Anomalous strong repulsive step-step interaction on slightly misoriented Si(113)

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We have used scanning tunneling microscopy to study Si(113) 0.2° misoriented towards $[\bar{1}10]$. Rapid quenching of this surface from 1500–1575 K to room temperature results in a uniformly stepped single-domain surface, whereas slower cooling gives rise to clustering of steps. The thermally induced step wandering and the terrace width distribution of the uniformly stepped surface are analyzed in order to determine the strength of the energetic and entropic step-step interactions. Beside the short-range attractive step-step interaction found by Song and Mochrie [Phys. Rev. Lett. **73**, 995 (1994)] on Si(113) misoriented 1°–5° towards [001], we found an anomalously strong long-range repulsive step-step interaction on Si(113) 0.2° misoriented towards $[\bar{1}10]$. The coexistence of a long-range repulsive and a short-range attractive step-step interaction may explain the transition from a uniformly stepped surface at high freeze in temperature to a faceted surface at lower freeze in temperatures. [S0163-1829(97)03012-9]

Misorientation of a crystal at a small angle with respect to one of its symmetry planes results in a vicinal surface. Because the effective interaction between steps is often repulsive, the vicinal surface usually consists of an array of uniformly distributed steps separated by high-symmetry terraces. However, if the effective interaction between the steps is attractive, a faceted surface will be found. The Si(113) surface is thermally stable and has a surface-free energy that is only slightly higher than the surface-free energy of the Si(111) and Si(001) surfaces.[1] The relatively low surface-free energy implies that this surface has potential as a substrate for crystal growth. Epitaxial growth on, e.g., {113} planes of III-V substrates has revealed crystal properties that are superior to those of the low-index surfaces.[2] During the past years there have been a number of studies devoted to the reconstruction of the Si(113) surface. Some experimental studies have found that the clean Si(113) reconstructs into a (3×2) pattern[3–5] while others have found a (3×1) surface unit cell.[6–8] Interestingly, several groups[9–11] found that the (3×2) reconstruction at 300 K converts into a (3×1) reconstruction due to contamination with residual gases. Despite this interest for the reconstruction of Si(113), the step edges, which are of key importance for many surface processes, remain relatively unexplored. There is however, one exception, namely, the particularly beautiful and detailed x-ray scattering study of Si(113) misoriented a few degrees (1.3°, 2.1°, 3.7°, −1.4°, and −5.2°) towards [001] by Song and co-workers.[12–16] They found a uniformly stepped Si(113) surface at temperatures above 1223 K, whereas at lower temperatures, a faceting transformation [step-free (113) facets coexisting with regions of high-step density] was found. As pointed out correctly by Song and Mochrie,[12] these observations can only be understood by assuming that there is an attractive interaction between the step edges. Although there is currently not a fully convincing theoretical understanding of the nature of these attractive step-step interactions, dipoles located at the step edges or a conduction-electron-mediated oscillatory interaction may be responsible for this type of attractive interaction.[17,18]

In this paper we will show that on slightly misoriented Si(113), an anomalously strong long-range repulsive interaction is present. As shown recently by Lässig,[19] the coexistence of a long-range repulsive interaction and a short-range attractive interaction can produce the complex orientational phase diagram of vicinal Si(113). Lässig[19] applied the Calogero-Sutherland model to an array of interacting steps and showed that the thermodynamic complexity of this system is related to the interplay of two distinct branches of solutions. The temperature dependence of the surface morphology arises from a crossover between one branch of solutions to the other.

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure in the mid 10^{-11}-Torr range. The chamber, which is mounted on pneumatic legs, is equipped with a home-built scanning tunneling microscope (STM). The Si(113) samples with dimensions $20\times4\times0.3$ mm^3 were ultrasonically rinsed in ethanol before loading them into the vacuum system. The misorientation of the surface with respect to the [113] direction was estimated to be about 0.2° in the [110] direction. After loading the samples in the UHV chamber they were outgassed at a temperature of about 875–975 K for at least 20 h. In order to obtain an atomically clean surface, the samples were repeatedly flashed at temperatures 1500–1575 K for several seconds followed by quenching to room temperature. We have compared rapid-radiation quenched surfaces (from 1500 to 500 K in a few seconds) with slowly cooled surfaces (rapid quench from 1500 to 1200 K in order to avoid contamination of the surface followed by a cooling rate of 5 K per sec). During flashing at 1500–1575 K, the pressure was kept in the mid 10^{-10}-Torr range. This procedure always resulted in clean single domain Si(113)-(3×2) surfaces. The rapid-quenching procedure results in a uniformly single-layer stepped surface, whereas the slow-cooling procedure results in larger terraces separated by step bunches. The step bunches vary in height from 1.64 up to 9.8 Å.

