Real-Time Measurements of the Deterministic Relaxation of an Initially Rough Si(111) Surface

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The smoothing of an initially scale-invariant, rough Si(111) surface was studied in real time using the high-resolution low-energy electron diffraction technique. At low annealing temperatures ($\leq$400 °C), the smoothing evolution shows a scaling behavior with a slow dynamics where the terrace width $L(t)$ grows as $\sim 1/\sqrt{\ln(t^{-1})}$. Consistent with the linear diffusion mechanism, the slow smoothing dynamics can be compared with that of the molecular beam epitaxial growth of Si/Si(111), where $L(t)$ decreases as $\sim 1/\sqrt{\ln(t)}$. At temperatures higher than 500 °C, the slower dynamics only occurs at the initial stage, which is followed by a faster evolution with $L(t) \sim t^{1/5}$, as driven by the line-tension force.

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Thin film growth processes can produce multilayer rough surfaces which exhibit scaling behaviors in both space and time [1]. The rough surface is a result of the competition between the surface diffusion-smoothing effect and the random fluctuation which is inherent in the growth processes and has amplitudes much greater than the thermal noise. The space scaling is shown by a scale-invariant height-height correlation function $\langle [z(\mathbf{r},t) - z(0,t)]^2 \rangle \sim r^{2\alpha}$, where $z(\mathbf{r},t)$ is the surface height of the planar position $\mathbf{r}$ and the exponent α describes surface roughness. Time scaling means that the surface roughness grows as $w \sim t^{\beta}$, where w is the interface width (root mean square surface height fluctuation, i.e., $w = \sqrt{\langle [z(\mathbf{r},t) - \langle z(\mathbf{r},t) \rangle]^2 \rangle}$). On the other hand, an initially rough surface can be smoothed below the roughening transition temperature through an annealing process. The key difference between an annealing process and a growth process is that random noise is negligible in an annealing process. Therefore, annealing is a deterministic process. The smoothing can be driven by the line tension of curved steps where straight step edges are thermodynamically more favorable [2,3]. The average terrace width during annealing was predicted to grow as $L(t) \propto t^{\chi}$, where the exponent χ varies from $\frac{1}{5}$ to $\frac{1}{3}$ depending on the models. The line-tension type of smoothing was observed recently on a Cu(100) surface [4]. In contrast to the above models applicable to smoothing processes driven by near-equilibrium forces, other studies concentrated on the far-from-equilibrium relaxation processes governed by deterministic Langevin equations [5]. In the past, deterministic models were applied to investigate surface diffusion [5–7] while recent theoretical studies [8,9] focused on the dynamic scaling behavior during annealing. In contrast to the growth case, the smoothing evolution exhibits a dynamic scaling depending on the initial scaling properties in the rough surface. So far, no experimental study has been reported on the dynamic scaling behavior in the annealing of initially scale-invariant surfaces. This experiment requires not only the monitoring of the morphology evolution in real time but also the preparation of an initially rough surface having space scaling properties.

In this Letter, we report on the experimental investigation on the smoothing of an initially scale-invariant, rough Si(111) surface using the high-resolution low-energy electron diffraction (HRLEED) technique [10]. At low annealing temperatures ($\leq$400 °C), the evolution shows a slow dynamics with the terrace width growing as $L(t) \sim 1/\sqrt{\ln(t^{-1})}$, which is consistent with a deterministic Langevin equation dominated by a linear diffusion mechanism. The relaxation process also demonstrates a dynamic scaling behavior that is comparable with that of the molecular beam epitaxial (MBE) growth of Si/Si(111). At temperatures higher than 500 °C, we found that the slow dynamics only occurs at the initial stage, which is followed by a faster evolution with $L(t) \sim t^{1/5}$. Such a faster relaxation towards equilibrium is believed to be driven by the line-tension force.

A rough Si(111) surface was prepared by *in situ* MBE growth of Si on a flat Si(111) surface at a temperature of 275 ± 5 °C, with a deposition rate of 8 ± 1 bilayer/min. The thickness of the deposited Si film ranges between 250 and 450 Å, where the growth-induced rough morphology was found to be scale invariant, as characterized by HRLEED. The steps in the Si(111) surface are predominantly biatomic (bilayer) steps. The detailed description of the growth experiment has been given elsewhere [11]. Immediately after the growth, the sample was quickly heated up to a fixed higher temperature within 2 min with overshooting less than 5 °C. The smoothing evolution of the surface morphology at different durations of annealing time t was monitored in real time by HRLEED.

