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Effects of external strain on the order-disorder phase transition and the hierarchical structure on the Si(001) surface

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Externally applied tensile strain on the Si(001)-$c(4\times2)$ surface was found to induce the flip-flop motion of the buckled dimers. This motion occurred cooperatively to form the disordered phase of the (2×1) structure. As the strain increased, the disordered phase grew and conversely the ordered phase of the $c(4\times2)$ structure shrank. The domain shape of the ordered phase depended on the tensile strain and its direction, which was governed mainly by the dependence of the domain wall energies parallel and perpendicular to the direction of the dimer bond on the strain.

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I. INTRODUCTION

On a clean Si(001) surface, the phase transition from $c(4\times2)$ to the (2×1) structure occurs at about 200 K.[1,2] The topmost atoms on the Si(001) surface form a dimer, and the dimer is buckled to stabilize the surface energy. Below the critical temperature, T_c, the buckled dimer is arranged in an antiferromagnetic order, which results in a $c(4\times2)$ structure. Above T_c, however, the buckled dimer appears symmetric due to the time average of the thermal flip-flop motion of the buckled dimer, resulting in a (2×1) structure.[3–6] Thus this transition is an order-disorder phase transition with respect to the arrangement of the buckled dimer. The formation of the dimer and the buckling of the dimer cause dipole interaction among the dimers and generate an atomic scale strain field in the surface layers.[7–10] The antiferromagnetic ordering of the buckled dimer results in a modulation of elastic strain over a range of several nanometers and the flip-flop motion of the buckled dimer disarrays this modulation. Near T_c, coexistence of the ordered and disordered phases forms a mesoscopic domain pattern of elastic strain on a terrace. On terraces separated by an odd number of monatomic-height steps, the directions of the modulation and the domain pattern are orthogonal. Thus the Si(001) surface exhibits a multiscale hierarchical structure regarding the elastic strain of the surface lattice. Such a hierarchical structure has the potential to form a higher-order structure of self-assembly and to generate multiple channels of surface reaction. One might expect that an external strain applied on the Si(001) surface would change the inner strain field and the hierarchical structure accordingly. Here we report how the external anisotropic strain affects the order-disorder phase transition and the hierarchical structure of elastic strain on Si(001).

II. EXPERIMENTAL PROCEDURES

In this experiment, an external strain was applied on a clean Si(001) surface under ultrahigh vacuum (UHV) by a three-point bending method; both edges of the sample, 0.3 mm thick, 8 mm wide, and 28 mm long, were loosely clamped through Ta spring wires, and the middle of the back of the sample was pushed by a wedge-shaped Ta anvil. The anvil was used to bend the sample on a high-precision micrometer. The convex surface was expanded in the longitudinal direction ([110] or [01] direction); a 0.27-mm deflection of the anvil corresponded to 1.0×10^{-3} tensile strain along the [01] direction at the middle of the sample. The tensile strain at the middle of the sample surface was varied between 0 and 2.5×10^{-3} depending on the deflection. Before applying the strain, the Si(001) surface was cleaned by Ar-ion bombardment (500 eV) for 4 min at the angle of incidence of 15° at room temperature, annealing at 900 K for 10 min, and repeated flash-heating at about 1500 K for 16 s, and then the sample was cooled by the liquid nitrogen reservoir. The surface structure was observed at the center of the sample by low-energy electron diffraction (LEED). The energy of the electron of incidence was 110 eV and 146 eV. As no significant difference was observed between the two results, only the result at 110 eV is shown below. The LEED intensity was measured by a computer-controlled data acquisition system equipped with an intensified charge-coupled device (CCD) video camera. As the surface structure of Si(001)-$c(4\times2)$ is very sensitive to surface contamination and to electron radiation,[2,11] the LEED measurements were accomplished under 1×10^{-8} Pa within 3 min. After relieving the strain, the sample was annealed at 900 K for 16 min to eliminate residual stress and was again cleaned by flash-heating at 1500 K.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the dependence of the LEED pattern of the Si(001) surface on the external strain. During the experiments, the surface temperature was kept constant at 169 K, which is below T_c (~200 K). In terraces separated by an odd number of monatomic-height steps, the orientation of the dimer bond is rotated by 90°. When the tensile strain is applied on the surface along the [01] direction, we referred to the terraces where the direction of the dimer bond is parallel to the [01] direction as the *A* terraces, and the terrace where the direction of the dimer bond is perpendicular to the [01] direction as the *B* terraces, as shown in Fig. 1(b). In Fig. 1, the quarter-order reflections of $3/4\ -1/2$ and $1/2\ -3/4$ were clearly observed; they originated from the ordered phases of the $c(4\times2)$ structure on the *A* and *B* terraces,

