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Reconstructions and step structures on vicinal Si(001) surfaces by interaction with Bi

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Abstract. Reconstructions and step structures on vicinal Bi:Si(001) surfaces are studied under various substrate temperatures and Bi coverages. The observed reconstructions are (2×1), (2×2), c(4×4), and (2×7) phases. For step distributions, alternative domain configurations with single layer steps are observed. The population ratios of A terrace to B terrace depend on the substrate temperatures. The observed reconstructions and step distributions are explained by the large size of the Bi atom compared with Si, the anisotropic stress tensor, and the local atomic structure in the S_B step.

Recently, considerable research effort has been concentrated on vicinal Si(001) surfaces because of their practical importance in epitaxial film growth [1–3] and fundamental interests [4–8]. As a result of many experimental and theoretical studies, the step structures and the reconstructions on vicinal Si(001) surfaces are well understood [4–8]. Vicinal Si(001) surfaces with single layer steps exhibit two types of step and also two types of terrace depending on the dimer row direction with respect to the step edge (see figure 1). For the A terrace, dimer rows are parallel to the step (S_A) edge and for the B terrace they are perpendicular to the step (S_B) [5–7]. Experimental and theoretical studies show that Si(001) surfaces exhibit tensile stress in the direction perpendicular to the dimer row and compressive stress along the dimer row [6–8]. Although *rebonded edge* and *non-rebonded edge* structures are possible candidates for a local atomic step structure of the S_B step with low energy, it is found experimentally and theoretically that the rebonded edge structure without a dangling bond which is eliminated by the reformed bond marked by an arrow in figure 1(a) has a lower energy than non-rebonded edge with dangling bond which is marked by an arrow in figure 1(b).

The reformed bond of the rebonded edge structure plays a key role in determining the distribution of the A terrace and B terrace [6, 7]. It is believed that the reformed bond induces a force dipole and then the induced force dipole is coupled with a force monopole at its neighbouring S_A step [6, 7]. This coupling between the force dipole and force monopole forces the B terrace to grow, resulting in the formation of the surface with asymmetric domain population [6–8]. It is believed that the step distribution on a Si(001) surface largely depends on the surface stress tensor as well as the local structure at the step edge [5–8]. Alerhand *et al* showed that a crystal surface with degenerate phases and an anisotropic surface stress tensor can lower its surface free energy by forming an ordered alternative domain configuration [8]. The reduction in the energy comes from a long-range elastic or strain relaxation.

Since adsorbates generally change surface stress tensors and local step structures, the adsorbed surfaces undergo a significant rearrangement to lower surface free energy by relaxing the additional strain induced by adsorbates [9–11]. Recently, the surface stress on Si(001)

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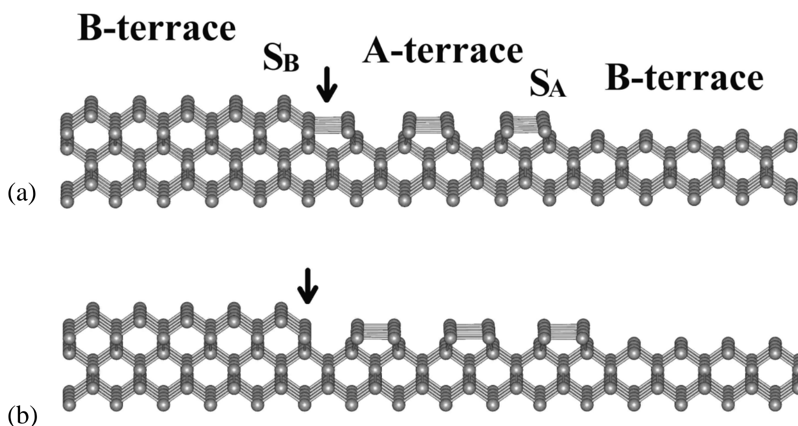

Figure 1. Schematic drawing of vicinal Si(001) surface with single layered step height, where two types of terraces of A terrace and B terrace and two types of steps S_A and S_B are shown. (a) clean Si(001) surface of rebonded edge structure with a reformed bond which is marked by an arrow. (b) clean Si(001) surface of non-rebonded edge structure without reformed bond, where the atom marked by an arrow has one dangling bond.

surfaces received considerable attention due to its apparent effects on reconstructions, step structures, alloying, and segregation as well as interfacial mixing [11–18]. The strain relaxation is accomplished by the change of reconstructions on the terrace and the rearrangement of step structures which require mass transport [15, 16]. In particular, As, Sb, and Bi among many adsorbates have attracted much attention because these elements can be used as surfactants in the epitaxial film growth on Si(001) surfaces [1–3]. Since As, Sb, and Bi belong to the same group but to different periods in the periodic table, they will show both similarities and differences in their chemical and physical properties. Indeed, these three elements show similar behaviours as surfactants in Ge/Si heteroepitaxy; on the other hand, they show different surface stresses due to their different covalent radii (Si: 1.17, As: 1.21, Sb: 1.41, Bi: 1.52 Å).