During annealing, the (00) beam angular profiles of the HRLEED intensity distribution were measured along the $[\bar{1}\bar{1}2]$ direction as a function of time. Figure 1 shows time-dependent intensity line shapes at an annealing temperature 350 ± 3 °C. The data shown in Fig. 1(a) were taken at an electron beam energy $E = 50$ eV, corresponding to a near out-of-phase condition $k_{\perp}c \approx 7.23\pi$. $k_{\perp}$ is the diffraction momentum transfer perpendicular to the surface and c is the bilayer spacing (3.135 Å) of Si(111). Figure 1(a) shows a continuous narrowing of the intensity profiles during annealing. To quantitatively demonstrate

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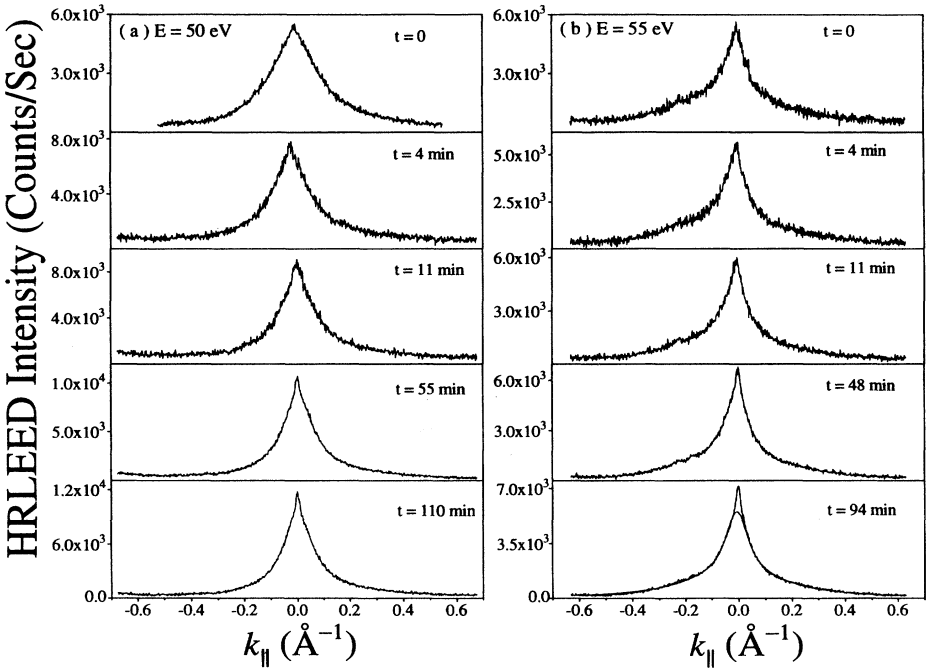

FIG. 1. Time-dependent angular profiles of the HRLEED (00) beam measured from a 10-min-deposited film annealed at 350 ± 3 °C. The incident beam is near the surface normal with a polar angle of 3.75° and an azimuthal scan along the $[\bar{1}\bar{1}2]$ direction. The data in (a) and (b) were taken at electron energies $E = 50$ and 55 eV, respectively, corresponding to $k_{\perp}c \approx 7.23\pi$ and 7.58π. To show the δ + diffuse characteristic, in (b) at $t = 94$ min, we plot the diffuse profile (a Lorenzian-like smooth curve) under the measured line shape. The δ component is the narrow peak near the maximum intensity of the line shape on top of the diffuse profile. The actual curve of the δ component, which has a FWHM of ~0.01 Å^{-1}, is not drawn here due to limited space.

such an evolution, in Figs. 2(a)–2(d), we plot the relationship between the annealing time t and the inverse of the full width at half maximum (FWHM) of the line shapes, at temperatures 550, 525, 500, and 400 °C, respectively. The corresponding FWHM is a measure of the average terrace width L, according to the relation [12] $L \propto 2\pi/\mathrm{FWHM}$. The increase of $2\pi/\mathrm{FWHM}$ shown in Fig. 2 thus indicates the growth of terrace size during annealing.

