growth processes involving two kinds of diffusing entities. In the presence of ES barriers, this model accounts successfully for both bunching and meandering in homoepitaxial growth of GaAs [15]. If in the case of Cu, dimers [20] would take the role of the "second particle," how large has their concentration to be? It is likely that dimers will be dissociated at high temperatures.

Our reported experimental investigation of the transition during step flow between meandering and faceting points to the fact that a 1D description of the growth might be insufficient. This result joins a recent theory of Politi and Krug [21], who have shown, within a full 2D theoretical treatment, that diffusion along *meandered* steps may induce a faceting of the surface. Since diffusion along kinked steps is an activated process with supposedly large activation energies, faceting should be induced only at relatively large temperatures, as experimentally observed. Moreover, the stabilizing effect of a 2D ES barrier is favored by wide terraces [1,14], while a step edge current-induced bunching [21] should naturally call for high step densities. In this picture, the instability should be shifted towards higher temperatures for larger

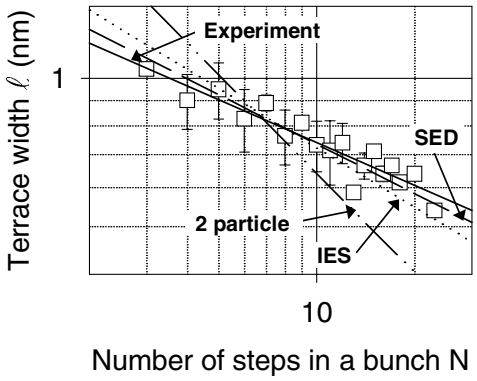

FIG. 4. Terrace width ℓ vs number of steps N in a bunch for the Cu (1, 1, 9) surface (□). Lines correspond to the power law behaviors $\ell \propto N^{-\gamma}$ predicted for different bunching mechanisms [22]: two particle model $\gamma = 2/3$, inverse Schwöbel barrier $\gamma = 2/5$ (IES), and step edge diffusion $\gamma = 1/3$. For the whole Cu (1, 1, 9) data set, the best fit power law exponent is $\gamma = 0.29 \pm 0.05$; see the text.

terrace widths; this has been checked explicitly with both HAS [7] and STM for the homoepitaxial step flow on Cu (1, 1, 17).

Our measurements of the mean terrace ℓ within a step bunch, Fig. 4, are also compatible with this picture. According to Pimpinelli *et al.* [22], this observable reflects the origin of bunching, through the coupling of step motion via the kinetic-channel-dependent diffusion field between steps. Our experimental data are best described by a power law, whose exponent $\gamma = 0.29$ compares favorably with the theoretical prediction $\gamma = 1/3$ [22] for bunching induced by step edge currents. The analysis of other faceting processes, i.e., the IES effect and the two particle model, reveals power law exponents $\gamma = 2/5$ and $\gamma = 2/3$, respectively [22]. While the latter lies outside the experimental error margin (Fig. 4), the exponent of the IES mechanism could describe our data as well. But again, this specific mechanism would lead to the appearance of *straight* bunched steps, which are not experimentally observed here. Therefore, the inverse 2D ES barrier as a source of bunching can be excluded.

In conclusion, the existence of both meandering and bunching instabilities during homoepitaxial step flow growth in a class of nonreconstructed metallic vicinal surfaces is reported. A detailed investigation of the transition between the morphologies with temperature reveals the 2D nature of this phenomenon. The meandering instability acts as a precursor to the bunching instability, indicating that a 1D description of step flow growth might not always be appropriate. Given the fact that these instabilities are observed in model metallic systems, the reported behavior may be intrinsic to step flow growth on vicinal surfaces in kinetically restricted systems.

We thank J. Krug, A. Pimpinelli, and J. Wollschläger for fruitful discussions, as well as P. Lavie and F. Merlet for continuous technical support.

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