Direct determination of the step-edge formation energies of the energetically stable and unstable double-layer step edges of Si(001)

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Scanning tunneling microscopy images of 4.5° misoriented double B stepped Si(001) have been analyzed to determine the double-layer step-edge formation energies of the energetically stable double step (B-type) as well as the energetically unstable double step (A-type). The ordering of the various single- and double-layer step-edge formation energies is in accordance with semiempirical tight-binding-based total-energy calculations performed by Chadi [Phys. Rev. Lett. **59**, 1691 (1987)]. Finally, the miscut angle at which the transition between the single- and double-layer stepped surface occurs as calculated using the experimentally obtained step-edge formation energies is in agreement with the experiments. [S0163-1829(96)05724-4]

One of the most intriguing and frequently studied surfaces is without any doubt Si(001). The Si(001) surface reconstructs to form rows of dimerized atoms. A rich variety of step structures have been reported in the literature over the past years. Among them are the transition from a hilly single-layer stepped surface to a surface containing coexisting areas with wavy single-layer steps and straight single-layer steps,[1] the transition from wavy and straight single-layer steps to straight single-layer steps only[2] and finally the transition from single-layer steps to double-layer steps.[3] Because of the symmetry of the diamond lattice, dimer rows are oriented in two perpendicular directions. Two types of single- and double-layer steps can be discriminated. Single-(double-) layer step edges are denoted S_A (D_A) when the dimer rows of the upper terrace run parallel to the step edge, whereas they are denoted S_B (D_B) when the dimer rows run perpendicular to the step edge. From a technological point of view double-layer steps on Si(001) are particularly interesting, because the growth of, e.g., GaAs on single-layer stepped Si(001) gives rise to disorder in the overlayer, whereas double-layer steps allow the growth of coherent Ga and As layers. The first real-space images of double-layer steps on Si(001) were reported by Wierenga, Kubby, and Griffith.[3] Their high-resolution scanning tunneling microscopy images have confirmed the rebonded geometry as proposed by Chadi.[4] Besides the atomic structure of the various types of step edges of Si(001) Chadi also calculated their formation energies using a semiempirical tight-binding-based total-energy calculation. The S_A step edge turns out to have the lowest formation energy because it is the only step edge that does not lead to large strains or to extra dangling bonds. The D_A step edge has the highest formation energy. Scanning tunneling microscopy images of single-layer stepped Si(001) have been analyzed to determine the step-edge formation energies directly. From the roughness of the S_B the formation energy of the S_A can be extracted and vice versa.[5,6] On double-layer stepped Si(001) only D_B-type steps occur. Determination of both D_A and D_B step-edge formation energies seems therefore *a priori* impossible. However, in this paper we will show that from the roughness of the D_B step edge alone *both* double-layer step-edge formation energies can be determined. Eaglesham *et al.*[7] measured the equilibrium shape of voids in Si formed by MeV He implantation and annealing. From this shape they were able to extract the surface energy, $\gamma(\theta)$. The step-edge formation energy for the D_B step edge obtained from $d\gamma/d\theta$ was determined to be 92 meV/$2a$. This value is in good agreement with the earlier mentioned theoretical calculation (100 meV/$2a$) by Chadi.[4] To the best of our knowledge the D_A step-edge formation energy has not been determined experimentally.

All experiments were carried 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, contains a home-built STM (scanning tunneling microscope). The B-doped p-type Si(001) samples (5–10 Ω cm) with dimensions $20\times4\times0.3$ mm^3 were 4.5° misoriented toward [110]. The azimuthal misalignment of the step edge with respect to the $[\bar{1}10]$ direction was estimated to be less than 0.5°. After loading the samples in the UHV chamber they were outgassed at a temperature of about 875–975 K for at least 20 h followed by flashing at temperatures above 1575 K for several seconds. After flashing the samples were either quenched immediately to room temperature by turning off the power supply or quenched to room temperature in a two-step process: first to a temperature varying between 600 and 825 K, kept there for about 15 min, followed by a second quench to room temperature. It turns out that, in agreement with previous work,[6] the different cooling procedures have no measurable influence on the observed step-edge roughness and kink distribution. During flashing the chamber pressure was kept in the 10^{-10}-Torr range. This procedure results in clean nearly single domain Si(001) 2×1 surfaces with a defect density as low as 0.5%.

