Step Capillary Waves and Equilibrium Island Shapes on Si(001)

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From low-energy electron microscopy measurements of step fluctuations and equilibrium 2D island shapes on Si(001), we determine the temperature dependence of the S_A and S_B step edge stiffnesses, free energies, and mobilities. A capillary wave analysis of step stiffnesses is in quantitative agreement with the 2D island shapes, demonstrating the direct relation between equilibrium thermal fluctuations and equilibrium structure. The analysis also suggests that step free energies vanish at ~1200 °C, providing direct evidence for a roughening transition. The combined exploration of step dynamics and equilibrium island shapes yields new insight into the basic thermodynamics of Si(001).

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The properties of atomic steps play an important role in determining the equilibrium morphologies of surfaces and the dynamics of processes such as crystal growth and surface faceting [1,2]. With advances in electron microscopy one can now analyze fluctuations of step edges for information on step stiffness and mobility and on the atomic transport mechanisms that mediate surface equilibration [3,4]. In principle, the same processes which govern the step fluctuations also govern how steps are arranged on the surface. For example, as we discuss here, the magnitude of equilibrium step edge fluctuations is directly related to the equilibrium shape of 2D islands on the surface. This relation has not been previously explored experimentally. Here we use low-energy electron microscopy (LEEM) to study step fluctuations and 2D equilibrium shapes on Si(001). We find that there is quantitative agreement between these two experimentally observable manifestations of step stiffness and free energy, showing the usefulness of the basic capillary wave theory of step fluctuations. In performing this work we have made use of the crystallographic anisotropy of the (100) surface of Si, which allows the comparison of two distinctly different types of steps, S_A and S_B.

The quantitative values extracted from our observations suggest that the step free energies approach zero at ~1200 °C, implying the presence of a surface roughening transition at this temperature. Indeed, roughening of the surface at this temperature has been observed in previous LEEM [5] and reflection electron microscopy experiments [6]. The possibility that this is a thermodynamic transition is a plausible alternative to previous suggestions that the roughening is a kinetic effect [5,6]. Usually a surface roughening transition is inferred from the scattered beam profiles in x-ray, electron, or atom diffraction experiments. To our knowledge this is the first time that the increased step fluctuations due to a vanishing of the step free energy (the defining criterion of a roughening transition [7]) have been directly quantified. Thus, the direct correlation of dynamic phenomena (step fluctuations) with equilibrium structural information (2D island shape) yields new insight into the basic thermodynamics of the Si(001) surface.

The LEEM used in these studies is described in Ref. [8]. The Si(001) surface studied in this paper was prepared by the usual procedure of repeatedly flashing to 1200 °C for several seconds. Sample LEEM images of the studied region are shown in Fig. 1. The terraces alternate from black to white because of the 90° rotation of the (2 × 1) reconstruction across the single-atomic-layer-height steps. The average terrace width in the studied region was 1300 Å.

Crystals were heated by electron bombardment from the rear. The temperature was measured using an optical pyrometer. Ten video sequences of the surface were recorded from 640 to 1210 °C. The analyzed sequences typically lasted 2 min (less at higher T). The temperature changed by less than 10 °C during this time. More than 35×10^6 step edge positions were marked during this study [9]. Below 1100 °C, overall motion due to sublimation was not detectable (i.e., step speeds were smaller than one average terrace width, 1300 Å, per minute). At 1170 °C, the sublimation rate is about 0.12 monolayer/sec. Islands were

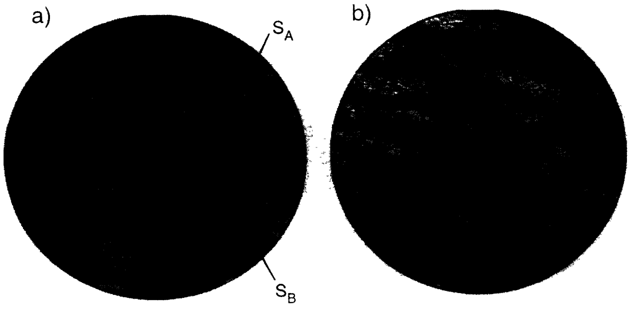

FIG. 1. LEEM images of Si(001) at (a) 860 °C and (b) 1210 °C. At 860 °C, S_A steps are much smoother than S_B steps. At 1200 °C, both types of step edges are rougher, and the difference between the steps is smaller. The field of view is 4 μm; the image was formed by using the $(\frac{1}{2},0)$ LEED beam at about 3.5 eV energy.

formed by room temperature deposition of Si, followed by island ripening at elevated temperature.

