Direct Determination of Step and Kink Energies on Vicinal Si(001)

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(Received 29 May 1990)

Scanning-tunneling-microscopy images of vicinal Si(001) with an equilibrium distribution of steps and kinks have been analyzed to determine the distribution of kink separations and kink lengths. From these distributions, step and kink energies have been directly determined.

PACS numbers: 68.35.Bs, 61.16.Di

There has been considerable interest recently in understanding the stability of vicinal surfaces.[1-4] The configuration of steps affects a number of surface phenomena, including the nature of the growth of epitaxial overlayers,[5] the chemical reactivity of surfaces,[6,7] and the usefulness of the surface as a template for heteroepitaxial growth of materials with significantly different lattice constants[8] or for creating specialized structures such as "quantum wires" that depend on preferential adsorption at steps.[9] The configuration of steps, their roughness, spacing, and the degree to which they meander on the surface is, of course, controlled by the boundary free energy of the steps; it is a long-standing problem[10] to determine the important contributions to the free energy. In general, one speaks of a generic "step-step" interaction or even "kink-kink" interactions, and it is recognized that entropy can be important, but quantitative information has been lacking.

Both theoretical and experimental effort has been made in understanding the step configuration of vicinal Si(001). The Si(001) surface reconstructs to form rows of dimerized atoms. Because of the symmetry of the diamond lattice, dimer rows are perpendicular to each other on terraces that are separated by an odd number of monatomic steps. If the surface is miscut with a surface normal tilted toward a [110] direction, adjacent steps are inequivalent. As can be seen in Fig. 1, alternate steps are smooth (so-called S_A) and rough (S_B). Dimer rows are respectively parallel and perpendicular to S_A and S_B steps. Kinks in one type of step are made up of segments of the other type of step. Theoretical treatments of the statistical mechanics of these steps have focused, in particular, on calculating their free energy and determining from it the equilibrium shape of Si islands grown on the surface[11] and the temperature of the phase transition between the single-atomic-height-step and double-atomic-height-step surface as a function of the vicinal angle.[12] These calculations use a model Hamiltonian

$$H=\sum_i J|h_i-h_{i+1}|+aC\ln\left[\frac{1}{\pi a}\cos\left(\frac{\pi h_i}{2l}\right)\right]. \qquad (1)$$

Here i is summed over the atoms in the step, and h_i is the perpendicular distance of the atom from the mean step position. The first term in the Hamiltonian is the energy to form kinks (excitations). For vicinal Si(001) cut toward [110] the choice of J for one step is the energy per unit length of the other step. The second term arises from the long-range strain fields that result when the step meanders away from its mean position. The influence of strain has been investigated both experimentally[13] and theoretically.[14]

In this Letter, we present scanning-tunneling-microscopy (STM) measurements of edge roughness of steps on vicinal Si(001) that allow a more complete determination of the contributions to the energy of the steps. The analysis shows that, in particular, a relatively large "corner energy" must be included that makes the excitation of kinks energetically much costlier and reduces the temperature dependence of the free energy. We present values for the various contributions to the step energy.

To determine the distribution of kinks, we measured the kinks and their separations on a large number of images like that of Fig. 1. After an initial thermal cleaning procedure,[15] which yields a surface defect density (chiefly vacancies) of $<5\%$, the sample is annealed at

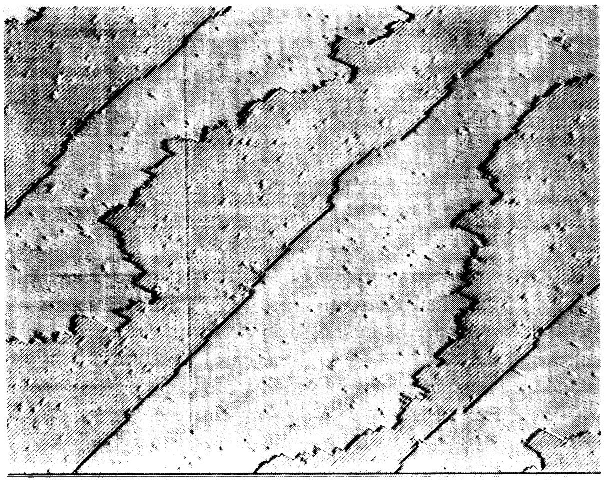

FIG. 1. A 1200-Å STM derivative-mode image of a Si(001) surface miscut 0.3° towards [100]. The surface steps down from left to right.