In Fig. 1 a detailed filled-state STM image of Si(113) is displayed together with the surface reconstruction model given by Dabrowski, Müssig, and Wolff.[4] The dangling bonds of the atoms numbered 1 and 4 as well as the dimer bond between atoms 2 and 3 appear in the filled-state STM image. The pentagon structure of the atoms labeled 8–12 can only be resolved in an empty-state STM image.[4] The dimer bond between atoms 2 and 3 is aligned along the [110] di-

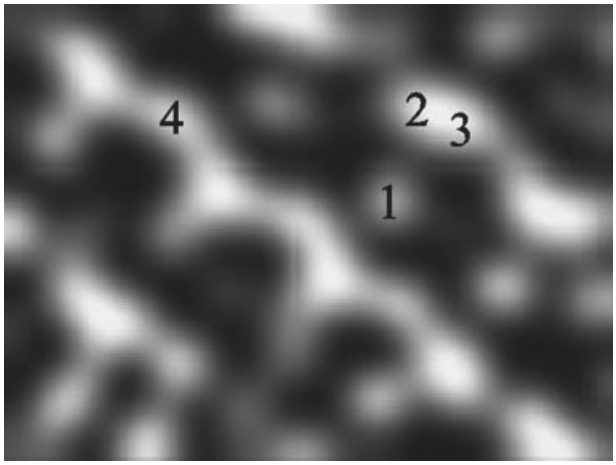

FIG. 1. (a) The Si(113)-3×2 reconstruction model given by Dabrowski, Müssig, and Wolff (Ref. 4). The surface unit cell, indicated by the dashed lines, contains atoms which are terminated like atoms of the (001) surface (labeled 2 and 3) and atoms which are terminated like atoms of the (111) surface (labeled 1 and 4). The length $a_\perp$ and width $a_\parallel$ of the unit cell are 12.76 Å and 11.54 Å, respectively. (b) High-resolution STM image (scan size 5×3.5 nm^2) of the Si(113)3×2 surface. The sample bias is −2 V and the tunneling current is 1 nA. The dimer bond between atoms 2 and 3 as well as the filled dimer bonds of atoms 1 and 4 are labeled in the figure.

rection. Large-area STM images of the rapidly quenched Si(113) surface reveal that this surface is uniformly stepped with an averaged terrace width of about 400 Å. In Fig. 2 two filled-state images with steps running perpendicular to the [110] direction are displayed. The measured height of most steps is 1.64 Å but steps with height 3.28 Å do also occur on the rapid quenched sample. Interestingly, if a step edge with the double height, i.e., 3.28 Å, occurs, a doubling of the *upper*-terrace width is found, hence the local miscut angle of the Si(113) is conserved. Slower quenching of this surface results into larger terraces separated by step bunches. Step bunches as high as 9.8 Å and terrace widths of about 2000 Å or more have been observed. The clustering of steps into step bunches is a clear sign of the presence of an attractive step-step interaction which dominates at small-step separation.

From the STM images as displayed in Fig. 2 it is clear that the Si(113)-(3×2) surface is single domain. Due to a misorientation of 25.2° from the (001) plane to the (113) plane, the degeneracy of the two, in principle equivalent, (001) terraces is lifted. The (001) terrace with the dimer bonds aligned along the [110] direction has the dimer bonds exactly perpendicular to the [113] direction, whereas the dimer bonds of the other terrace made an angle of 25.2° with the [113] direction.

In Fig. 3, the normalized distribution of step-step separations is shown. This distribution contains information about both the thermal excitations of the step edge and the nature and strength of the step-step interactions. Let us first consider the entropic step-step repulsion which arises due to the fact that steps are not allowed to cross each other. Bringing steps close to one another decreases the amount of wandering, and thus lowers the configurational entropy, leading to an effective entropic step-by-step *repulsion*. The strength of this entropic repulsive interaction can be estimated by using