To analyze the step fluctuations, we follow the approach of Ref. [4]: If the step edge position as a function distance y along the step edge is $x(y,t)$, we define the Fourier components $x_q(t)$ by $x(y,t) = \sum_q x_q(t) \exp(iqy)$ and measure the correlation functions $G_q(t - t') = \langle |x_q(t) - x_q(t')|^2 \rangle$. We fit these correlation functions to

$$G_q(t) = A(q)\{1 - \exp[-t/\tau(q)]\}. \qquad (1)$$

Equipartition of energy among the capillary modes of the steps predicts [10] that

$$A(q) = 2kT/L\tilde{\beta}q^2, \qquad (2)$$

where L is the length of the analyzed step, and the step edge stiffness $\tilde{\beta}$ is related to the step free energy $\beta(\theta)$ through $\tilde{\beta}(\theta) = \beta(\theta) + d^2\beta/d\theta^2$.

Equation (2) in principle allows the step edge stiffnesses to be deduced from the Fourier amplitudes of the capillary waves. In determining the stiffnesses from these amplitudes, it is important to use only wave numbers which have time constants sufficiently small that the corresponding modes are in equilibrium. This restriction is increasingly important at lower temperature. In addition, the fluctuations must occur on time scales slower than video rates; otherwise, the fitted amplitudes are anomalously small because of temporal averaging. This problem limits the wavelengths that can be studied at high temperature. These constraints emphasize the importance of making *dynamic* observations of step motion, so that the time constants can be measured. We restricted our amplitude analysis to time constants in the range 5 to 0.1 sec. The inverse of the amplitude, $A^{-1}(q)$, within this range of time constants is plotted vs q^2 in Fig. 2 for several different step edges at 860 °C. As predicted by Eq. (2), the plots are approximately linear. The slopes give the stiffnesses. (The small intercepts can be interpreted in terms of the step-step interactions [9].) At this temperature, S_A steps are about 7 times as stiff as the S_B steps.

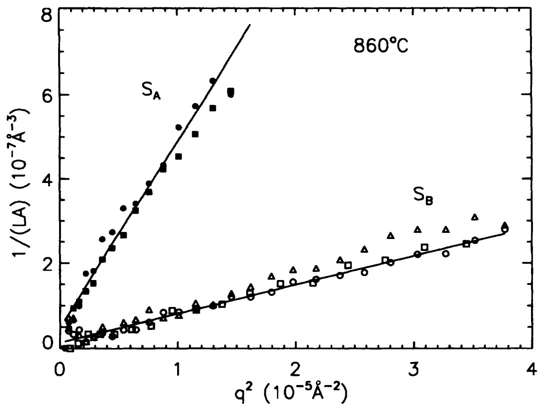

FIG. 2. The inverse of the amplitude of the step capillary fluctuations plotted vs q^2 at 860 °C. Each different symbol corresponds to a different step edge: solid symbols correspond to S_A steps; and open symbols correspond to S_B edges. Using Eq. (2), the slopes of the lines give the step edge stiffnesses at this temperature to be $0.013kT$/Å and $0.09kT$/Å for the S_B and S_A steps, respectively.

Figure 3 shows the temperature dependence of the S_A and S_B step edge stiffnesses, respectively, determined from plots such as Fig. 2. The ratio of the stiffnesses drops dramatically by about a factor of 5 in the studied temperature range. Since the anisotropy in step free energies which determine the step stiffnesses also governs the equilibrium shape of islands, an *independent* measurement of the ratio of the step stiffnesses can be obtained from measurement of the shapes of islands grown on large terraces [11]. Figure 4 shows how the shapes of these islands vary with temperature. The measured aspect ratio changes from about 0.39 at 700 °C to 0.685 at 1100 °C. The observed ratios at low temperatures are consistent with the range of 1/3 to 1/2 observed with scanning tunneling microscopy (STM) at room temperature by Mo *et al.* [12] and the 1/2.6 ratio observed previously with LEEM during growth at 530 °C [13]. The high-temperature ratios are consistent with the value of 0.7 to 0.8 observed for sublimation holes by reflection electron microscopy [6,14]. The ratios are much different from the 1:15 ratio expected at zero temperature on the basis of tight-binding calculations [15].