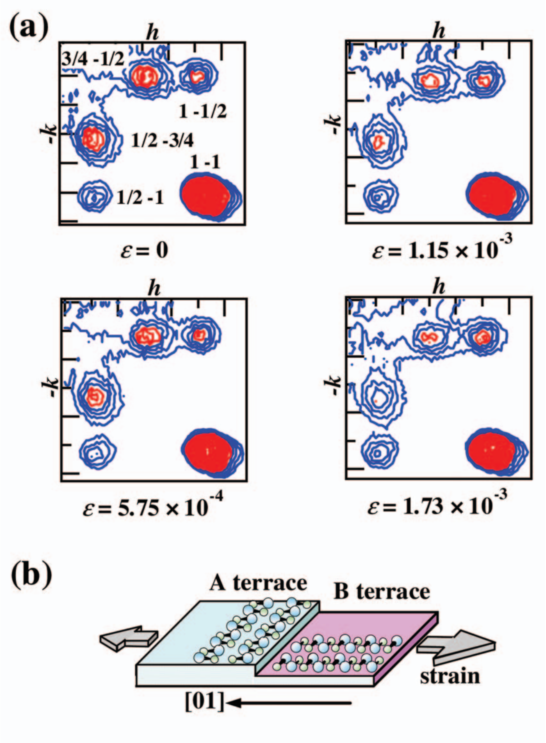

FIG. 1. (Color) (a) The dependence of the LEED pattern of Si(001) on the external strain, at 169 K. The intensity distribution was represented in contour. The external tensile strain was applied along [01] direction. (b) The relationship between the directions in the tensile strain and the dimer bond.

respectively. The $1/2\ -1/2$ reflection corresponding to the $p(2\times2)$ structure was never observed during the entire experiment. Thus, the $p(2\times2)$ structure, even if it was present, did not construct a large domain but existed only at the antiphase domain boundary. From Fig. 1(a), it can be seen that the intensities of the quarter-order reflections and their distribution strongly depended on the strain. However, the integrated intensities of the half-order reflections of $1/2\ -1$ and $1\ -1/2$ which originate from the dimers on the *A* and *B* terraces, respectively, were independent of the strain (the quantitative data are not shown). In the Si(001) surface, the integrated intensity of the half-order reflection is proportional to the number of dimers on the terrace (i.e., the area of the terrace). Thus, the result indicates that the area of each terrace does not depend on the strain; the ratio of the areas of the *A* and *B* terraces remained at a constant ratio of about 1.10. This result is in contrast with the dependence of the terrace population on the external strain at an elevated temperature. At a surface temperature well above T_c where the disordered phase of the (2×1) structure is stable, the external strain produces unequal populations of the (2×1) and (1×2) terraces.[12] These reconstructed terraces have the anisotropic intrinsic surface stress which produces long-range strain fields. When an anisotropic external strain is applied to the surface, the energy in these strain fields can be minimized by changing the configuration of the two terraces.[13] This requires the motion of monatomic steps caused by thermal activation. In this experiment, however, the surface temperature was too low $(<T_c)$ for the steps to move. As shown in Fig. 2, the integrated intensities of the $3/4\ -1/2$ and $1/2\ -3/4$ reflections decreased with an increase in the strain. According to the kinematical theory of electron diffraction, the integrated intensity of the quarter-order reflection, $I^{\text{integr}}(\mathbf{q})$, is expressed as, $I^{\text{integr}}(\mathbf{q})=4(S/A_u)\times(f_+-f_-)^2\theta_{c(4\times2)}$, where $\mathbf{q}$ is the wave vector at a quarter-order reflection, S is the area of the terrace from which the reflection originates, A_u is the area of the unit cell of (4×2), f_+ and f_- is the structure factors for the two buckled-dimer orientations, and $\theta_{c(4\times2)}$ is the coverage of the ordered phase of the $c(4\times2)$ structure. During the entire experiment, no fractional order reflections other than those corresponding to the $c(4\times2)$ or (2×1) structures were ever observed; the surface consisted of the ordered phase of the $c(4\times2)$ structure and the disordered phase of the (2×1) structure. Then we can define $\theta_{c(4\times2)}$ as the order parameter. Since the area of the terrace, S, is constant with the strain, the decrease in the integrated intensities of both quarter-order reflections means that on both the *A* and *B* terraces, $\theta_{c(4\times2)}$ decreases and conversely the disordered phase of the (2×1) structure increases, with the increase in the strain. In the disordered phase of the (2×1) structure, the buckled dimer spatiotemporally fluctuated by flip-flop motion is energetically more favorable than the static buckled dimer disorderly arranged.[3–6] Thus, this result strongly suggests that the flip-flop motion of the buckled dimers is induced by the strain. According to the first-principles calculations of the surface stress of the clean Si(001) surface,[14,15] the (2×1) surface is less tensile along the dimer bond direction and is more compressive in the direction perpendicular to the dimer bond than the $c(4\times2)$ surface. Thus, the (2×1) surface is more favorable for elastic energy than the $c(4\times2)$ surface when the external tensile strain is applied on the Si(001) surface. This is probably the reason why the disordered phase of the (2×1) structure increases with the strain. This qualitative interpretation is based on the concept proposed by Alerhand *et al.* that anisotropy in the surface stress tensor and degeneracy in the reconstructed phase can lead to the spontaneous formation of elastic-stress domains on the surface.[13] The influence of the step on the phase transition can also be ex-