600 °C for 5 min and then radiation quenched to room temperature. The lengths of the kinks $n=|h_i-h_{i+1}|$ and their separations s are tabulated for both types of steps. The analysis of the smooth step is complicated by the fact that there are so few kinks. We will first therefore restrict ourselves to a discussion of the rough step. The measured distributions for the rough step are displayed in Fig. 2. As shown in the inset, n and s are measured perpendicular and parallel to the nominal edge, respectively. Figure 2(a) is a plot of the measured probability $P(s)$ of finding two adjacent kinks separated by s atoms versus s. Because of the symmetry of the (2×1) reconstruction, kinks always occur separated by an integral number of dimer rows. Figure 2(b) is a plot of the number of kinks of length n atoms, $N(n)$, vs n. Again the kink lengths come only in multiples of two atoms because of the way in which the step must terminate at the lower terrace, which has a periodicity of 2 perpendicular to the step.

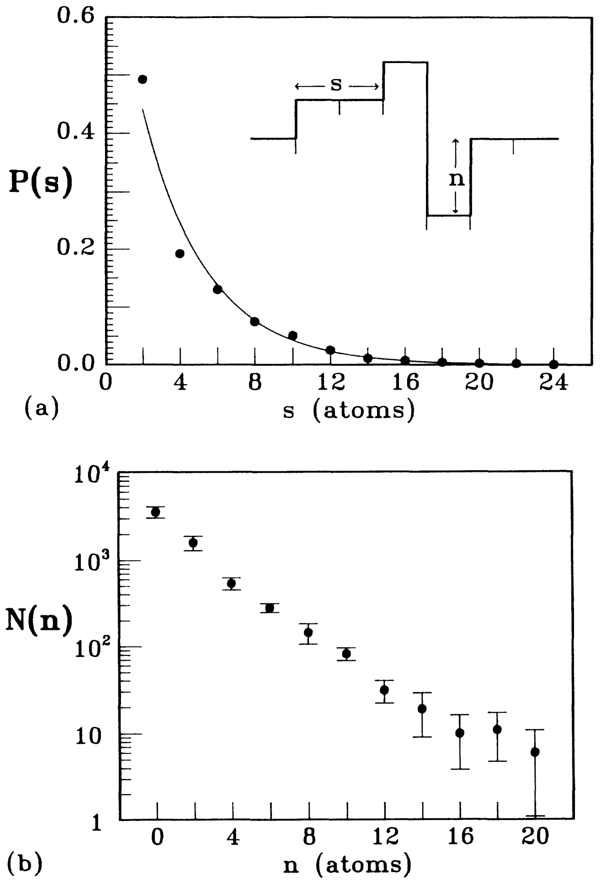

FIG. 2. (a) Measured probability that two adjacent kinks along the nominal step direction are separated by s atoms vs s. The solid line is the expected form if all of the kinks are independent (see text). Inset: Schematic picture of a typical step showing the directions of s and n, parallel and perpendicular to the nominal step direction, respectively. A kink is any inside corner followed by an outside corner (or vice versa), and can be of varying lengths, n. (b) Measured number of kinks of length n atoms vs n. The value at $n=0$ is the number of sites at which there is no kink. The error bars are given as the sum of the statistical $(\sqrt{N})$ error and a systematic counting error determined by counting an identical data set several times.

The simplest interpretation of these data is to assume that the excitations are statistically independent, i.e., that every possible kink site along the edge is independent of all others. Under this assumption, the probability $P(s)$ of two kinks, separated by s, would be given by $P(s)=P_k(1-P_k)^{s/2-1}$, where P_k is the probability that a kink exists at a potential kink site. The solid line in Fig. 2(a) is this function using P_k equal to the measured number of kinks divided by the total number of possible kink sites. Thus there is no adjustable fitting parameter used in Fig. 2. One might have expected that interactions between kinks would change the probability of two kinks appearing close to each other, causing a systematic deviation of the data from the solid line at small separations. This is not observed within the experimental uncertainty of the data and therefore we conclude that it may be appropriate to consider each potential kink site as independent. The exponential form of $P(s)$ is only a necessary condition for kink independence. Another condition is the lack of correlations in the kink lengths and kink directions. Within the uncertainties due to extrinsic constraints, e.g., azimuthal miscut, the directions of nearest-neighbor kinks are uncorrelated. That is, a kink directed into the terrace is equally likely to be followed either by a kink directed into or out of the terrace.

