

Experimental Study of Smoothing Kinetics on a Rough Surface

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The smoothing kinetics of a rough surface have been studied using time-resolved high resolution low energy electron diffraction. By depositing ~ 100 monolayers of Cu on Cu(100) near room temperature, a rough surface results with an initial morphology of multilevel, roughly circular terraces separated by monatomic steps. Upon annealing at elevated temperatures, two growth regimes are distinguished for the average terrace width $L(t)$ versus time t : The earlier one varies as $t^{1/3}$, consistent with kinetics driven by the line tension of curved step edges, and the later one follows $t^{1/5}$. Also, in the $t^{1/3}$ growth regime, scaling is observed.

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When a single-crystal surface is rough, as after sputtering or epitaxial deposition, annealing is often employed to make it smooth. The detailed description of the smoothing process and the driving forces controlling the mass transport in smoothing kinetics have been attracting great attention [1–8]. The importance of understanding this phenomenon arises from both practical and fundamental interests such as surface preparation, thin-film growth, and the smoothing transition when a crystal surface is cooled from its roughening temperature. So far, many theoretical efforts [1–8] have been devoted to explore this problem with pioneer work by Mullins [1], but experimental tests are lacking. In these theoretical works, two fundamental behaviors have been predicted. The first behavior is the time-dependent growth of the average terrace width $L(t)$, which has been generally shown to follow a power law

$$L(t) \propto t^x. \quad (1)$$

The exponent x depends on the driving force governing the mass transport in the smoothing kinetics. For a surface with an initial morphology consisting of multilevel, circular terraces of various sizes separated by monatomic steps, the mass transport in the smoothing process is suggested to be driven by the line tension of curved step edges [3–6]. In this case, the exponent x is shown to be $\frac{1}{3}$ [3–5], analogous to the Lifshitz-Slyozov mechanism [9], i.e., atoms diffuse from terrace edges with small radii to those with larger radii in order to reduce the line tension of curved step edges. However, with the same driving force but a different expression of step chemical potential, the x is shown to be $\frac{1}{2}$ or $\frac{1}{5}$ if the mass transport rate is controlled by step mobility or surface diffusion, respectively [6]. This line-tension driving force, which is dominant in the step chemical potential [4,6], vanishes for an initial surface morphology such as parallel grooves with essentially straight step edges. In this case, step-step interactions become the driving force for morphological evolution [2,5–7]. The exponent x is shown to be $\frac{1}{5}$ or $\frac{1}{4}$ for diffusion-limited or step-attachment-limited step propagation, respectively, in a discrete model [7] and to

be $\frac{1}{2}$ in a continuous model [2]. The second prediction for the behavior of smoothing kinetics calls for scaling [3–5]. Scaling means that although the average terrace width expands with time, the functional form of the terrace width distribution remains unchanged as the smoothing progresses.

In this Letter, we present the first experimental test for the smoothing kinetics of a system with an initial morphology consisting of multilevel, circular terraces of various sizes separated by monatomic steps. This system is prepared by depositing Cu on Cu(100) using molecular beam epitaxy (MBE). The probe used is a time-resolved high resolution low energy electron diffractometer (HRLEED) with an instrument response width of $\sim 0.006 \text{ \AA}^{-1}$ and an angular profile acquisition time of a few seconds. In this study, two power-law growth regimes are distinguished: The earlier one with $x \sim \frac{1}{3}$ in agreement with Villain's prediction where the smoothing is driven by the line tension of curved step edges [3–5], and the later one with $x \sim \frac{1}{5}$ for which the physical origin has been discussed in several possibilities. Also, scaling is observed in the $x \sim \frac{1}{3}$ growth regime, but breaks down after the growth switches to the $x \sim \frac{1}{5}$ growth regime.

