Faceting of ⟨010⟩ steps on Si(001) and Ge(001) surfaces

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We have used scanning tunneling microscopy to study the faceting of ⟨010⟩ oriented steps on Si(001) and Ge(001) surfaces. The ⟨010⟩ oriented steps on Si(001) tend to facet into local S_A and S_B step segments, whereas ⟨010⟩ oriented steps on Ge(001) meander along the mean ⟨010⟩ direction. We show that the step faceting behavior of the Si and Ge(001) surfaces is fully governed by the next-nearest-neighbor (NNN) interaction between the substrate dimers. Only in the case of a repulsive NNN interaction, as for Si(001), faceting occurs.

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INTRODUCTION

Surface steps play an important role in many equilibrium surface processes. Amongst them are, for instance, thermal roughening and faceting.[1] Also, in many nonequilibrium surface processes, such as crystal growth and etching, surface steps play a prominent role.[1] At zero temperature the step free energy equals the step formation energy. With increasing temperature thermal kinks are generated and the step free energy decreases. Although kink generation costs energy, the thermal generation of kinks decreases the total free energy because of the strong entropy effect involved.[2] Thermal roughening will occur if the step free energy vanishes. For many surfaces, however, the roughening temperature exceeds the melting point and this transition can therefore rarely be observed experimentally.

Another surface morphological phase transition is faceting.[3–11] A facet will spontaneously break up in a hill-and-valley structure consisting of different facets and steps if that leads to a reduction of the total (projected) surface free energy. To understand this transition, knowledge of the step free energy is also essential. In this paper we will address the step faceting transition. To the best of our knowledge this transition has been observed,[12] but has not been discussed theoretically in the literature before.

Faceting of a step oriented along a high symmetry direction will occur if it is energetically favorable to form a combination of differently oriented steps that have the same overall azimuthal direction. Because step faceting does not necessarily occur at zero temperature, knowledge of the step free energy as a function of the azimuthal direction is required. As an example we address the step faceting of ⟨010⟩ oriented steps on the well-studied Si and Ge(001) surfaces. We show that the ⟨010⟩ oriented steps on Si(001) facet into local [110] and [$-$110] segments in contrast to the ⟨010⟩ steps on Ge(001). We will demonstrate that this difference is easily understood in terms of a simple solid-on-solid model that incorporates nearest-neighbor (NN) and next-nearest-neighbor (NNN) interactions. Faceting of the ⟨010⟩ steps only occurs for repulsive NNN interactions [as for Si(001)].

STEP FREE ENERGIES

At zero temperature, in the absence of entropy effects, minimization of free energy requires a minimization of step length. This means that steps will be as straight as possible. The only kinks present at zero temperature are so-called forced kinks. These forced kinks are necessary to accommodate the misalignment of a step with respect to the crystal high-symmetry axes.

We consider single layer S_A or S_B steps of Si and Ge(001) surfaces that are perfectly aligned along the ⟨110⟩ direction. At elevated temperatures the S_A or S_B step edges become rough due to the thermal generation of kinks. When viewed along the step edge, there are two types of kinks: protruding (positive kinks) and intruding ones (negative kinks). The formation of these additional kinks allows the step to wander. This increases the entropy and thereby decreases the free energy of the step. At zero temperature the step free energy equals the step formation energy. Despite the fact that there are two different positions where the dimer rows of the upper terrace can end with respect to the lower terrace, a unit of two dimers has been chosen as the basic building block of the (2×1) reconstructed (001) surface. Dimer rows can end in the troughs between the dimer rows of the underlying terrace or on top of the dimer rows. Both types of terminations have been found, but there is a strong preference for the dimer rows to terminate in the troughs of the underlying terrace. Kinks are therefore generally found on a (2×2) lattice, resulting in a natural unit of two dimers to represent the surface layer.[13] In our discussion we only consider NN and NNN interactions between these elementary (2×2) units. The symbols $\varepsilon_{\parallel(\perp)}$ refer to the NN interaction energy between a unit building block along (perpendicular) to the substrate dimer row direction. The diagonal NNN interaction energy is denoted by δ.