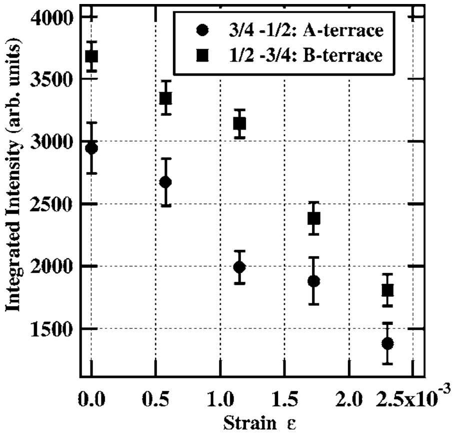

FIG. 2. The dependence of the integrated intensities of the quarter-order reflections on the external tensile strain.

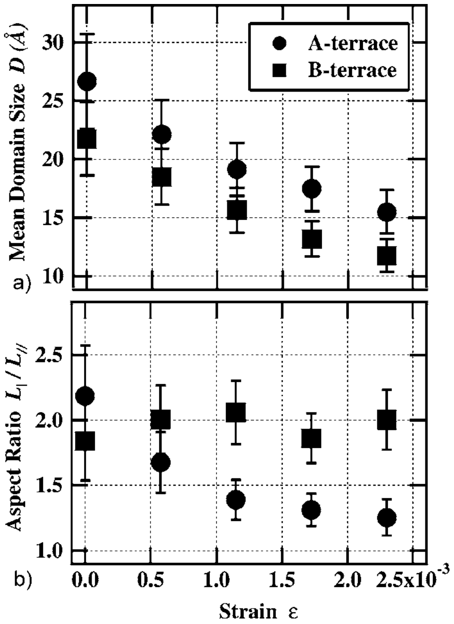

FIG. 3. The dependence of the mean domain size and the aspect ratio of the ordered domain of the $c(4\times2)$ structure on the external tensile strain.

plained by this interpretation. In the scanning tunneling microscopy (STM) images at 177 K, about 20 K below T_c, the disordered domains of the (2×1) structure were found near the ledge of the straight S_A steps on the B terrace, whereas the $c(4\times2)$ structure was observed in the other region; the ledge of the straight S_A step inhibited ordering of the buckled dimer on the lower terrace near the S_A step.[16] Here the S_A step was assumed as a single atomic step which is perpendicular to the dimer row on a lower terrace of the step.[17] On the lower terrace of the S_A step, the area near the S_A step is compressed along the dimer row direction.[18] Because the (2×1) surface is more compressive in the direction parallel to the dimer row than the $c(4\times2)$ surface, at the area near the S_A step, the (2×1) structure is energetically more favorable than the $c(4\times2)$ structure. When the surface is strained by the three-point bending method, together with the strain on the surface, the shear strain arises along a depth only in the middle of the sample. In the $c(4\times2)$ structure, the long-range atomic relaxation deep into the bulk plays a crucial role in stabilizing $c(4\times2)$.[9,15] Thus, the shear strain along the depth direction accompanied by externally applied tensile strain on the surface also destabilizes the $c(4\times2)$ surface structure.