Under the assumption of independent kinks, $N(n) \propto \exp[-E(n)/kT]$, where $E(n)$ is the energy of a kink of length n atoms. In Fig. 3 we plot $E(n) = -\ln[N(n)/2N(0)]$ from four different data sets. The factor of 2 arises from the degeneracy of the excited states; i.e., there are two possible kink directions, either into or out of the terrace. These data can be fitted by

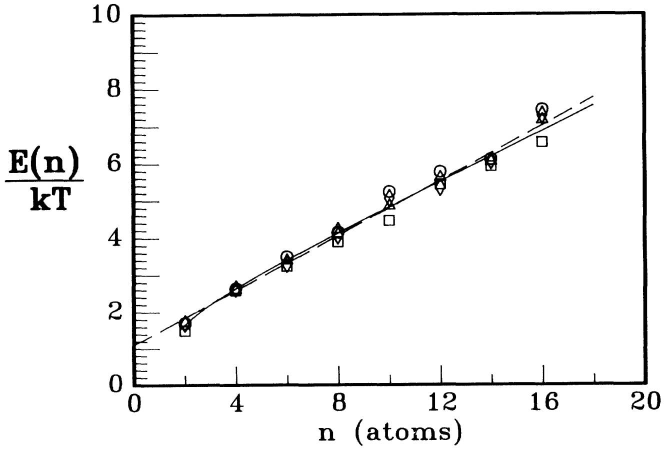

FIG. 3. The measured energy of a kink of length n atoms vs n from four data sets for the rough step. The dashed line is a fit by the form $E(n)=n\epsilon_{s_A}+C$ and the solid line is a fit by the form $E(n)=n\epsilon_{s_A}+C-B/n$.

the functional form $E(n)=n\epsilon_{S_A}+C$. The values of the parameters are $\epsilon_{S_A}/kT=0.37\pm0.03$ (atom)$^{-1}$, and $C/kT=1.1\pm0.3$. The errors reflect the statistical fit by a linear model. A somewhat better fit by $E(n)/kT$ can be obtained with an additional term inversely proportional to n, $E(n)=n\epsilon_{S_A}+C-B/n$. The values of the parameters for this model are $\epsilon_{S_A}/kT=0.33\pm0.04$ (atom)$^{-1}$, $C/kT=1.6\pm0.6$, and $B=1.3\pm1.3$ atom. The addition of the third term may, however, not be statistically justifiable. The value of ϵ_{S_A} can be interpreted as the energy per atom of an infinite, straight, smooth, type-S_A step. The slope of the data, given by the dashed line in Fig. 3, gives ϵ_{S_A}, which is the same as the coupling constant J used in Eq. (1). The constant C, given by the intercept of the dashed line, can be thought of as corresponding to the additional energy due to the corners of the kinks. (Finally, the possible B term, which describes the deviation of the data at small n from a straight line, can be thought of as the attractive interaction between the ends of a kink.)

As mentioned earlier, the analysis of the smooth step is hampered by the fact that there are so few kinks. The samples used in this study have a slight azimuthal misorientation, $<5°$, which geometrically forces a certain number of nonthermally excited kinks. The number of "forced" kinks is a small fraction of the total number of kinks in the rough step and therefore has little effect on the kink distribution. However, the forced kinks comprise a significant fraction of the total kinks in the smooth step. It is difficult, therefore, to analyze the functional form of the kink length distribution. We can, nevertheless, extract the value of the kink energy for the smooth step with a few simple assumptions. It was demonstrated above that kinks in the rough step are independent and noninteracting. This should be even more valid for the smooth step where kinks have a greater separation. We assume a functional form for the energy of a kink in the smooth step identical to that for the rough step, $E(n)=n\epsilon_{S_B}+C$. Kinks in the smooth step are comprised of segments of S_B step. We will take the value of C as identical to that measured on the rough step, for the corners of kinks on either step are microscopically indistinguishable. We eliminate the problem of forced kinks by dealing only with the thermally excited "unforced" kinks that are in the direction opposite to the kinks caused by the azimuthal misorientation.