When the kink energy is comparable to the temperature, exact calculations of the equilibrium crystal shape of 2D islands for the anisotropic 2D Ising model [16] and the body centered solid on solid model [17] show that the islands are essentially elliptical. Figure 4 shows that at all studied temperatures deviations from ellipses are negligible. Given the elliptical shape, the ratios of step free energies from the two measurements can be compared directly. From the Wulff construction of equilibrium shapes [18], the step free energies β_A and β_B are directly proportional to the length of the corresponding semiaxes: $\beta_{A,B} = \lambda R_{A,B}$, where λ is a constant. In equilibrium the Gibbs-Thomson chemical potential, the stiffness multiplied by the step

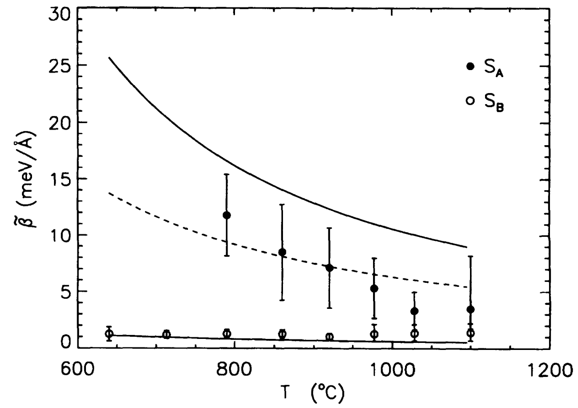

FIG. 3. The temperature variation of the S_A and S_B step stiffnesses as deduced from the capillary fluctuations of the steps in the manner shown in Fig. 2 are shown by solid and open symbols, respectively. The solid lines show the prediction for the stiffnesses using Swartzentruber kink energies; the dashed line shows the results of the modified model discussed in the text.

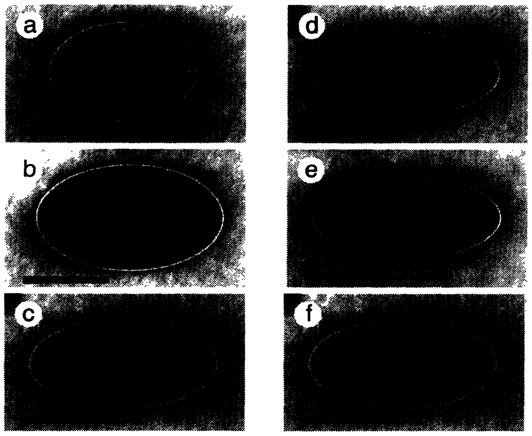

FIG. 4. The evolution of equilibrium island shapes on Si(001) with temperature: (a) 1060 °C; (b) 1010 °C; (c) 960 °C; (d) 860 °C; (e) 800 °C; and (f) 750 °C. The white lines are fits to ellipses, from which the data points in Fig. 5 were deduced. In (a), R_A and R_B indicate the semiaxes of the ellipse.

curvature, is equal to λ everywhere along the island edge [10]. The curvatures of an ellipse in the two principal directions are equal to $R_{A,B}/R_{B,A}^2$. The constraint of constant chemical potential then implies that $\tilde{\beta}_{A,B} = \lambda R_{B,A}^2/R_{A,B}$. Thus, the step free energies can be computed from the stiffnesses using

$$\beta_{\mathrm{A,B}} = \tilde{\beta}_{\mathrm{B,A}}^{2/3}\tilde{\beta}_{\mathrm{A,B}}^{1/3}. \qquad (3)$$

The ratios of the step free energies computed directly from the shapes of the islands, and indirectly from the step fluctuations using the data of Fig. 3 and Eq. (3) are compared in Fig. 5(a). The agreement is good: The capillary wave analysis of step fluctuations works. The values of $\beta_{\mathrm{A,B}}$ from Eq. (3) are shown in Fig. 5(b).

