Dynamics of Rough Ge(001) Surfaces at Low Temperatures

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Mass transport by surface diffusion on rough Ge(001) surfaces is characterized using *in situ* scanning tunneling microscopy. Rough starting surfaces with nearly constant step densities are prepared by low-energy ion etching at 270 °C; the characteristic in-plane length scale of the roughness is varied from 37 to 118 nm. These surfaces are subsequently annealed at 245–325 °C for times between 10 min and 6 h and imaged at room temperature. The activation energy for surface smoothing is 1.9 ± 0.25 eV. The dependence of the relaxation rate on the in-plane length scale is inconsistent with the continuum model of Mullins: the time constant τ of the smoothing process increases with increasing lateral length scale L as $\tau \propto L^n$, $n = 2.2 \pm 0.4$. [S0031-9007(96)00204-9]

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The dynamics of crystalline surfaces has been a topic of continued interest for more than four decades [1,2]. Recently, the shrinking scale of microelectronic devices and the need to control the morphology of epitaxial interfaces have provided a strong technological impetus for developing a deeper understanding of surface dynamics on nanometer length scales. Mass transport by surface diffusion also plays a critical role in the synthesis of semiconductor nanostructures by growth on nonplanar substrates [3], pattern formation during low temperature epitaxy [4,5], and the self-assembly of monodisperse islands in strained-layer epitaxy.

To study the dynamics of mass transport on a semiconductor surface on nanometer length scales, we use scanning tunneling microscopy (STM) to quantify the relaxation of multilayer roughness on Ge(001) surfaces following thermal annealing. The in-plane length scale of the roughness is controllably varied from 37 to 118 nm, extending earlier work on semiconductor surfaces to a much smaller lateral length scale and therefore lower temperatures than have been studied previously.

A complete theoretical description of the relaxation of rough surfaces at temperatures below the roughening transition does not currently exist [6]. Understanding the dynamics of morphology evolution requires an understanding of the thermodynamic driving force and the mechanism of mass transport. The connection between surface morphology and surface chemical potential was first described by Herring [1]. While the application of Herring's work by Mullins [2] is rigorously valid only for describing the relaxation of surface roughness at temperatures above the roughening temperature $T > T_R$, Mullins' description is known to be in good agreement with experiments [7] on the smoothing of micron-sized features on Si produced by photolithography. Extensions of the Herring-Mullins approach to $T < T_R$, as discussed by Rettori and Villain [8] and by Ozdemir and Zangwill [9], begin with the thermodynamic free energy of a crystal facet. Other theoretical efforts have emphasized the importance of step curvature on the chemical potential of the steps, and the possibility that the smoothing kinetics are determined by the mobility of steps rather than the mobility of point defects such as adatoms or vacancies [10,11]. Little consensus exists regarding which of these approaches best describes surface dynamics at low temperatures and on small length scales.

The relaxation of rough surfaces at low temperatures has recently been reported for Cu(001) [12], TiO_2(001) [13], and Si(111) [14] using high-resolution electron diffraction, a real-time probe that is complementary to our "quench-and-look" studies. These diffraction studies yield the rms surface roughness and the average terrace size within the coherence width of the electron source; the decay of the surface roughness and the growth of the average terrace size typically follows a weak power law dependence on annealing time t^α, with $0.2 < \alpha < 0.33$. We believe that the interpretation of these power laws is greatly complicated by the fact that the variation of the step density in the plane of the surface, i.e., the lateral characteristic length scale of the roughness, is essentially unknown. Using STM, we measure the height of the surface with high spatial resolution over large lateral length scales, and therefore the STM data provide a nearly complete description of the surface morphology. A unique aspect of our experiments is our ability to produce starting surfaces with different characteristic in-plane length scales L but nearly constant average step densities [15]. These starting surfaces give us a way of quantifying the dependence of smoothing kinetics on L for $L \sim 100$ nm.

The Ge(001) samples are typically 1.5×1.5 cm^2 and are In bonded to a Mo plate that is subsequently attached to a 3.5 in. diameter Mo sample block using alumina spacers for thermal isolation. After sample introduction, the entire sample block is outgassed at 600 °C for 3 h. During ion etching and annealing, the sample is heated by electron beam bombardment of the Mo backing plate. Temperatures are measured using infrared pyrometry in a wavelength band near 5 μm with a precision of ±5 °C. The pressure in the chamber is $\sim 8 \times 10^{-10}$ torr during annealing; the dominant components of the residual gases are H_2 and CO + N_2.