Experiments were performed in an UHV chamber with a base pressure of $\sim 4.0 \times 10^{-11}$ Torr. The chamber contains HRLEED, Auger electron spectroscopy (AES), and a Cu evaporation source. The Cu(100) substrate, oriented within 0.2° to the (100), was cleaned by Ar^+ sputtering and then annealed at $\sim 500^\circ\text{C}$ for 5–10 min. After cleaning, no impurities were detected with AES. For the well-annealed Cu(100) surface, the average terrace width is estimated typically to be $\sim 550 \text{ \AA}$ from the full width at half maximum (FWHM) of the (00) LEED beam under conditions for which the scattering is out of phase from adjacent terraces separated by single-height steps. Temperature was measured with W-5%Re-W-26%Re thermocouple wires attached to two small holes near the edge of the Cu(100) surface.

Cu was deposited on the Cu(100) substrate with a fixed deposition rate of ~ 0.7 monolayer per minute

(ML/min) near room temperature. This homoepitaxial overlayer has the same orientation as the substrate. In the submonolayer range, individual LEED beams at out-of-phase conditions for single step height show a roughly square intensity band surrounding a central sharp spike. Figure 1 is an example of the (00) beam with such a shape shown in the cross section of a pseudo-three-dimensional plot at $k_{\perp}d=7\pi$ and coverage $\Theta\sim 0.42$ ML, where k_{\perp} is the momentum transfer perpendicular to the surface and $d=1.808$ Å is the single step height. The roughly square shape of the beam implies roughly square domains in the overlayer. This is probably due to the square unit mesh of the Cu(100) substrate on which the adatoms are registered. The well-resolved diffraction intensity band indicates a narrow distribution of either the width or separation of deposited Cu domains [10–12]. The central spike reflects the long-range order over the surface [12], and its FWHM is limited by the average terrace width of the substrate. When the coverage Θ increases through 0.5 to 1 ML, the central spike first reduces to zero at 0.5 ML, then recovers to an intensity equal to 82% of the zero-coverage intensity at 1 ML. The zero intensity of the central spike at 0.5 ML was used to calibrate the coverage with the fixed deposition rate. With increasing coverage, an oscillatory behavior of the central spike intensity is observed. However, the oscillatory amplitude is gradually damped over several monolayers. This implies an imperfect layer-by-layer growth mode for Cu grown on Cu(100) near room temperature at the given deposition rate, consistent with the previous observation for similar growth conditions [13]. Continuing deposition first makes the roughly square diffraction band become a circular ring, then the ring shrinks, and finally the diffraction beam develops a broad Lorentzian-like shape which is round about the central axis. Shown in Fig. 2 are the angular profiles of the (00) beam measured at both the in-phase and out-of-phase conditions after ~ 100 ML deposition near room temperature. At in-phase conditions ($k_{\perp}d$ =even integer multi-

ple of π), the profile exhibits a sharp instrument response function, whereas at out-of-phase conditions ($k_{\perp}d$ =odd integer multiple of π), the profile can be fit by a broad Lorentzian, where the in phase or out of phase is calculated using single step height. This indicates [14] that (1) even though the surface is rough, it is still single crystal, and (2) the continuing deposition with the imperfect layer-by-layer growth mode eventually leads to a morphology consisting of multilevel, roughly circular terraces of various sizes separated by monatomic steps. From the FWHM of the out-of-phase profile, the average terrace width is estimated to be ~ 30 Å in all directions. Similar behavior is also observed for other beams.

The roughened morphology just described provides the starting point for our study of smoothing kinetics. After ~ 100 ML deposition, the sample is quickly heated to and held at an elevated temperature where obvious evolution of the surface morphology occurs through diffusion. By measuring the FWHM and angular profile of the (00) beam as a function of time, we are able to determine the growth law of Eq. (1) and the scaling behavior. Plotted in Fig. 3(a) is $1/\text{FWHM}$ ($\sim L(t)/2\pi$) vs t in a log-log scale at the out-of-phase condition of $k_{\perp}d=7\pi$ for seven different annealing temperatures. Basically, the data can be divided into two power-law growth regimes. In the earlier growth regime, the exponent x in Eq. (1), extracted from the least-squares fit to the slopes of data as shown in solid lines, is in the range of $(0.29-0.31) \pm 0.01$ for temperatures 333–353 K. These values are in good agreement with Villain's predicted value of $\frac{1}{3}$ for kinetics driven by the line tension of curved step edges [3–5]. For temperatures $T \geq 360$ K, the slopes seem to gradually decrease. This decrease in x is due to the effect of the initial terrace width $L(t_0)$ just after the up-quench which is not negligible for $T \geq 360$ K. When this initial $L(t_0)$ is included, the $x = \frac{1}{3}$ growth law of Eq. (1) should read [5]