These results can be compared with predictions using the kink energies deduced from STM observations at room temperature. By assuming an equilibration temperature of 600 °C and measuring the Boltzmann factors for the various kink excitations, Swartzentruber *et al.* [19] found that the kinks on the S_B and S_A step edges cost 28 and 90 meV per atom of their length, respectively. In addition, creating the kink corner costs 80 meV. The solid lines in Figs. 3 and 5 show the predictions using these energies, computed from analytic expressions for the step partition function neglecting overhangs [1,20]. (Very near roughening the neglect of overhangs, and islands and holes on the terraces, cause the step free energy to vanish more slowly than this approximation would suggest [20].) Obviously there are significant differences between these predictions and the data. The Swartzentruber kink energies result in values for both the step stiffness and step free energy which are significantly higher than our experimental observations. Both of these problems can be corrected by a small change in the kink energies, however. Reducing the kink energy of the S_A step from 90 to 70 meV (well within the quoted 35% uncertainties [19]) and keeping the corner energy the same, gives the dashed lines in Figs. 3 and 5. The slightly modified S_A kink energy clearly accounts for our observations. Although this change in the kink energy is small, it has a dramatic consequence. As seen in Fig. 5(b), at high enough T the step free energy predicted using these values vanishes. Vanishing of step free energies and the consequent proliferation of steps cause surface roughening transitions [7]. For the original kink energies, roughening occurs at 1430 °C. For the energies extracted from the data, it occurs at only 1230 °C. As shown in Fig. 1(b), step edges do indeed become very rough at 1210 °C. (As reported in Ref. [5], all contrast is lost at slightly higher temperatures.) This roughness has been proposed [6] to be an example of a kinetic instability due to increased sublimation (sublimation holes appear in the terraces as a prelude to the roughening). However, our observations of increasing step fluctuations below 1100 °C, when sublimation is very small, suggest that the roughening has a thermodynamic origin.

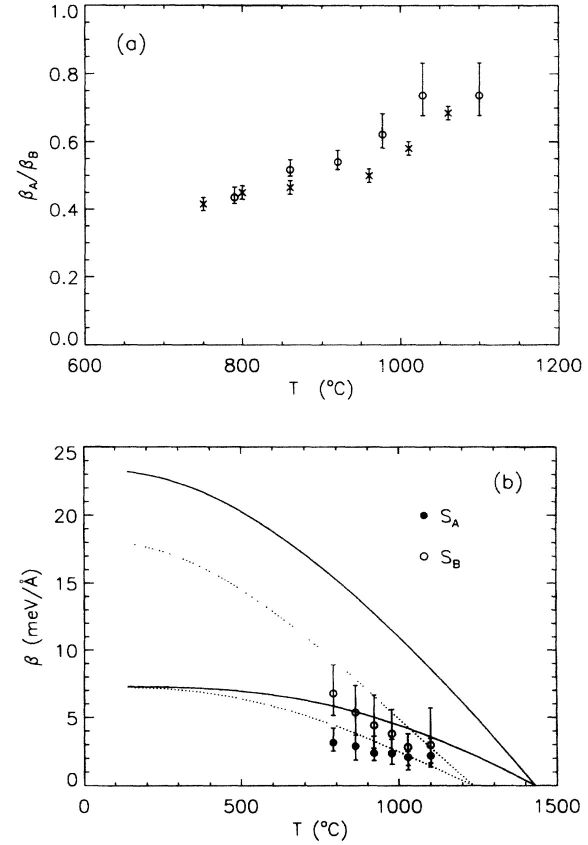

FIG. 5. Panel (a) gives the ratio of the step free energies. The circles show the results of the analysis of the capillary fluctuations, the crosses were deduced from the shape of the islands. Panel (b) shows the temperature dependence of the step free energies deduced from the stiffnesses with the assumption that the equilibrium island shape is elliptical at all T. The solid and dashed lines are the predictions of the same models as in Fig. 3.