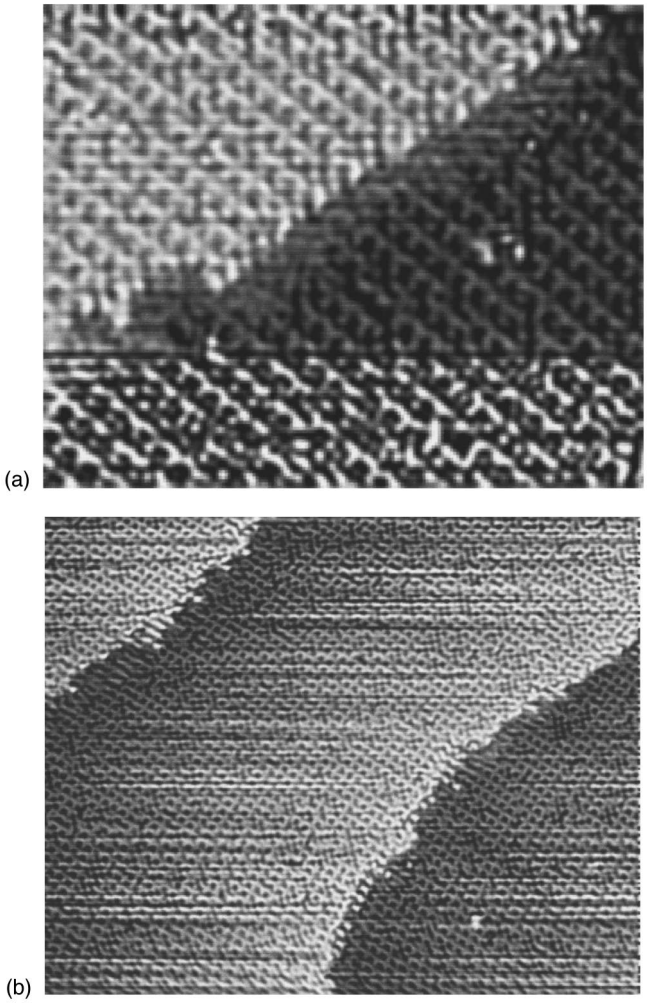

FIG. 2. Filled-state STM images of the Si(113) surface with a misorientation of about 0.2° in the [110] direction. The sample bias is −2 V and the tunneling current is 1 nA. (a) Scan size 25×20 nm^2, (b) scan size 65×50 nm^2.

the simple, but particularly elegant approach introduced some years ago by Fisher and Fisher.[20] Because steps are not allowed to cross each other step collisions result in a decrease of the entropy with about $k_b \ln 2$. If L is the averaged step-step separation and $\langle k^2 \rangle$ is the mean-square length of the kinks, then the typical distance between collisions is given by $L^2/2\langle k^2 \rangle$, assuming that both steps perform independent one-dimensional random walks. Hence, the free-energy increase per unit length along the step edge is about $2\langle k^2 \rangle k_b T_f \ln 2/L^2$ (where T_f is the freeze in temperature of the step-edge roughness).[21] Because the step edges on Si(113) are imaged with sufficient resolution, the mean-square length of the kinks can be measured microscopically. Our experimental data yield $\langle k^2 \rangle = 0.8 a_\parallel^2$ and $L = 35 a_\parallel$ resulting in a free-energy increase of only $9 \times 10^{-4} k_b T_f$ per unit length, $a_\perp$, measured along the step edge. If this entropic step-step repulsion would be the only step-step interaction present, a cosine-squared terrace width distribution would have been found. As is immediately clear from Fig. 3, this is definitely not the case. In most cases energetic step-step interactions, such as elastic and dipole-induced interactions, are also present. Including a step-step interaction potential of

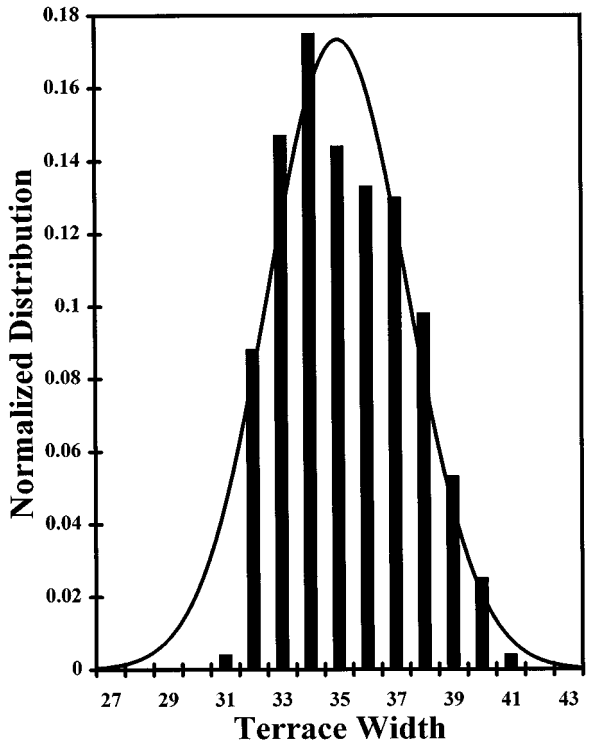

FIG. 3. Terrace-width distribution in units of $a_{\parallel}$ for the Si(113) surface with a misorientation of about 0.2° in the [110] direction. The average terrace length corresponds to approximately $35a_{\parallel}$. The bold line is a Gaussian fit of width $w=2.3a_{\parallel}$.