$$L^3(t) - L^3(t_0) = A(T)(t - t_0)^{3x} \quad (3x = 1 \text{ for } x = \frac{1}{3}), \quad (2)$$

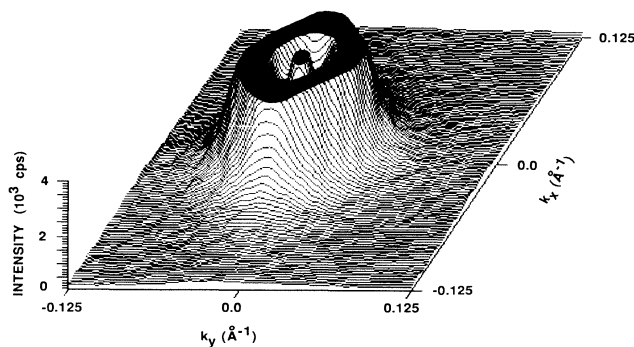


FIG. 1. A pseudo-three-dimensional plot of the (00) beam at $k_{\perp}d=7\pi$ diffracted from the Cu(100) deposited with ~ 0.42 ML Cu. The plot has been truncated at the 75% intensity level to reveal a cross section of the beam shape.

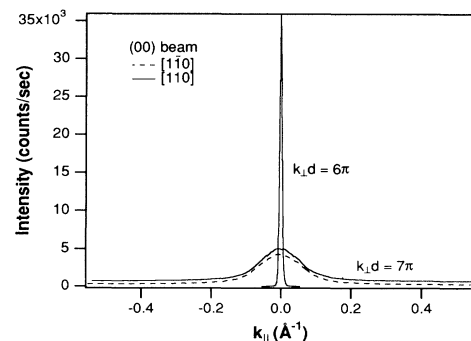


FIG. 2. The angular profiles of the (00) beam at both the in-phase and out-of-phase conditions from a rough surface of ~ 100 ML Cu deposited on the Cu(100) near room temperature. For $k_{\perp}d=7\pi$, the profiles scanned in two directions are shown, where the [110] profile is vertically offset for clarity.