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To prepare the starting surfaces, we first ion etch the Ge crystal for 1 h at 430 °C. The relatively high temperature of this preparation method creates a nearly ideal starting surface with large terraces separated by atomic-height steps. The average terrace width is ~100 nm and reflects the miscut of the Ge crystal, ~0.1° in the ⟨100⟩ direction. The surface is then etched by 240 eV Xe ions at a sample temperature of 270 °C to produce multilayer surface roughness. Etching times of 10, 42, or 180 min are used to produce surface morphologies with characteristic in-plane length scale L of 37, 65, and 118 nm, respectively. The roughening of Ge(001) by low-energy ion etching has been studied by x-ray reflectivity [16] and STM [15].

After ion etching, the surface is annealed at various temperatures and times; ≃40 sec is needed to heat a sample from 270 to 295 °C, and ≃70 sec from 270 to 325 °C with 5 °C overshoot. Cooling rates of the samples are $\simeq 1\ ^\circ\mathrm{C\,sec}^{-1}$ at 325 °C and $\simeq 0.3\ ^\circ\mathrm{C\,sec}^{-1}$ at 245 °C. Samples are then moved to the STM and imaged at room temperature.

To quantify the roughness, we evaluate the height difference correlation function [6], $G(\rho) = \langle (h_j - h_i)^2 \rangle$, and the height-height correlation function $H(\rho) = \langle h_j h_i \rangle$ where h_j and h_i are the heights of the surface at two locations labeled by i and j separated by a distance ρ. The brackets signify an average over pairs of points i, j separated by ρ. $G(\rho)$ is related to $H(\rho)$ by $G(\rho) = 2\langle W^2 \rangle - 2H(\rho)$ where $\langle W^2 \rangle = \langle (h_i - \langle h_i \rangle)^2 \rangle$. STM images with scan areas of 720 × 720 nm^2 are used to calculate $G(\rho)$ and $H(\rho)$.

$G^{1/2}(\rho)$ for our three rough starting surfaces are shown in Fig. 1(a). A measure of the average step density is given by $G^{1/2}(\rho)/\rho a$ in the limit of small ρ where a is the step height. The data shown in Fig. 1(a) show that the average step density of the three rough surfaces is nearly identical. We define a characteristic in-plane length scale L by the position ρ of the first local maximum in $H(\rho)$ [see Fig. 1(b)]; L corresponds to the separation or repeat distance between dominant features in the surface morphology. Consistent with our observation that the average step density is nearly constant, the amplitude of the surface roughness as measured by $G^{1/2}(L/2)$ increases nearly linearly with L. $G^{1/2}(L/2)$ is 0.32, 0.50, and 0.80 nm for $L = 37$, 65, and 118 nm, respectively, giving a power law of $G^{1/2}(L/2) \propto L^{0.8}$. The reproducibility of both the vertical roughness and in-plane length scale is better than 10%. For example, three separate samples of the $L = 37$ nm surface gave $L = 37 \pm 3$ nm and $G^{1/2}(L/2) = 0.32 \pm 0.03$ nm.

Example STM images of an annealing experiment are displayed as Fig. 2. The starting surface with $L = 65$ nm is shown in Fig. 2(a)—Figs. 2(b)–2(d) are for surfaces annealed at 270 °C for 20 min, 1 h, and 6 h. Higher magnification images show that all of the surfaces are made up of narrow (001) terraces separated by atomic-height steps. Individual terraces are clearly observed in Figs. 2(b)–2(d).