The above analysis has shown consistency in the step free energies determined using the completely different approaches of analyzing step fluctuations and island shape. A similar correspondence can be made between the time constant for step wandering [Eq. (1)] and the rate of change of the 2D island area due to equilibration with the nearby step edges. For the step fluctuations at high temperature, we find that the equilibration time constant $\tau(q)$ can be approximated by

$$\tau_{A,B}(T,q) = kT/\Gamma\tilde{\beta}_{A,B}q^2, \qquad (4)$$

where the temperature dependence of the step mobility Γ is given by $\Gamma_0 e^{-E_0/kT}$, with $E_0 = 1.2$ eV for *both* S_A and S_B steps [9]. The form of Eq. (4) is characteristic of step fluctuations limited by attachment and detachment at the step edges [3,4]. Island dissolution limited by detachment rates at the island edges should lead to a linear decrease in island area with time [21]. Measurements of the dissolution rates of isolated islands from 860 to 1010 °C confirm this prediction [9].

Knowledge of the time constants given by Eq. (4) is crucial to the interpretation of static images of surface morphology. For example, a consistent interpretation of the STM experiments must take into account the step-edge dependence of the equilibration time constants. It was assumed in Ref. [19] that the step morphology was frozen in at 600 °C. However, because the time constants given by Eq. (4) scale inversely with stiffness, the S_A step equilibrates faster than the S_B step, giving rise to a lower freeze-in temperature. If we set the characteristic freeze-in time constant τ_0 (related to cooling rate in the STM experiment) equal for S_A and S_B steps, we find

$$e^{-E_0/kT_A^{\mathrm{freeze}}}(\tilde{\beta}_A/\tilde{\beta}_B) = e^{-E_0/kT_B^{\mathrm{freeze}}}(T_A^{\mathrm{freeze}}/T_B^{\mathrm{freeze}}). \qquad (5)$$

Using $T_B^{\mathrm{freeze}} = 600\,^\circ\mathrm{C}$, and $\tilde{\beta}_A/\tilde{\beta}_B = 20$ (as deduced directly from the STM data), we find that $T_A^{\mathrm{freeze}} = 457\,^\circ\mathrm{C}$. Reanalyzing the data of Swartzentruber *et al.* [19] for the S_A step with this reduced value of T_A^{freeze}, we find the S_A kink energy to be 74 meV, in excellent agreement with the value we derive directly from the LEEM experiments.

In conclusion, we have used the real-time, high temperature imaging capabilities of low-energy electron microscopy to study equilibrium step fluctuations and 2D island shapes over a wide range of temperatures. We find full consistency between the physical parameters derived from these two sets of observations, demonstrating the quantitative accuracy of capillary wave theory. The step free energies obtained from our data vanish at ~ 1200 °C, providing strong evidence for the thermodynamic origin of the surface roughening observed at this temperature. We believe that the direct relation between step dynamics and step morphology demonstrated in this Letter will enable a deeper understanding of a range of surface processes, including crystal growth and surface faceting.

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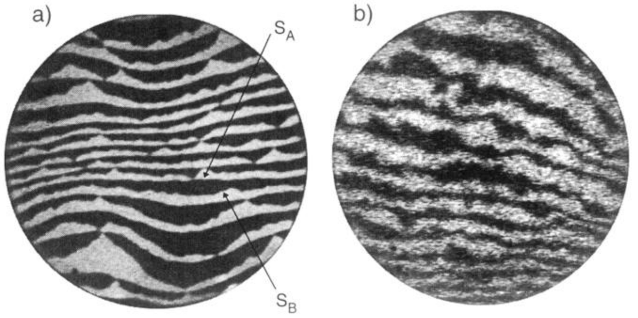

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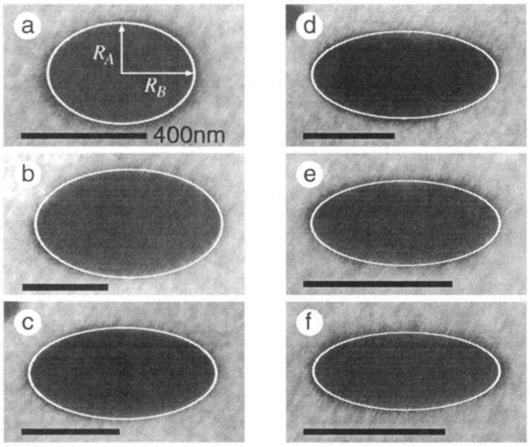

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