The step formation energy for an S_A (S_B) step edge is[2,14]

$$E_{S_A(S_B)}=\frac{\varepsilon_{\perp(\parallel)}}{2}+\delta. \tag{1}$$

The kink formation energy for a kink with a length of i units ($i\geqslant1$) in an S_A (S_B) step is[2,14]

$$E_{\mathrm{kink},S_A(S_B)}(i)=i\,\frac{\varepsilon_{\parallel(\perp)}}{2}+(i-1)\,\delta. \tag{2}$$

Because both the step and kink formation energies can be expressed in terms of the NN and NNN interaction energies,

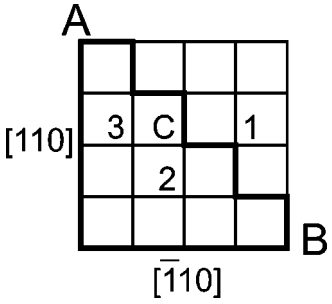

FIG. 1. Schematic diagram of ⟨110⟩ and ⟨010⟩ oriented steps. Bold lines refer the mean ⟨110⟩ and ⟨010⟩ directions. At point C the step can proceed in three different directions labeled 1, 2, and 3. Only the pathways C1 and C2 are taken into account. Pathway C3 is energetically very unfavorable.

the step free energy can also be written in terms of these interaction energies. The approach that we will take relies on elementary statistical physics. The step free energy F per unit length and per unit step height is defined as

$$F = -kT \ln Z = -kT \ln\left(\sum_i e^{-E_i/kT} \right), \tag{3}$$

where the summation runs over all possible step configurations and E_i refers to the formation energy of the ith configuration. The partition function Z of an S_A (S_B) step edge is given by[2,14]

$$Z_{S_A(S_B)} = e^{-E_{S_A(S_B)}/kT} \left(1 + 2\sum_{i=1}^{\infty} e^{-E_{\mathrm{kink},S_A(S_B)}(i)/kT} \right) \tag{4}$$

and hence

$$F_{S_A(S_B)} = \frac{\varepsilon_{\perp(\parallel)}}{2} + \delta - kT \ln\left(1 + \frac{2e^{-(\varepsilon_{\parallel(\perp)}/2kT)}}{1 - e^{-(\varepsilon_{\parallel(\perp)}/2+\delta)/kT}} \right). \tag{5}$$

The strength of the NN and NNN interaction of Si and Ge(001) surfaces have previously been extracted from an analysis of the step roughness. Because the roughness of the steps is frozen in at an elevated temperature T_F (the freeze in temperature) the NN and NNN interaction energies are expressed in terms of $kT_F/2a$ (NN interaction terms) or kT_F (the diagonal NNN interaction term). For Si(001) the following values have been found: $\varepsilon_\parallel = 5.7 \pm 0.3\, kT_F/2a$, $\varepsilon_\perp = 3.6 \pm 0.2\, kT_F/2a$, $\delta = -1.0 \pm 0.3\, kT_F$, and $T_F = 775 \pm 100$ K.[14,15] For Ge(001) we have found: $\varepsilon_\parallel = 4.1 \pm 0.3\, kT_F/2a$, $\varepsilon_\perp = 1.7 \pm 0.3\, kT_F/2a$, $\delta = -0.1 \pm 0.3\, kT_F$, and $T_F = 575 \pm 75$ K.[16]

In order to find the step free energy of a 100% kinked step oriented along the ⟨010⟩ direction we consider the case of an isotropic NN interaction ε ($= \varepsilon_\parallel/2 + \varepsilon_\perp/2$) and an attractive NNN interaction ($\delta \geqslant 0$). We only take into account the two energetically most favorable pathways, because all the other pathways involve significantly more step edge length and are therefore much higher in energy (see Fig. 1). The step edge energies per unit length $\sqrt{2}a$ (measured in the ⟨010⟩ direction) are then $\varepsilon/2 + \delta/2$ and $\varepsilon/2 + \delta$, respectively. The partition function of a ⟨010⟩ step is given by[17]

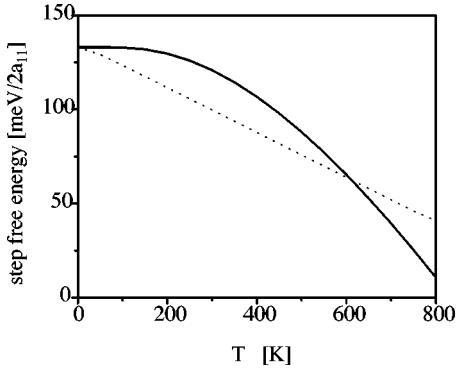

FIG. 2. Plot of the step free energies of Ge(001) versus temperature. The solid curve refers to a pair of S_A and S_B steps and the dotted curve refers to a ⟨010⟩ step.

$$Z_{\langle 010\rangle} = e^{-(\varepsilon/2+\delta/2)/kT} + e^{-(\varepsilon/2+\delta)/kT}. \tag{6}$$

The free energy of a ⟨010⟩ step per unit length $2a$ ($2a = 8$ Å, the spacing between adjacent dimer rows) is then represented by

$$F_{\langle 010\rangle}(T) = \sqrt{2}\left[\left(\frac{\varepsilon+\delta}{2} \right) - kT \ln(1 + e^{-\delta/2kT}) \right]. \tag{7}$$

In Eqs. (6) and (7) only the two energetically most favourable pathways are included. At low temperatures this is a good approximation. In the case of Ge(001), for instance, the step free energy decreases by an amount of about 0.2 meV/$2a$ at the step edge freeze-in temperature (575 K) if short overhangs are included. The additional terms in Eq. (6) are $e^{-[(3\varepsilon+3\delta)/2]/kT} + e^{-[(3\varepsilon+4\delta)/2]/kT}$. However, at a temperature of 1150 K this free energy difference has increased to 4 meV/$2a$.