At temperatures higher than 500 °C, as shown in Figs. 2(a)–2(c), there exists two stages in which the terrace width slowly increases initially and then starts to grow more rapidly. The linear relationships in the log-scaled plots indicate that the growth proceeds in a form of power law $L(t) \propto t^{\chi}$, except that χ is different at different stages. For the initial stage, the slopes give $\chi \leq 0.07$. The second stage starts at $t = t_0$, so that the growth law $L(t) \propto t^{\chi}$ has to be replaced [2] by $L(t)^{1/\chi} - L(t_0)^{1/\chi} \propto t - t_0$. The data in Figs. 2(a)–2(c) can indeed be fitted by the equivalent expression $\mathrm{FWHM}(t) = \mathrm{FWHM}(t_0)[1 + A(t - t_0)]^{-\chi}$, where χ and A are adjustable parameters. The best fits give $\chi \approx 0.20 \pm 0.02$.

There are two existing models relevant to the dynamics of $t^{1/5}$ law, a step-step repulsion model [13] and a line-tension model [3]. Since the step repulsion model considers only the interaction between parallel straight steps, it is not suitable to describe a rough surface where most of step edges are neither straight nor parallel. In contrast, the line-tension model does not contradict our

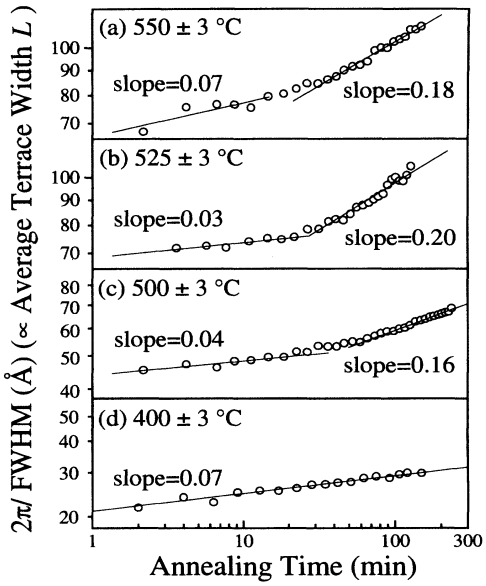

FIG. 2. The annealing time-dependent $2\pi/\mathrm{FWHM}$ or average terrace width L at different annealing temperatures, where the FWHMs of the (00) beam line shape were measured along the $[\bar{1}\bar{1}2]$ direction at $E = 50$ eV. Note the log-log scale. The uncertainty in the measurement is comparable with the size of the data points.

present observation. In this model, the topmost terraces shrink continuously due to the diffusion of their atoms to lower terraces as driven by line-tension force. The repetition of shrinking to vanishing of the top terraces leads to the formation of small top facets which grow as $t^{1/5}$.

So far, no model exists that can explain the observed slow dynamics region. This slow process occurs during the first 30 min for temperatures above 500 °C but is the only one at below 400 °C in the time interval studied. As shown in Fig. 2(d), fast growth does not occur and the surface is still relatively rough even after a long annealing time: $L \sim 30$ Å at 150 min as compared to $L \sim 22$ Å at 2 min. Such a slow dynamics involves a far-from-equilibrium process dominated by a relaxation mechanism different from the equilibrium line-tension force. Initially, the size of terraces in the rough surface is small and the step edges are more meandered and randomly shaped. The relaxation process tends to rearrange and smoothen the step shapes as driven by local atomic diffusion. The growth of the terraces is therefore slower. The line-tension driving force can become effective only when the step edges are smoothly shaped and the terrace sizes reach the critical size for nucleation, which is the case in the later stage for annealing at $T > 500$ °C.