the form A/L^2 will result in an almost perfect Gaussian shape of the terrace width distribution.[22,23] The width of this Gaussian is given by

$$w(T_f,L)=L\left(\frac{\langle k^2\rangle k_b T_f}{48Aa_{\perp}}\right)^{1/4}.$$

We found $w(T_f,L)=(2.3\pm0.2)a_{\parallel}$, resulting in $A=(9\pm3)10^2 k_b T_f a_{\parallel}^2/a_{\perp}$.[24] For $L=35a_{\parallel}$ the ratio of energetic step-step repulsion (which is defined as the second derivative of the interaction potential, i.e., $6A/L^4$) over entropic step-step repulsion is about 4. Thus the energetic step-step interaction on Si(113) turns out to be much stronger than the entropic step-step repulsion on Si(113) as well as the energetic step-step repulsion on the closely related low-index Si(001) and Si(111) surfaces.[25] At first sight, this anomalous strong step-step repulsion seems to be in disagreement with the attractive step-step interaction found by Song and Mochrie.[12] However, Song and Mochrie[12,13] already introduced a temperature dependence of step-step interaction such that above a critical temperature, the effective step-step interaction is repulsive and below this critical temperature the effective step-step interaction is effectively attractive. Moreover, Lässig[19] has shown already that just the combination of a *long-range repulsive* and a *short-range attractive* interaction between steps can produce an orientational phase diagram that compares favorably with the orientational phase diagram of Si(113), including the faceting transition found by Song and Mochrie.[12] Lässig[19] pointed out that as the temperature is lowered, the step fluctuations increases substantially and hence the probability of a step being close to one of its neighbors becomes larger. The development of step bunches on Si(113) after slow cooling can therefore be related to the existence of a short-ranged attractive step-step interaction. Finally, in the case of Song and Mochrie,[12] the misorientation is towards the $[\bar{0}01]$ direction, whereas our misorientation is towards the [110] direction. It is reasonable to assume that there might be a dependence of the step-step interaction on the azimuthal orientation.

In summary, we have shown that there is a strong long-range repulsive interaction between single height steps on the slightly misoriented Si(113) surface. Fully consistent with the single-domain character of Si(113) surface, we were able to find only step heights which were quantized in units of 1.64 Å. Most of the steps on the rapid quenched Si(113) surface have the minimum height, i.e., 1.64 Å. Slower quenching of the surface, however, results in step bunching and larger terrace widths. The entropic as well as the energetic step-step interaction between steps with the minimal step height of 1.64 Å are determined. The energetic step-step interaction between the single-layer step edges on Si(113) is much stronger than the entropic step-step repulsion on Si(113) as well as the energetic step-step interactions on the closely related Si(001) and Si(111) surfaces. The coexistence of a short-range attractive and a long-range repulsive step-step interaction on Si(113) compares favorably with the experimentally determined orientational phase diagram by Song and Mochrie.

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[21] The STM images are taken at room temperature. At this temperature no rearrangement events at step edges can be observed. The roughness of the step edges on Si(113) is frozen in at a much higher temperature [on Si(001), for example, step edge rearrangement events can be observed on a time scale of seconds at temperatures around 700 K]. Following the orientational phase diagram depicted in Ref. 12 uniformly stepped Si(113) is found at freeze in temperatures above 1150–1225 K.
[22] Because all step edges wander simultaneously, the step-step distribution is a slightly distorted Gaussian distribution. Among the differences with a perfect Gaussian are an algebraic rise, an extended tail for separations beyond L, and a slightly shifted peak position [for details, see B Joós *et al.*, Phys. Rev. B **43**, 8153 (1991)].
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[24] On Si(100), because of the alternating 2×1 and 1×2 periodicity, the step-step interaction decays as $\ln(L)$. If all the domains are isotropic, as in the Si(113) case, no strain relaxation due to domain rotation can occur and therefore this type of step-step interaction must be ruled out.
[25] On Si(001) and Si(111), the entropic and energetic step-step repulsion are roughly of the same order of magnitude; for a comprehensive review, see, e.g., E. D. Williams, Surf. Sci. **299/300**, 502 (1994). We still do not have a satisfying explanation for the occurrence of such a strong step-step repulsion on Si(113).