We analyzed the dependence of the line profiles of the quarter-order reflections on the strain. For the quarter-order reflection, the full width at half maximum (FWHM) of the line profile, Δ_{FWHM}, can be expressed as $\Delta_{\mathrm{FWHM}}=2\sqrt{\ln 2}(a_0/\pi L)$, where Δ_{FWHM} is in the reciprocal-lattice units, a_0 is the Si lattice parameter (3.84 Å along the [01] and [10] directions), and L is the correlation length assuming the correlation function Gaussian. STM measurements of Si(001) revealed the presence of a domain pattern consisting of $c(4\times2)$ and (2×1) domains, under an external strain-free condition.[4] A similar domain pattern was also observed on Ge(001).[19] Then the correlation length can correspond to the average length of the ordered domain of the $c(4\times2)$ structure.[20] Assuming that the shape of the ordered domain is rectangular, the mean size of the ordered domain, D, can be defined by $D=\sqrt{L_\parallel L_\perp}$, where $L_\parallel$ and $L_\perp$ are the lengths of the ordered domain parallel and perpendicular to the dimer bond direction, respectively. On both the A and B terraces, D decreased with an increase in the strain [Fig. 3(a)], which was associated with the decrease in the coverage of the ordered phase. The dependence of the aspect ratio of the ordered domain, $L_\perp/L_\parallel$, on the strain was different between the A and B terraces; $L_\perp/L_\parallel$ on the A terrace went down to unity with decreasing strain, and that on the B terrace slightly increased or was maintained virtually constant with the strain [Fig. 3(b)]. From Refs. 13 and 21, the elastic energy per unit area of an ordered domain on the N terrace $(N=A,B)$ under the external tensile strain ε, $E^{unit}_{el,N}$, can be expressed as

$$\begin{aligned} E^{unit}_{el,N} = {} & \frac{2}{D}\left(cE_\perp + \frac{E_\parallel}{c}\right) + \frac{1+\nu}{\pi D\eta}\Bigg\{\left[g(c)F_\parallel^2 + h(c)F_\perp^2 + i(c)F_\parallel F_\perp\right] \\ & - 2(1-\nu)\left[cF_\parallel^2 + \left(\frac{1}{c}\right)F_\perp^2\right]\ln\left(\frac{D}{a_0}\right)\Bigg\} \\ & + \frac{\varepsilon}{2}\Bigg\{(\delta_{A,N}+\nu\delta_{B.N})\left[\sigma_{(2\times1)\parallel} + \left(\frac{D}{L_{\parallel,0}c}\right)F_\parallel\right] \\ & + (\nu\delta_{A,N}+\delta_{B,N})\left[\sigma_{(2\times1)\perp} + \left(\frac{Dc}{L_{\perp,0}}\right)F_\perp\right]\Bigg\}, \end{aligned} \tag{1}$$

where $c^2=(L_\perp/L_\parallel)$ is the aspect ratio; $E_\parallel$ and $E_\perp$ the formation energies of the domain wall, which we named domain wall energies, per unit length parallel and perpendicular to the dimer bond, respectively; $\nu=0.218$ the Poisson's ratio; $\eta=0.81$ eV/Å^2 the Young's modulus of the substrate; $F_\parallel=0.108$ eV/Å^2 and $F_\perp=0.231$ eV/Å^2 the force densities along the domain wall parallel and perpendicular to the dimmer row,[14] respectively; $g(c)$, $h(c)$, and $i(c)$ the