To quantitatively understand the slow relaxation dynamics, we recall a continuous model for MBE growth, which is described by a type of Langevin equation [14]

$$\partial z(\mathbf{r},t)/\partial t = -\kappa\nabla^4 z(\mathbf{r},t) + \eta\,, \qquad (1)$$

where the ∇^4 term represents local diffusion with diffusion coefficient κ. η is white noise simulating random fluctuations during growth. Without the noise $\eta = 0$, Eq. (1) becomes a deterministic equation that models diffusion relaxation as proposed by Mullins [5]. Differing from the line-tension model, the relaxation in Eq. (1) relies on a local rule shown by the ∇^4 term. Equation (1) captures the essential features in surfaces that have strong chemical bonding (such as in Si), where surface atoms at low temperature can only relax to the nearby kink sites and, therefore, the relaxation proceeds in a slow manner.

The use of Eq. (1) was shown to be successful in our studies on both MBE growth [11] and ion-sputtering [15] processes. Assuming an infinitely large surface size and then solving Eq. (1) analytically using Fourier transform, we can calculate rigorously the height-height correlation function that combines the annealing ($t \geq 0$, $\eta = 0$) process and the initial MBE ($\eta \neq 0$) process that produces a rough surface before $t = 0$,

$$H(\mathbf{r},t) = \langle[z(\mathbf{r},t) - z(0,t)]^2\rangle \sim \int_0^{1/b_c} dq\,[1 - J_0(qr)]\,\frac{1 - e^{-2\kappa_g t_g q^4}}{q^3}\,e^{-2\kappa_a t q^4}, \qquad (2)$$

where $J_0(x)$ is the zeroth order Bessel function, t_g denotes the duration for initial MBE deposition, and b_c is the short length-scale cutoff with an order of the lattice constant. κ_g and κ_a are the diffusion coefficients for MBE and annealing processes, respectively. For the initial MBE-growth-induced rough surface ($t = 0$), Eq. (2) exhibits a dynamic scaling behavior [14,16]. The space scaling exists in short range, $H(\mathbf{r},0) \sim (r/L_g)^{2\alpha}$, where $\alpha = 1$ and $L_g \sim 1/\sqrt{\ln(t_g)}$. The time scaling can be shown as $w(0) \sim t_g^{\beta}$, with $\beta = \frac{1}{4}$. We will show in the following that, as the annealing proceeds ($t > 0$), Eq. (1) for $\eta = 0$ describes a novel slow dynamics which is consistent with that observed in our present experiment.

From Eq. (2), we obtain the mean-square step density or the mean-square slope

$$\langle(\nabla z)^2\rangle \sim \ln[(t + t_c + \tau)/(t + t_c)],$$

where $t_c = b_c^4/\kappa_a$. The time constant $\tau = \kappa_g t_g/\kappa_a$ depends on the deposition time as well as both the annealing temperature and the MBE growth temperature. Usually, the transient region $0 \leq t < t_c$ is short. We are more interested in the steady growth region $t \gg t_c$, where $\langle(\nabla z)^2\rangle \sim \ln(1 + \tau/t)$. Since $\sqrt{\langle(\nabla z)^2\rangle} \sim 1/L$, one has $L(t) \sim 1/\sqrt{\ln(1 + \tau/t)}$. Note that at $t_c \ll t \ll \tau$, the growth law becomes $L(t) \sim 1/\sqrt{\ln(\tau/t)}$, which implies that χ would be ~ 0 if one attempted to use a power law $L(t) \propto t^{\chi}$. To quantitatively examine this growth law, in Fig. 3(a), we plot the measured FWHM vs t at $E = 50$ eV for a low annealing temperature, 400 °C, where the two sets of data correspond to different initial conditions. The open squares represent the smoothing from an initially rougher surface prepared by 17-min Si deposition, whereas the open circles are from an initially less rough surface with 10-min deposition. The solid curves represent the fits using a form FWHM $\sim \sqrt{\ln(1 + \tau/t)}$, where the fitting parameter τ for the rougher case is about 1.10×10^4 min while for the less rough case, $\tau \approx 0.64 \times 10^4$ min. A similar plot at 350 °C (from the less rough surface) is shown in Fig. 3(b), where $\tau \approx 0.85 \times 10^4$ min. Note that the transient region was found negligibly short ($t_c < 0.5$ min) for all cases. It is concluded that the initial rough surface condition and annealing temperature can only change the time constant τ but cannot alter the growth law given by $L(t) \sim 1/\sqrt{\ln(\tau/t)}$.