In this paper, we present scanning tunneling microscopy measurements of the step-edge roughness of the D_B step that allows a determination of the step-edge formation energies of both types of double-layer step edges. In Figs. 1(a) and 1(b) two filled-state STM images of 4.5° misoriented Si(001) are displayed. Areas with rebonded D_B double steps coexist with areas where the double step has split into pairs of singles (S_B+S_A). To determine the distribution of step con-

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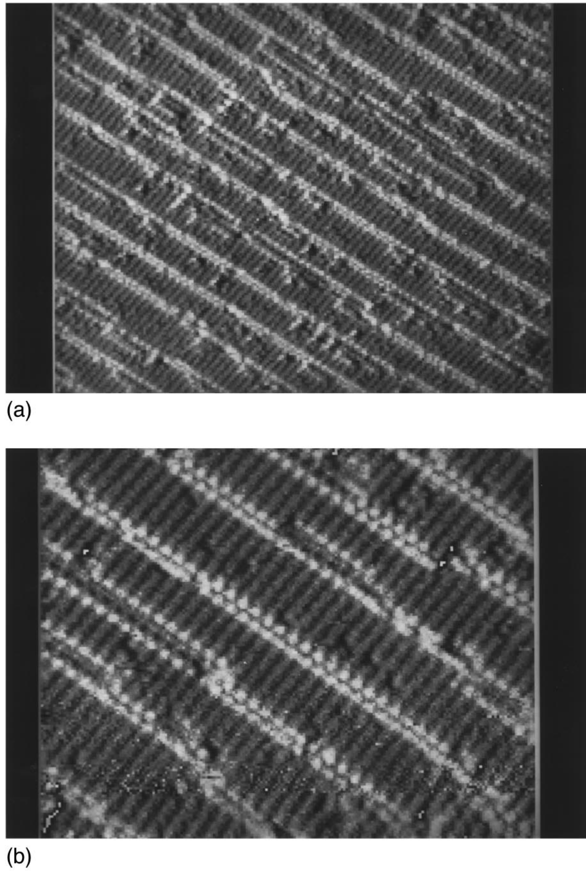

FIG. 1. Scanning tunneling microscopy images of 4.5° vicinal Si(001) tilted toward [110]. Sample bias −2 V and tunneling current 1 nA. (a) Scan size 40×32 nm^2; (b) scan size 20×16 nm^2.

figurations, we have measured the probability of finding various step-edge geometries. We have, however, only counted several types of different step-edge geometries [see Figs. 2(a)–2(c)]: the rebonded D_B step geometry (denoted n_{D_B}), a combination of two single-layer step edges separated by $2a$ (=7.7 Å) from each other (denoted $n_{S_A+S_B}$), and finally kinks with length $2a$ consisting of a D_A piece of step edge (denoted n_{D_A}). Under the assumption of independent kinks and no azimuthal misalignment of the step edge with respect to the [$\bar{1}$10] direction (no forced kinks), the probability of finding a certain type of kink is $\propto g_i \exp[-E(n)/kT]$, where T is the freeze in temperature of the step-edge roughness [estimated to be about 775 K (Ref. 6)], $E(n)$ is the energy difference between the kink position under consideration and a rebonded D_B position (our reference), and g_i arises from the degeneracy of the excited states; i.e., there are in general two possible kink directions, either into or out of the terrace. For the n_{D_A} type of kink the two possible kink directions occur with the same probability, indicative of no azimuthal misalignment of the step edge. The difference in energy between a rebonded D_B step edge and an n_{D_A} type of kink of length $2a$ (=7.7 Å) is just the formation energy of a D_A step edge per $2a$