The partition function Z considered in Eq. (6) deals with a line segment of length $\sqrt{2}a$ in the ⟨010⟩ direction and therefore the factor $\sqrt{2}$ is needed in Eq. (7) in order to convert the step free energy to an energy per unit length $2a$ in the ⟨010⟩ direction.

The condition for a ⟨010⟩ step to facet into straight segments oriented along ⟨110⟩ directions is

$$F_{S_A} + F_{S_B} < \sqrt{2} F_{\langle 010\rangle}. \tag{8}$$

We now consider this faceting transition in more detail for three different cases ($\delta = 0$, $\delta > 0$, and $\delta < 0$).

Case I ($\delta = 0$). Because the NNN interaction is assumed to be zero this case is appropriate for Ge(001). In Fig. 1 a schematic diagram of a step oriented along the ⟨010⟩ and ⟨110⟩ direction is shown. At zero temperature all pathways (from A to B) require a minimum energy of $N(\varepsilon_\parallel + \varepsilon_\perp)/2$ (where $N \times N$ is the cell size). Thus the formation energy of a pair of straight steps is exactly the same as the formation energy of a step oriented along the ⟨010⟩ direction. However, with increasing temperature the entropy term of a ⟨010⟩ step is larger than that of the sum of the two ⟨110⟩ oriented steps. Hence the ⟨010⟩ oriented steps will not facet into straight ⟨110⟩ oriented step segments. In Fig. 2 a plot of the step free energies for a ⟨010⟩ and a pair of ⟨110⟩ steps of Ge(001)

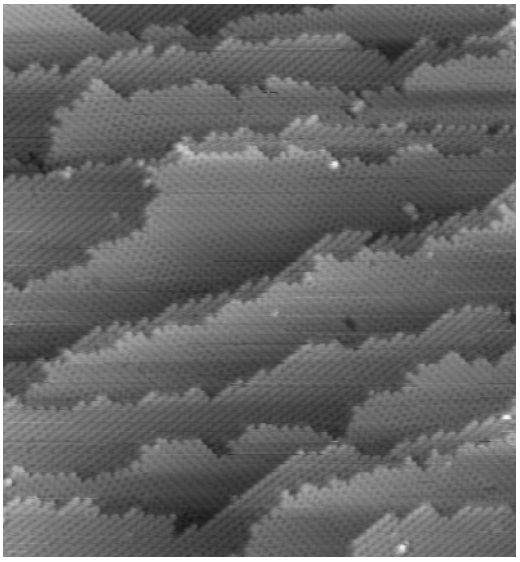

FIG. 3. STM image of ⟨010⟩ oriented steps on Ge(001). The ⟨010⟩ steps meander along their mean direction. Image size 53 nm $\times$56 nm. The sample bias is -1.6 V and the tunneling current is 1 nA.

versus temperature are shown. The freeze in temperature at which step edge roughness of Ge(001) is frozen is estimated to be $\sim$575 K. At this temperature it is energetically still favorable to have a ⟨010⟩ oriented step meandering around its mean direction. However, at temperatures above $\sim$630 K the ⟨010⟩ step will tend to facet into ⟨110⟩ step segments. Because the free energy differences between the two different step configurations is small compared to kT both configurations will coexist at these temperatures in perfect agreement with the experimental observations (see Fig. 3).

Case II ($\delta>0$). The step edge formation energy of a ⟨010⟩ oriented step is $N(\varepsilon_{\parallel}+\varepsilon_{\perp})/2+N\delta$, whereas a faceted step requires an energy $N(\varepsilon_{\parallel}+\varepsilon_{\perp})/2+2N\delta$. Because $\delta>0$ it is always more favorable to have a perfectly aligned ⟨010⟩ step rather than a facetted step. Thus for an attractive NNN interaction faceting will in general not occur.