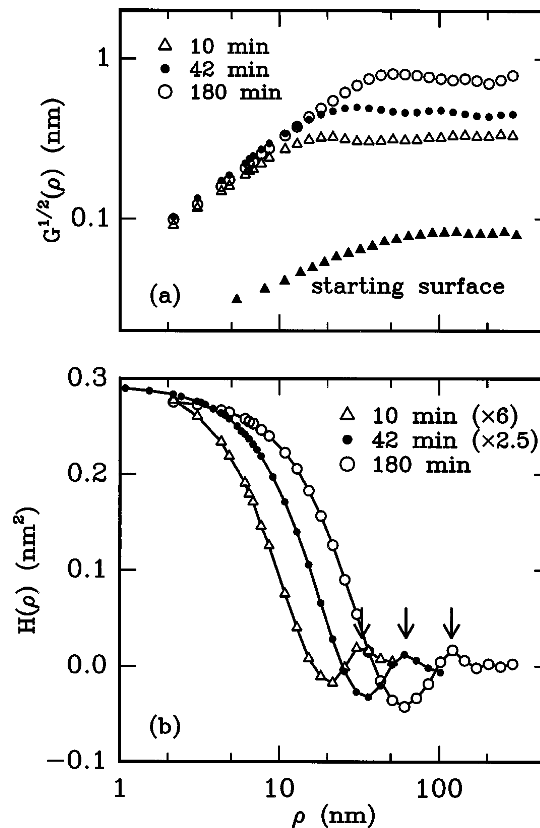

FIG. 1. (a) Square root of the height difference correlation function for the three rough starting surfaces, etching times of 10 min, 42 min, and 3 h corresponding to $L = 37$, 65, and 118 nm, respectively. Data for the initial flat surface are shown for comparison. (b) The height-height correlation function for the three rough starting surfaces shown in (a).

The activation energy for surface smoothing is found by analyzing the relaxation of the $L = 65$ nm starting surface as a function of annealing temperature. Empirically, we have found that the evolution of $G(\rho, t)$ can be described to a good approximation as $G(\rho, t) = f^2(t/\tau)G(\rho, 0) + G_f(\rho)$, where G_f describes the roughness of a surface following a relatively high temperature, long time anneal, 325 °C for $t = 6$ h. Since the largest ratio of $G(\rho, 0)/G_f(\rho)$ occurs at a lateral length scale near $\rho = L/2$, we use the time dependence of $G(L/2, t)$ to extract $f(t/\tau)$. Quantifying the activation energy for the decay time constant τ does not require an exact functional form for $f(t/\tau)$, but we have found that a power law of the form $f(t) = (1 + t/\tau)^{-1/2}$ describes the decay of the roughness quite well (see Fig. 3).

Figure 3(a) shows the relaxation of the surface roughness, as measured by $G^{1/2}(L/2, t)$, for the $L = 65$ nm starting surfaces as a function of both time and temperature. Each data point in Fig. 3 constitutes a complete cycle of experiments: preparation of a flat surface at elevated temperature, roughening the surface by etching at 270 °C, annealing, and imaging by STM at room temperature. Assuming that τ is thermally activated, $\tau = \tau_0 \exp(E_a/k_B T)$, E_a and τ_0 are adjusted to simultaneously obtain the best

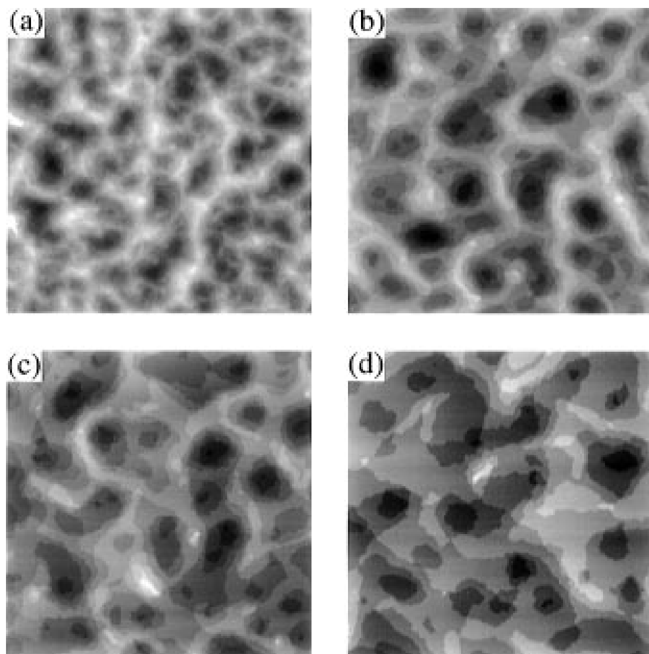

FIG. 2. STM images of Ge(001) following (a) etching at 270 °C for 42 min corresponding to 32 monolayers etched from the surface; (b) subsequent annealing at 270 °C for 20 min; (c) 1 h; and (d) 6 h. All scan areas are 360×360 nm^2. Black-to-white grey scales in (a)–(d) are 2.11, 1.6, 1.32, and 0.84 nm.

fit at $T = 245$, 270, and 325 °C. We obtain $E_a = 1.9 \pm 0.25$ eV and $\tau_0 = 3 \times 10^{-15\pm2}$ s.