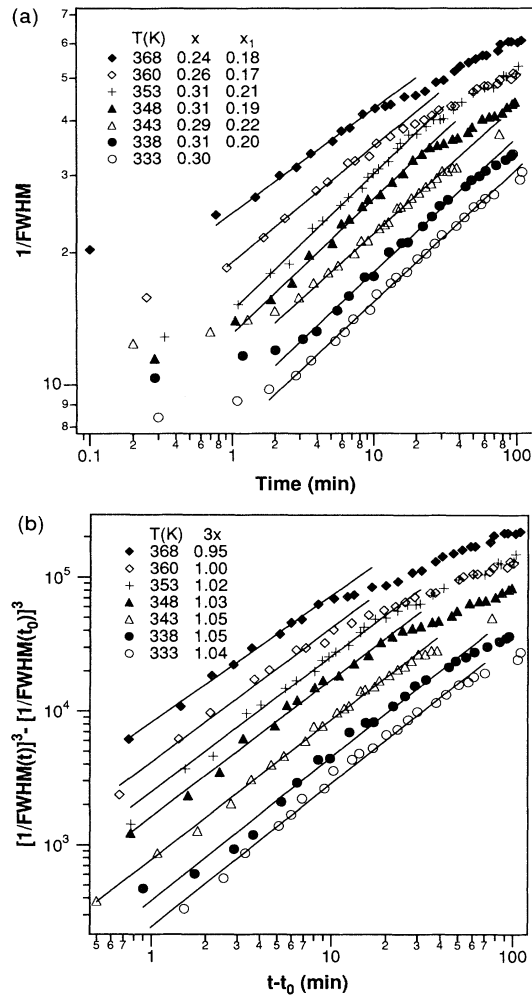


FIG. 3. (a) A log-log plot of $1/\text{FWHM}$ vs time t from the (00) beam at $k_{\perp}d=7\pi$ for different annealing temperatures. Two power-law growth regimes are distinguished: the earlier one with $x \sim \frac{1}{3}$ and the later one with $x_1 \sim \frac{1}{3}$. (b) The same data in (a) are replotted according to Eq. (2) with $L(t) \propto 1/\text{FWHM}$ and $3x \sim 1$ is extracted, where t_0 corresponds to the first data point in (a). In both (a) and (b), the solid lines are the least-square fits to the data in the earlier growth regime.

where $A(T) \propto (1/T)\exp[-(E_d + E_0)/k_B T]$ is a temperature-dependent factor [3], E_d is the activation energy for surface diffusion, and E_0 is the energy for an atom evaporated from a straight step edge onto the lower adjacent terrace. For the higher annealing temperatures, on the one hand, it takes more time to reach the desired temperature and on the other hand, diffusion is faster. Therefore, when the heating reaches the desired temperature, the initial terrace width $L(t_0)$ is already appreciable and cannot be neglected. In order to correct this initial effect, the data have been replotted in Fig. 3(b) in the form of Eq. (2), i.e., $[1/\text{FWHM}(t)]^3 - [1/\text{FWHM}(t_0)]^3$ vs $(t - t_0)$. In such a plot, the exponent $3x$ in Eq. (2), ex-

tracted for all temperatures in this earlier regime, are in the range $0.95-1.05 \pm 0.02$, consistent with $3x=1$ for $x = \frac{1}{3}$ in Eq. (2). This confirms that the $x \sim \frac{1}{3}$ growth is independent of the annealing temperature, and a trend of the decreasing value of x for $T \geq 360$ K in Fig. 3(a) is indeed due to the effect of initial $L(t_0)$ which is not negligible for those higher temperatures. From this example, it is apparent that neglect of initial conditions can lead to an incorrect interpretation. In addition, from the least-squares fit to our data [solid lines in Fig. 3(b)], the pre-factor $A(T)$ in Eq. (2) was obtained for all temperatures, which allows us to extract the energy $E_d + E_0 = 1.10 \pm 0.03$ eV through an Arrhenius plot of $\ln[TA(T)]$ vs $1/T$ in this earlier regime. The activation energy E_d for surface diffusion is determined to be ~ 0.28 eV in helium atom scattering [11] and ~ 0.40 eV in both thermal energy atom scattering [13] and low energy ion scattering [15], thus, E_0 must be in the range $0.82-0.70$ eV.

In the later growth regime, the exponent x_1 is determined to be in the range $0.17-0.22 \pm 0.01$, or roughly $\frac{1}{5}$, as listed in Fig. 3(a). We suggest several possibilities for this slower growth. (1) When the terrace width grows large enough, the step edges straighten so that the line-tension driving force is greatly reduced. In this case, the radius of large outer terraces may be nearly fixed since their change due to the atom flow from inner smaller-terrace edges can be negligible, while the topmost smaller terraces still shrink to disappear. Therefore, the change in diffraction now is only attributed to the expansion of topmost terraces which has been shown [6] to increase as $t^{1/5}$ and seems consistent with the values we measured. Also, this process will change the terrace width distribution and result in the breakdown of scaling. (2) The step-step repulsion driving force could become important after the line-tension driving force becomes weak. However, in this later regime, the average terrace width is already quite large, for example, for $T=368$ K, $L(t) \sim 2\pi/\text{FWHM} > 250$ Å. For such large step separation, the step-step interaction would not exist, and thus this possibility can be ruled out. (3) The entropic term in the surface free energy may become comparable to the excess free energy due to the line tension of curved step edges in this later regime. With a fixed internal energy, the surface free energy will be lowered by increasing the surface configurational entropy which promotes surface roughening. Therefore, the competition between the line tension and entropic driving forces could slow the smoothing process, and eventually will lead to terrace width distribution to an equilibrium distribution of the well-annealed surface, which will make the $x = \frac{1}{3}$ scaling break down. So far, there is no detailed theory to discuss this problem, and we hope that our work will stimulate theoretical interest.