The growth law for average terrace width only characterizes short-range relaxation. On the long-range scale, the smoothing evolution is characterized by the interface width w. From Eq. (2), we can obtain w in an explicit form

$$2w^2 \sim \sqrt{1 + t/\tau} - \sqrt{t/\tau}\,.$$

Such a novel long-range growth law can be readily tested in our experiment.

In general, the diffraction profile away from the out-of-phase diffraction conditions has a "δ + diffuse" type of line shape, as shown in Fig. 1(b), which is characteristic of diffraction from a rough surface having a finite interface width w [17]. w can be estimated from the ratio R of the integrated δ intensity to the total integrated intensity, based on the relationship [17] $R \approx e^{-w^2|k_\perp c - 2m\pi|^2}$ or $w^2 = -\ln(R)\,|k_\perp c - 2m\pi|^{-2}$, where m is an integer with $|k_\perp c - 2m\pi| \leq \pi$. In Fig. 4, we plot w^2 vs time at 350 °C from measured R with $|k_\perp c - 8\pi| \approx 0.42\pi$. It is found that w only reduces to ~ 5.0 Å after 113 min

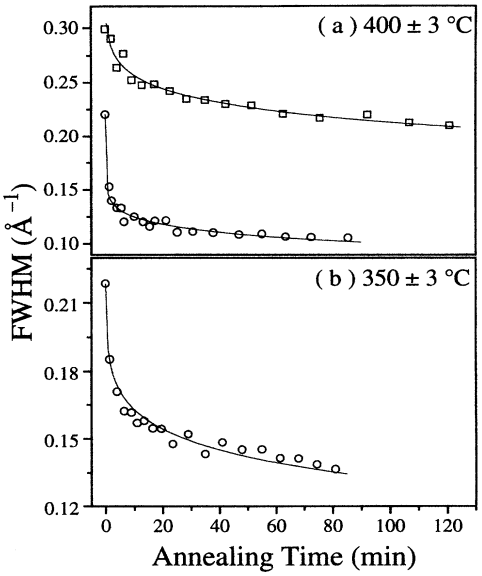

FIG. 3. The FWHM vs time for low annealing temperatures measured at $E = 50$ eV, where the open squares represent the smoothing from an initially rougher surface prepared by 17-min Si deposition, whereas the open circles are from an initially less rough surface with 10-min deposition. $t = 0$ denotes the moment at which the sample starts up quenching to an annealing temperature. The solid curves are fits based on the growth law FWHM $\sim \sqrt{\ln(1 + \tau/t)}$.

annealing, as compared with $w \sim 5.3$ Å for the initial rough surface. This indicates that, as a result of local atomic diffusion, the relaxation process on the long-range scale is very slow. The data in Fig. 4 (open circles) are fitted well by the growth law shown as the solid curve, where $w^2 = w_0^2(\sqrt{1 + t/\tau} - \sqrt{t/\tau})$, with $w_0 \approx 5.2$ Å and $\tau \approx 0.71 \times 10^4$ min.

From Eq. (2), we can show that space scaling exists in short-range scale, i.e., $H(\mathbf{r}, t) \sim (r/L)^{2\alpha}$, with $\alpha = 1$. For a surface described by $H(\mathbf{r}, t) \sim (r/L)^{2\alpha}$, we showed

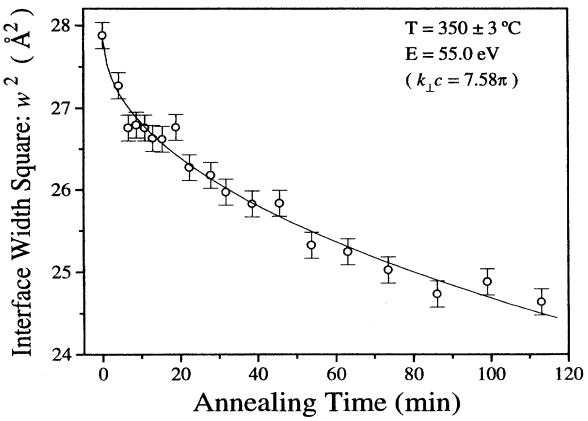

FIG. 4. w^2 vs time measured at 350 °C from a film with a 10-min deposition. The data were taken at 55 eV, corresponding to $|k_\perp c - 8\pi| \approx 0.42\pi$. The solid curve is a fit using the form $w^2 = w_0^2(\sqrt{1 + t/\tau} - \sqrt{t/\tau})$.

previously [17] that FWHM $\sim L^{-1}|k_\perp c - 2m\pi|^{1/\alpha}$. For the present experiment, we measured the FWHM of the diffuse profiles as a function of $k_\perp$ and found that for low annealing temperature ($T < 450$ °C), the relationship at any annealing time does agree with the power-law form $|k_\perp c - 2m\pi|^{1/\alpha}$, with $\alpha \approx 1$.