Our value of E_a can be directly compared to data by Blakely and co-workers [7] on the decay of micron-sized 1D sinusoidal profiles on Si(001), $E_a = 2.3 \pm 0.2$ eV. The ratio of the activation for surface smoothing on Ge(001) (this study) to that of Si(001) (Ref. [7]) is $1.9/2.3 = 0.83$; we note that the ratio of the activation energy for sublimation of Ge and Si has a similar value [17]. E_a is usually interpreted as the sum of the formation energy E_f of the surface point defect that dominates mass transport on the surface and the energy barrier for surface migration E_m of the defect $E_a = E_f + E_m$. While the activation energy for diffusion of single adatoms [18] is $E_m^{\text{adatom}} \simeq 0.67$ eV and for dimers [19] $E_m^{\text{dimer}} \simeq 1.0$ eV, we are unaware of any measurement of the formation energies of these surface species.

To determine the dependence of τ on the in-plane length scale of the surface roughness L, we study the relaxation of the three rough starting surfaces with $L = 37$, 65, and 118 nm at a fixed annealing temperature $T = 270$ °C [see Fig. 3(b)]. Here, we assume that the time constant of the smoothing process $\tau \propto L^n$ and adjust n to obtain the best fit to all of the data. We find $n = 2.2 \pm 0.4$.

If the continuum model of Mullins applied to our experiments $n = 4$ is expected, an exponent that we believe lies outside our experimental uncertainties. Therefore, we must consider other models to describe our experiments. Theoretical descriptions of the relaxation of surface roughness at $T < T_R$ can be classified as either "diffusion limited" or "step-mobility limited." In a diffusion-limited model, the rate-limiting step for mass transport is the diffusion of surface defects across each terrace; in a step-mobility-limited model, the creation or annihilation of surface defects at step edges is the rate-limiting step.

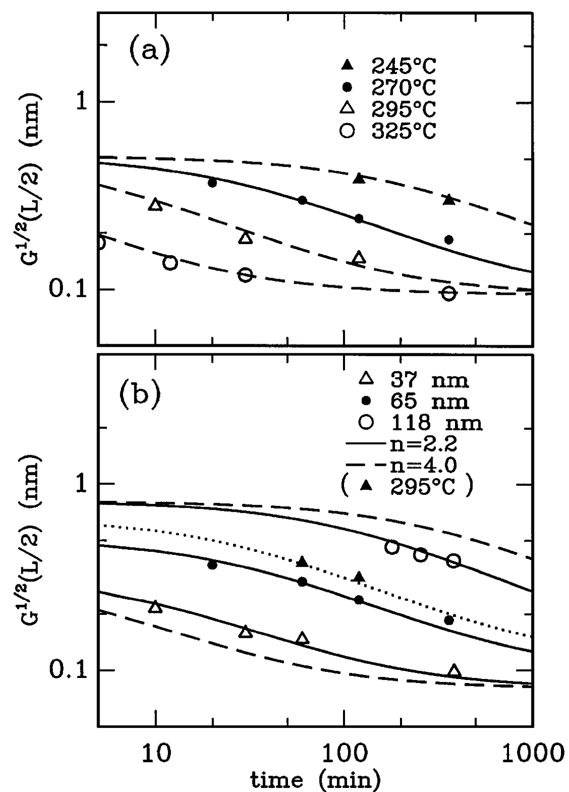

FIG. 3. (a) Decay of the surface roughness as measured by $G^{1/2}(L/2)$ as a function of temperature for the $L = 65$ nm starting surface. Dashed lines show scaling by an activation energy of 1.9 eV. (b) Decay of the surface roughness as a function of lateral length scale L for an annealing temperature $T = 270$ °C; $L = 37$ nm (open triangles), $L = 65$ nm (filled circles), $L = 118$ nm (open circles). Assuming $\tau \propto L^n$, the solid line shows the calculated decay using $n = 2.2$; the dashed line is calculated using $n = 4.0$. The filled triangles are additional data for a surface with $L = 118$ nm and $z_0 = 0.65$ nm annealed at $T = 295$ °C; the dotted line is the predicted relaxation curve for this surface based on the scaling $\tau \propto L^2(L/z_0)^2$, and an activation energy of 1.9 eV.

Diffusion-limited models [8,9] predict that the lifetime τ of a 1D surface morphology should scale as $\tau \propto L^5/z_0$, where L is the lateral length scale of the morphology and z_0 is the initial amplitude of the surface roughness. For a 2D morphology, $\tau \propto L^3 z_0$. Since our three rough starting surfaces have $z_0 \propto L^{0.8}$, these diffusion-limited models also predict $n \simeq 4$.