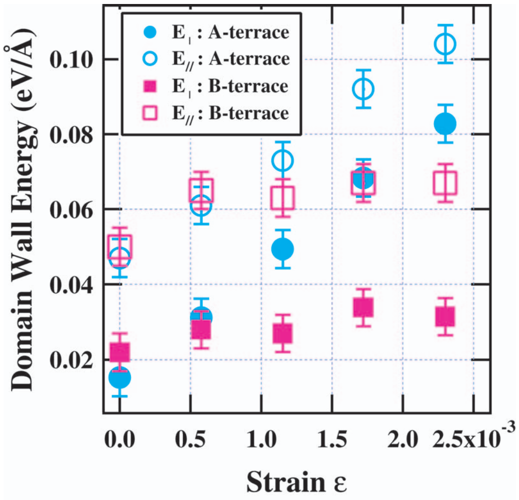

FIG. 4. (Color) The dependence of the domain wall energies on the external tensile strain. $E_\parallel$ and $E_\perp$ are the domain wall energies parallel and perpendicular to the dimer bond, respectively.

dimensionless geometric factors which depend on the domain aspect ratio c^2;[22] $a_0=3.84$ Å the microscopic cutoff length in the range of the surface lattice constant; $\sigma_{(2\times1)\parallel}$ and $\sigma_{(2\times1)\perp}$ the stress tensors of the (2×1) surface parallel and perpendicular to the dimer row, respectively; and $L_{\parallel,0}$ and $L_{\perp,0}$ are $L_\parallel$ and $L_\perp$ at $\varepsilon=0$, respectively. In the right-hand side of Eq. (1), the first term is the domain wall energy, the second term is the elastic relaxation energy, and the third term is the gain of the energy by applying the external strain. For a given external strain ε, E_{el}^{unit} is minimized with respect to $L_\parallel$, $L_\perp$, $E_\parallel$, and $E_\perp$. From the experiments, we can know the dependence of $L_\parallel$ and $L_\perp$ on ε. Then we can estimate $E_\parallel$ and $E_\perp$, depending on ε, to minimize E_{el}^{unit}. Figure 4 shows the dependence of the domain wall energies on ε for each terrace. On the *A* terrace, both $E_\parallel$ and $E_\perp$ increased, and the ratio of $E_\parallel/E_\perp$ went down to unity as ε increased. Both $E_\parallel$ and $E_\perp$ on the *B* terrace, however, were only weakly dependent on ε. In either terrace, the dependence of the ratio of $E_\parallel/E_\perp$ on ε was very similar to that of the aspect ratio of $L_\perp/L_\parallel$ on ε. This suggests that the dependence of the aspect ratio of the ordered domain on ε is strongly affected by the dependence of the domain wall energy on ε.

IV. CONCLUSIONS

In conclusion, we have elucidated the influence of the external strain on the order-disorder phase transition of the Si(001) surface. The externally applied tensile strain on the Si(001) surface destabilized the ordered phase of the $c(4\times2)$ structure. Consequently the ordered phase shrank, and the disordered phase of the (2×1) structure grew below T_c, with an increase in the strain. The domain shape of the ordered phase strongly depended on the strain and its direction. When the direction of the tensile strain was parallel to the dimer bond, the anisotropic shape became isotropic as the strain increased. When the direction of the tensile strain was perpendicular to the dimer bond, however, the shape was insensitive to the strain. The dependence of the shape of the ordered domain on the strain was due mainly to that of the domain wall energies parallel to and perpendicular to the dimer bond on the strain.

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[22] The geometric factors, $g(c)$, $h(c)$, and $i(c)$, are given by

$$g(c) = (1-\nu)\left(c \ln \frac{\sqrt{c^2+\frac{1}{c^2}}+c}{\sqrt{c^2+\frac{1}{c^2}}-c} - 2c \ln \frac{c}{e} \right) + 2(1-2\nu)\left(\frac{1}{c} - \sqrt{c^2+\frac{1}{c^2}}\right),$$

$$h(c) = (1-\nu)\left(\frac{1}{c} \ln \frac{\sqrt{c^2+\frac{1}{c^2}}+\frac{1}{c}}{\sqrt{c^2+\frac{1}{c^2}}-\frac{1}{c}} - \frac{2}{c} \ln \frac{1}{ec} \right) + 2(1-2\nu)\left(c - \sqrt{c^2+\frac{1}{c^2}}\right),$$

$$i(c) = 4\nu\left(c + \frac{1}{c} - \sqrt{c^2+\frac{1}{c^2}}\right).$$