In conclusion, the slow relaxation process observed in the present experiment is consistent with Eq. (2), based on linear diffusion dynamics. The terrace width $L(t)$ grows as $\sim 1/\sqrt{\ln(t^{-1})}$. Such a slow dynamics is compared with the Si/Si(111) MBE process where the terrace width $L(t)$ decreases as $\sim 1/\sqrt{\ln(t)}$ in a similar temperature region. The space scaling behaves as $H(\mathbf{r}, t) \sim \ln(t^{-1})r^2$ for the annealing case, compared with $H(\mathbf{r}, t) \sim \ln(t)r^2$ for the growth case. On the long-range scale, the interface width during MBE growth exhibits a time scaling $w(t) \sim t^{1/4}$, while during annealing $w^2 \sim \sqrt{1 + t/\tau} - \sqrt{t/\tau}$, which, in the asymptotic case of $t \gg \tau$, recovers a scaling form $w(t) \sim t^{-1/4}$. Clearly, the relaxation proceeds in a comparable fashion with respect to the MBE growth, as a result from the same relaxation mechanism governed by Eq. (1). In our previous experiment [11], we found that, below 300 °C, the MBE growth induces a roughening evolution that exhibits a dynamics scaling behavior consistent with Eq. (1). The results from our present annealing process thus give new evidence that the ∇^4 term plays a key role in far-from-equilibrium processes.

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[1] For review, see *Dynamics of Fractal Surfaces*, edited by F. Family and T. Vicsek (World-Scientific, Singapore, 1990), and references therein.
[2] J. Villain, Europhys. Lett. **2**, 531 (1986).
[3] M. Uwaha, J. Phys. Soc. Jpn. **57**, 1681 (1988).
[4] J.-K. Zuo and J. F. Wendelken, Phys. Rev. Lett. **70**, 1662 (1993).
[5] W. W. Mullins, J. Appl. Phys. **28**, 334 (1957); **30**, 77 (1959).
[6] K. Yamashita *et al.*, Appl. Phys. **25**, 231 (1981).
[7] M. E. Keeffe *et al.*, Mater. Res. Soc. Symp. Proc. **237**, 205 (1992).
[8] J. Krug and H. Spohn, Phys. Rev. A **38**, 4271 (1988).
[9] J. G. Amar and F. Family, Phys. Rev. E **47**, 1595 (1993).
[10] U. Scheithauer *et al.*, Surf. Sci. **178**, 441 (1986); J.-K. Zuo *et al.*; Appl. Phys. Lett. **51**, 250 (1987).
[11] H.-N. Yang *et al.*, Phys. Rev. Lett. **73**, 2348 (1994).
[12] T.-M. Lu and M. G. Lagally, Surf. Sci. **120**, 47 (1982).
[13] M. Ozdemir and A. Zangwill, Phys. Rev. B **42**, 5013 (1990).
[14] D. E. Wolf and J. Villain, Europhys. Lett. **13**, 389 (1990); Z.-W. Lai and S. Das Sarma, Phys. Rev. Lett. **66**, 2348 (1991); L.-H. Tang and T. Nattermann, *ibid.* **66**, 2899 (1991); A. Zangwill *et al.*, Surf. Sci. **274**, L529 (1992).
[15] H.-N. Yang *et al.*, Phys. Rev. B **50**, 7635 (1994).
[16] J. G. Amar *et al.*, Phys. Rev. E **47**, 3242 (1993).
[17] H.-N. Yang, T.-M. Lu, and G.-C. Wang, *Diffraction From Rough Surfaces and Dynamic Growth Fronts* (World-Scientific, Singapore, 1993).