$$n_{D_A}/n_{D_B} = 2e^{-E_{D_A}/kT}. \quad (1)$$

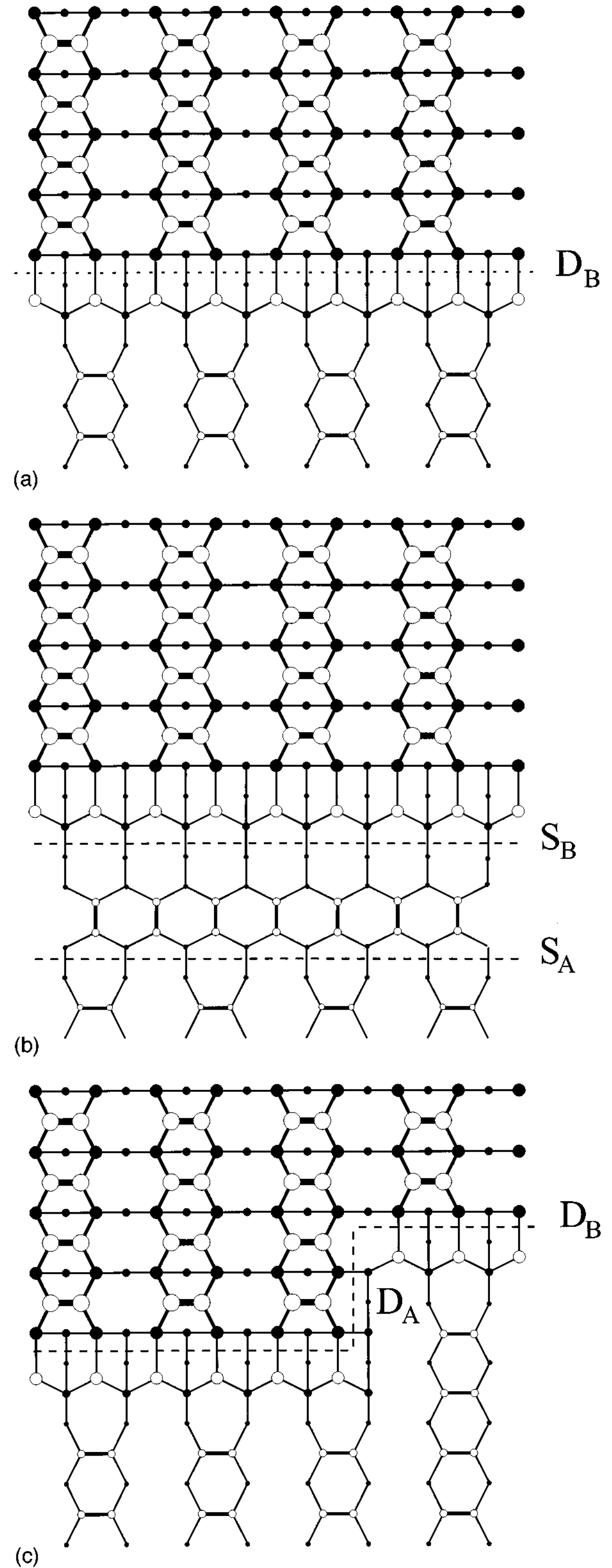

FIG. 2. Configuration of various step geometries. (a) n_{D_B} step-edge geometry; (b) $n_{S_A+S_B}$ step-edge geometry; (c) n_{D_A} kink position.

We have counted in total more than 2000 step-edge positions (n_{D_B}=1521, n_{D_A}=33, and $n_{S_A+S_B}$=472). From these numbers we extract a ratio n_{D_A}/n_{D_B} of 0.022 resulting in a D_A step-edge formation energy of 300 meV/$2a$. As we will see

below the D_A step-edge formation energy is substantially higher than the formation energy of a D_B type of step edge in agreement with the experiments that no D_A step edges are observed after cleaning Si(001). In order to extract the D_B step-edge formation energy we focus our attention on the probability of occurrence of a step-edge geometry where the two single-layer step edges are separated by $2a$. The difference in energy between a rebonded D_B step edge and this combination of two single-layer step edges separated by $2a$ is $E_{S_A}+E_{S_B}+E_{\mathrm{strain}}-E_{D_B}$ (Refs. 8 and 9)

$$n_{S_A+S_B}/n_{D_B}=e^{-(E_{S_A}+E_{S_B}+E_{\mathrm{strain}}-E_{D_B})/kT}. \tag{2}$$