Case III ($\delta<0$). This case holds for the Si(001) surface at zero temperature. It is energetically more favorable to have the faceted pair of ⟨110⟩ steps rather than the 100% kinked ⟨010⟩ step. In Fig. 4 a plot of the step free energies for a ⟨010⟩ and a pair of ⟨110⟩ steps of Si(001) versus temperature is shown. We have considered a square cell with a size of 4 by 4 unit cells (see Fig. 1). The steps are constrained to start and end at points A and B, respectively. The free energy for this situation is

$$F=2\left(\frac{\varepsilon_{\perp}+\varepsilon_{\parallel}+2\delta}{4}-k\frac{T}{8}\ln\left[\begin{matrix}e^{\delta/2kT}+4e^{\delta/kT}+12e^{3\delta/2kT}+18e^{2\delta/kT}+\\18e^{5\delta/2kT}+12e^{3\delta/kT}+4e^{7\delta/2kT}+e^{4\delta/kT}\end{matrix}\right]\right).$$

The lower (solid) curve in Fig. 4 refers to the free energy of a pair of steps oriented along ⟨110⟩ directions. Note that, increasing the cell size from 4×4 to 8×8 only reduces the

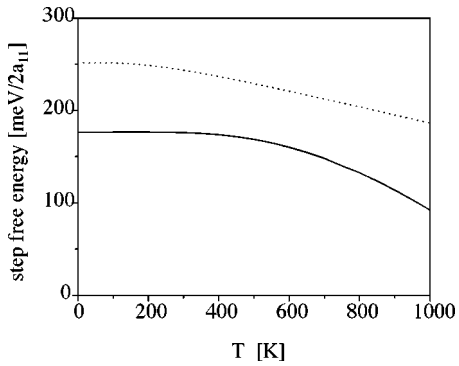

FIG. 4. Plot of the step free energies of Si(001). The solid curve refers to a pair of S_A and S_B steps and the dotted curve refers to a ⟨010⟩ step.

step edge free energy at the step edge freeze-in temperature of Si(001) (775 K) from 206 meV/2a for a 4×4 cell to 196 meV/2a for a 8×8 cell. Over the full temperature range, i.e., from 0 K to the thermal roughening temperature of Si(001), the faceted configuration is favored. This is in perfect accordance with the experimental STM observations (see Fig. 5).

To quantify the amount of faceting of ⟨010⟩ oriented steps on Si(001) and Ge(001) surfaces we introduce the average corner density, denoted by $\langle c\rangle$. For a perfectly straight [010] step one has $\langle c\rangle=1$, whereas a perfectly straight [110] step has a ⟨c⟩ value of 0. By analyzing several large scale STM images we find $\langle c\rangle=0.30\pm0.03$ for Si(001) and $\langle c\rangle=0.62\pm0.06$ for Ge(001), illustrating the different degrees to which [010] steps are faceted for these surfaces. We take these numbers as direct evidence in support of our model, in which the degree of faceting of [010] steps is determined by the strength and sign of NNN interactions. In the absence of a NNN interaction one finds for a meandering ⟨010⟩ step an average corner density of exactly 0.5. The fact that the Ge(001) ⟨010⟩ steps exhibits a higher value might be as-

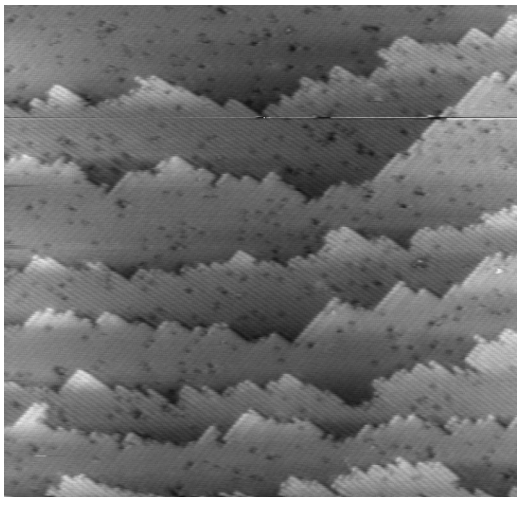

FIG. 5. STM image of ⟨010⟩ oriented steps on Si(001). The ⟨010⟩ steps facet into local ⟨110⟩ step segments. Image size 75 nm $\times$75 nm. The sample bias is -2 V and the tunneling current is 1 nA.

cribed to, for instance, leaving out of consideration of overhangs and kink-kink interactions.

CONCLUSIONS

Within the framework of a solid-on-solid model that incorporates NN and NNN interactions we have addressed the faceting of ⟨010⟩ oriented steps on a cubic (001) surface. For a repulsive NNN interaction ⟨010⟩ steps will tend to facet into ⟨110⟩ step segments. Faceting of ⟨010⟩ steps does not occur for a vanishing or attractive NNN interaction. As an example we have presented data of ⟨010⟩ oriented steps on Si and Ge(001) surfaces. In the case of Si(001) the ⟨010⟩ steps are faceted, whereas the ⟨010⟩ steps do not facet for Ge(001). These observations are in perfect agreement with the available data of the NNN interaction energies between the substrate dimers of Si and Ge.

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