In the following, we will examine the scaling behavior during the smoothing process. As is known, the line shape of a diffraction angular profile reflects the terrace

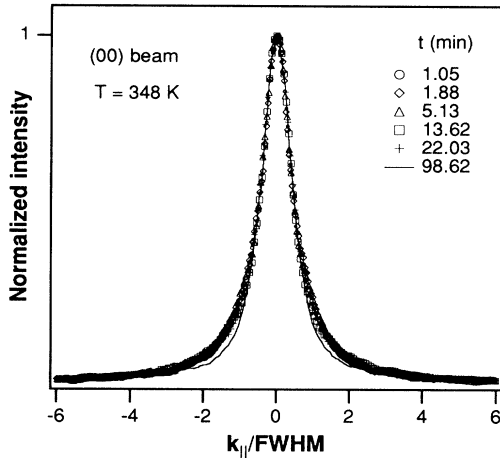


FIG. 4. The scaling profiles of the (00) beam at different growth times for the case of $T=348$ K, which represents the $F(z)$ in Eq. (3) with $z = k_{\parallel}/\text{FWHM}$.

width distribution. With scaling, the angular profile diffracted from a rough surface can be expressed in the form [16]

$$I(\mathbf{k}, t) = L^2(t)F(z) \propto I_p F(z), \quad (3)$$

where $F(z)$ is a scaling function with $z \equiv k_{\parallel}/\text{FWHM}$ independent of time, and the peak intensity I_p will be proportional to $L^2(t)$ if scaling exists. Equation (3) implies that if the normalized angular profiles, $I(\mathbf{k}, t)/I_p \propto F(z)$, are plotted against z , they should superpose on each other, i.e., independent of time, if scaling exists. Shown in Fig. 4 is such a plot for the case of $T=348$ K. As we can see, the profiles coincide with each other very well in the $x \sim \frac{1}{3}$ growth regime as compared to the data in Fig. 3. This indicates that scaling indeed exists in the $x \sim \frac{1}{3}$ growth regime due to the unchanged functional form of the terrace width distribution. Scaling can also be confirmed by checking whether $I_p \propto L^2(t)$ holds or not [16]. This can be done by substituting $L(t) \propto I_p^{1/2}$ into Eq. (2),

$$I_p^{3/2}(t) - I_p^{3/2}(t_0) \propto A(T)(t - t_0)^{3x} \quad (3x = 1 \text{ for } x = \frac{1}{3}). \quad (4)$$

In a log-log plot of $I_p^{3/2}(t) - I_p^{3/2}(t_0)$ vs $(t - t_0)$, we indeed obtained the exponent $3x$ very close to 1 in the range 0.91–0.99, confirming the existence of scaling. However, deviation from previous scaling profiles is observed after the growth matures to the $x_1 < \frac{1}{3}$ regime; see the solid curve in Fig. 4. This breakdown of scaling is understandable because of the change in terrace width distribution as discussed above.

In conclusion, using time-resolved HRLEED, smooth-

ing kinetics have been investigated on a surface consisting of multilevel, roughly circular terraces of various sizes separated by monatomic steps formed by depositing ~ 100 ML Cu on a Cu(100) substrate near room temperature. Smoothing upon annealing at elevated temperatures first follows at $t^{1/3}$ law for the average terrace width $L(t)$, in agreement with the prediction by Villain for the kinetics driven by the line tension of curved step edges. In this growth regime, scaling is observed. However, when $L(t)$ becomes large, growth switches to a $t^{1/5}$ law. Several possibilities for this slower growth have been discussed. Also, in this slower growth regime, breakdown of scaling occurred due to the change in the terrace width distribution.

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