We now write the probability P_{un} of having an unforced kink of any length in S_A,

$$P_{\text{un}}=\frac{\sum_{n=1}^{\infty}e^{-\beta(C+n\epsilon_{S_B})}}{1+2\sum_{n=1}^{\infty}e^{-\beta(C+n\epsilon_{S_B})}}\,. \tag{2}$$

Solving for ϵ_{S_B}/kT yields

$$\epsilon_{S_B}/kT=\ln[e^{-\beta C}(1/P_{\text{un}}-2)+1]\,. \tag{3}$$

The value of ϵ_{S_B}/kT determined from the STM images is 1.2 ± 0.1 (atom)$^{-1}$.

If we assume that the quench rate is sufficiently rapid and the kinetics below 600 °C sufficiently slow that our step configuration represents equilibrium at this temperature, then we can use this annealing temperature to translate the parameters into energy units. This gives $\epsilon_{S_A}=0.028\pm0.002$ eV/atom, $C=0.08\pm0.02$ eV, and $\epsilon_{S_B}=0.09\pm0.01$ eV/atom. The values of ϵ_{S_A} and ϵ_{S_B} can be compared with Chadi's calculated values of 0.01 and 0.15 eV/atom.[16] Uncertainty in the equilibrium temperature will, of course, affect these energies but not their ratios. In practice, the freeze-out temperature for the steps is lower than the annealing temperature. We know from growth and coarsening measurements[11] that the kinetics are insignificant below 300 °C. Using this value as a (very generous) lower bound lowers the measured energy values of the parameters by $\sim35\%$.

An interpretation based on the assumption of independent kinks cannot be completely correct since it predicts that the steps would statistically meander over the whole area available to them. In fact, the distribution of step positions is more sharply peaked around the midpoint between adjacent steps because of the long-range strain fields[13,14] than would be expected from purely entropic considerations.[17] However, the fact that the independent-kink model does describe the data well suggests that, within a segment of the step of length small compared to the separation between steps, the fluctuations are governed primarily by the kink energies. The gross meandering of the average position of these segments, on a scale like the terrace widths, is then governed by the long-range strain fields. In the present results the Boltzmann factor rather than the long-range strain fields limits kinks of large n. We are currently studying the effect of sample vicinality on the kink distributions to determine at what point the presence of the strain energy and finite terrace size introduces sufficient correlations to affect our measured distributions.

In conclusion, we have measured the kink energy as a function of length for steps on a Si(001) surface by examining the distribution of kink lengths. The energy fits the form $E(n)=n\epsilon+C$ where the parameters can be described as ϵ, an energy per unit length of the step, and C, a constant, effective corner energy. We suggest that this is the appropriate form for the excitation energy to be used in the Hamiltonian when calculating the free energy of a step. In particular, the inclusion of a corner energy will increase the energy of kinks relative to that in the Hamiltonian of Eq. (1). The energy of the short-length excitations, which are the dominant ones at experimentally accessible temperatures, will be increased by up to about a factor of 3. This will make the free energy of the steps fall much more slowly with temperature than Eq. (1) predicts. Attempts to justify equilibrium island shapes of Si deposited on Si(001) in terms of step energies[11] and to quantify the single-atomic-height-step to double-height-step transition with vicinal angle in

Si(001) will be aided by such a slower falloff.[12]

With this work, we have demonstrated that STM can be used to extract quantitative microscopic information about surfaces. We believe that this method of counting kinks can be used to determine step and kink energies on many surfaces. Analogous experiments, combined with statistical analysis, should be a powerful tool also for investigating other kinetic or thermodynamic phenomena for which the degree of surface disorder is a signature.

This research was supported by ONR, Physics Program, and in part by NSF Grant No. DMR 87-20778.

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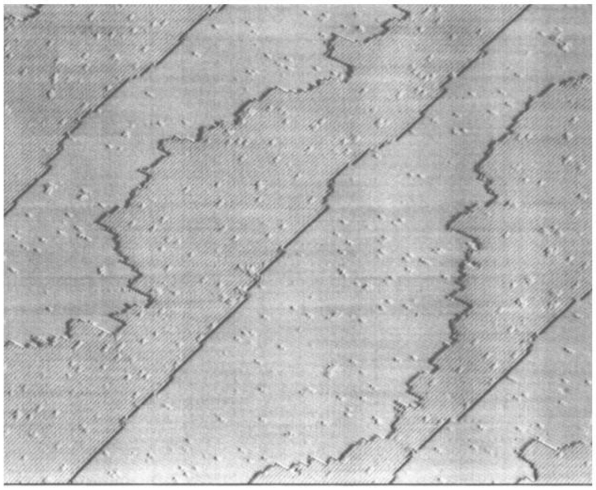

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