From the experiments we extract a ratio $n_{S_A+S_B}/n_{D_B}$ of 0.31. The strain relaxation energy per unit step length, E_{strain}, can be written as[8]

$$E_{\mathrm{strain}}=-2C\ln\left[\frac{l+L}{2\pi a}\sin\left(\frac{\pi l}{l+L}\right)\right], \tag{3}$$

where l (=7.7 Å) is the width of the minority domain and L $(=[2.72\text{Å}/\tan(4.5°)]-7.7\text{Å}=26.9\text{ Å})$ the width of the majority domain. C is a function of the elastic constants and of the difference of the surface stress within the two types of 2×1 domains and a_0 is a microscopic cutoff length (e.g., the lattice constant).[8] From various experiments C is determined to be about 25 meV/$2a$,[9,10] resulting in a strain relaxation energy of only 4 meV/$2a$. The step-edge formation energies of the single-layer steps have been determined earlier[5,6] to be 120 and 52 meV/$2a$ for the S_B and S_A step edges, respectively. Plugging these values into Eq. (2) gives a step-edge formation energy of 100 meV/$2a$ for the D_B step edge. This experimentally determined D_B step-edge formation energy is in good agreement with the experimental value reported by Eaglesham *et al.*[7] as well as the theoretical calculation by Chadi.[4]

In order to give an estimate of the critical angle at which the transition between the single-layer stepped surface and the double-layer stepped Si(001) surface one should realize that the double-layer stepped Si(001) surface is a single-domain structure where all the terraces have the same orientation, and no strain relaxation can occur. On the other hand, a single-layer stepped Si(001) surface exhibits two different terraces, whose orientation alternates. The corresponding stress tensor (the 2×1 reconstruction has an anisotropic stress tensor) rotates at each single-layer step edge, resulting in a strain relaxation energy (per unit area) for the single-layer stepped surface with an averaged terrace width λ of $C\ln(\lambda/\pi a)$. With decreasing miscut angle the strain relaxation becomes large enough to make a combination of two single-layer steps (formation energy 172 meV/$2a$) energetically more favorable as compared to a single double-layer step (formation energy 100 meV/$2a$). The miscut angle, θ_c, where the transition occurs from a single-layer stepped to a double-layer stepped Si(001) surface can be extracted from the following equation:

$$E_{D_B}=E_{S_A}+E_{S_B}-2C\ln(\lambda_c/\pi a), \tag{4}$$

where λ_c $[=2.72\text{Å}/\tan(\theta_c)]$ is the critical terrace width. Plugging the values for E_{D_B,S_A,S_B} (100, 52, and 120 meV/$2a$) and C (25 meV/$2a$) in Eq. (4) results in a critical miscut angle θ_c of 1.5° in good agreement with the experimental observations. Because thermal fluctuations of the step edges have not been taken into account here this result only holds for $T=0$ K. The entropy of the two wandering single-layer steps is larger as compared to the entropy of the wandering double step resulting in a decrease of the critical terrace width λ_c and thus an increase of the critical angle θ_c.

In summary, scanning tunneling images of double-layer stepped Si(001) are analyzed in order to determine the step-edge formation energies of the two types of double-layer step edges. The D_B step-edge formation energy is estimated to be about 100 meV/$2a$, whereas the energetically unfavorable D_A step edge has a formation energy of about 300 meV/$2a$. The D_B step-edge formation energy is in good agreement with the experimental value of Eaglesham *et al.*[7] as well as the theoretical calculation by Chadi.[4] Moreover, the ordering of the two single- and two double-layer step-edge formation energies is in accordance with the ordering reported by Chadi.[4] Finally, using these values of the step-edge formation energies as well as a value of the strain relaxation energy of the 2×1 domains we are able to estimate quite accurately the miscut angle for which the transition between single stepped Si(001) to double-layer stepped Si(001) occurs. The calculated miscut angle of 1.5° is in agreement with the experimental observations.

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