Step-mobility-limited models can be further broken down into two classifications: "conserved" or "nonconserved" [20]. This terminology refers to the *local* conservation of mass—transport is said to be conserved if a surface defect generated at a step edge eventually annihilates at the same step or at one of the two adjacent steps. Thus, the motion of adjacent steps is coupled. Based on

these assumptions, the 1D model of Nozières [10] predicts $\tau \propto L^4$, independent of z_0 [21]. In a "nonconserved" model, the motion of adjacent steps is uncorrelated; i.e., surface defects generated at a step edge can annihilate at *any* step edge on the surface. Uwaha [11] has considered this case and found $\tau \propto L^2(L/z_0)^2$; i.e., for our experiments Uwaha predicts $\tau \propto L^{2.4}$ (since $z_0 \propto L^{0.8}$), in good agreement with our observations.

Since Uwaha's presentation [11] is more general than we require, we rederive his result (in a slightly altered form) and summarize the assumptions of this model. The step chemical potential is defined by $\zeta = dE/dn$, where E is the surface free energy per unit area and n is the step density. For a 1D morphology, and to second order in n, $\zeta = \beta + \gamma n^2$ where β is the free energy per unit length of a single step and γ describes the strength of step-step interactions. The step velocity v is given by $v = -\eta d\zeta/dx$, where η is the step mobility [22].

To obtain an expression for the surface velocity $\partial z/\partial t$, we replace the step density n by the spatial derivative of the surface height $z_x = \partial z/\partial x$ and the height of a single step a: $|z_x| = an$. Since $\partial z/\partial t = -van$,

$$\partial z/\partial t = (2\eta\gamma/a^2)z_x^2\partial|z_x|/\partial x\,. \qquad (1)$$

We can then examine the time evolution of the shape-preserving solution by separating variables, $z(x,t) = u(x)\omega(t)$, where $u(x)$ is the profile of the shape-preserving solution, and $\omega(t)$ describes the time evolution. The ordinary differential equation for ω, $d\omega/dt = -\alpha\omega^3$, yields a power law solution, $\omega(t) = (1 + t/\tau)^{-1/2}$, which is the functional form we use to fit the relaxation data. Furthermore, using dimensional analysis, $z_t \sim z_0/\tau$, and $z_x \sim z_0/L$, we find $\tau \propto L^2(L/z_0)^2$ as discussed above.

As an additional test of the model, we prepared a starting surface (by etching at a higher temperature, 295 °C) with the same in-plane length scale $L = 118$ nm as one of the previous surfaces, but a smaller roughness amplitude $G^{1/2}(L/2) = 0.65$ nm. This surface was annealed at 295 °C; the data are plotted in Fig. 3(b) as filled triangles. The dotted line shows the predicted relaxation behavior (with no adjustable parameters) using the scaling relationship $\tau \propto L^2(L/z_0)^2$ and an activation energy of 1.9 eV. The good agreement gives us further confidence that the proposed dependence of τ on z_0 correctly describes the experiments.

The agreement of Uwaha's model with the data may be fortuitous, particularly considering the complex step structures we observe. For example, highly anisotropic, elongated terraces are formed when adjacent regions of the 2×1 reconstruction are shifted relative to one another, and the resulting antiphase boundary restricts the motion of steps. Antiphase boundaries are also formed during low temperature epitaxial growth of Si(001) [23] and are therefore a common feature on Si(001) and Ge(001) prepared by low temperature processes. The presence of antiphase boundaries, however, apparently has a relatively weak effect on the activation energy for surface smoothing. Activation energies determined in previous studies of step relaxation on Si(001) [24] ($E_a = 2.2 \pm 0.3$ eV) and the decay of micron-sized 1D profiles on Si(001) [7] ($E_a = 2.3 \pm 0.2$ eV) are similar to our results for Ge(001) despite the absence of antiphase boundaries in the Si(001) experiments [7,24].

Finally, we emphasize what we believe is the most important conclusion of this work. While the continuum model of Mullins [2] adequately describes the relaxation of surface roughness on micron length scales, the Mullins approach does not describe our low temperature, nanometer-scale annealing experiments [see, in particular, Fig. 3(b)]. The nonconserved, step-mobility-limited model of Uwaha [11] may provide a first approximation to a more complete theory for the surface dynamics of nanostructured semiconductor surfaces.

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