As-covered Si(001) surfaces (henceforth As:Si(001)) showed a clear (2×1) phase with low vacancy density [11–16] and Sb:Si(001) surfaces exhibited a disordered (2×1) phase including many vacancies [17–19]. Contrary to the cases of As:Si(001) and Sb:Si(001), the Bi:Si(001) surface showed a disordered (2×2) phase at low coverages and a $(2\times n)$ or a highly disordered (2×1) phase at a saturated coverage, where n ranges 5–15 [20–25]. These phases have been explained as resulting from the dimerization of adsorbates. In addition to the change of reconstruction, the step structures of original Si(001) surfaces will be changed by interactions with adsorbates [11, 13–17]. Comparing the surface stress tensors for these adsorbate covered surfaces, the As:Si(001) surface is under tensile stress in the directions both parallel and perpendicular to the As dimer row [13], while the Sb:Si(001) and Bi:Si(001) surfaces are under tensile stress in the direction perpendicular to the dimer row but under compressive stress in the parallel direction [13, 17–25]. Thus, the As:Si(001) surfaces prefer the double-step structure with low step density to the single-step structure because there is no elastic strain relaxation in either the single- or double-domain surface [11, 13–15]. However, the Sb:Si(001) and Bi:Si(001) surfaces can lower the surface free energy by forming alternative domain configurations of A and B terrace [11, 17]. It is expected that the energy gain from the strain relaxation by the formation of double-domain surfaces with single steps will exceed the energy cost by the higher step density, compared to that of the single-domain surfaces with double steps. For the local step structures, since the S_A step has an energy lower than the S_B step [5–7],

the structure of the S_A step is affected less than the S_B step by the interaction with adsorbates.

It was found that the substrate step structures in the initial stage of film growth are very important in determining the growth mode [13]. The step structures of As:Si(001) surfaces have been extensively studied by varying substrate temperatures and As coverages, while the step structures of Sb:Si(001) surface and especially Bi:Si(001) have not. The main purpose of this study is to understand the effects of strain induced by Bi on reconstructions and step structures on Bi:Si(001) surfaces. In the present work, the Bi:Si(001) surfaces were studied by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) varying substrate temperatures and Bi coverages.

The measurements of reconstructed phases and step distributions were made with a conventional four-grid LEED optics equipped with a charge-coupled device (CCD). The CCD enables us to measure the diffracted beam intensity and to analyse the shape quantitatively. For AES, a double pass cylindrical mirror analyser was used. The sample used in this experiment is a commercial mirror-polished Si(001) wafer with a miscut angle of 2° toward the [110] direction. The sample was heated and annealed resistively and the temperature was measured with a thermocouple and infrared pyrometer. Bi (purity of 99.999%) was deposited from a pre-outgassed quartz tube; during deposition the chamber pressure was less than 3×10^{-10} Torr. The coverage of Bi was determined by the AES peak-to-peak ratio of Bi to Si referenced to that on the surface which was obtained by a deposition above 700 K. The saturation coverage of the surface deposited above 700 K has been reported to be about 6/7 monolayer (ML) [22–25], where 1 ML was defined as 6.78×10^{14} atoms cm^{-2}.

After flashing the sample to 1500 K several times and then annealing it at 1100 K, sharp integral-order and half-order LEED spots appeared and no impurities were detected by AES signal. When Bi was deposited on the substrate held below 350 K, a (2×2) LEED pattern with diffuse half-order spots was observed up to 0.7 ML. The (2×2) spots are sharpest at about 0.5 ML. In order to analyse the (2×2) phase quantitatively, the line profile technique was employed. A schematic drawing of the LEED pattern is given in figure 2(a) to represent the direction of line profiles. From the broad and diffuse peak of half-order spots with high background intensity as shown in figure 2(b), it can be concluded that the (2×2) phase includes many vacancies. This observation is consistent with the result of STM by Noh *et al.* [24]. It is expected that the large misfit of 30% between Bi layer and Si substrate induces a large strain on the surface and lets the surface relax the strain by placing the Bi dimers apart from each other. However, since the substrate temperature of 350 K is too low for Bi dimers to diffuse enough to form a well ordered (2×2) phase, the (2×2) phase including many vacancies is formed at below 350 K. Thus, it is expected that the strain on the Bi:Si(001)-(2×2) is not fully relaxed because the diffusion of Bi dimers is limited due to the low substrate temperature. Since Bi atoms are always observed in the form of dimers on the Si(001) surface, the Bi dimer is taken to be the basic unit [24, 25].

In order to completely relax the strain on terraces by increasing the diffusion of Bi dimers on the Si(001) surface, Bi was deposited on the surface and held at a slightly elevated temperature of 400 K. In this case, a c(4×4) phase was observed at about 1/4 ML and a (2×1) phase appeared above 0.3 ML. The intensity profile of the c(4×4) pattern shows clear and sharp fractional spots with a lower background intensity compared to that of (2×2) (figure 2(c)). This means that the well ordered c(4×4) phase is formed uniformly in wide regions. This observation is very interesting because the c(4×4) phase resulting from the ordered Bi adlayer has not been reported and the (2×2) phase has been suggested as a ground state of the Bi:Si(001) surface at low coverages [21, 24]. Considering the fact that Bi dimers on a Si(001) surface are more mobile at 400 K than at 350 K, the well ordered c(4×4) phase can be explained. Comparing two Bi coverages of (2×2) and c(4×4) phase, it is clear that the average distance

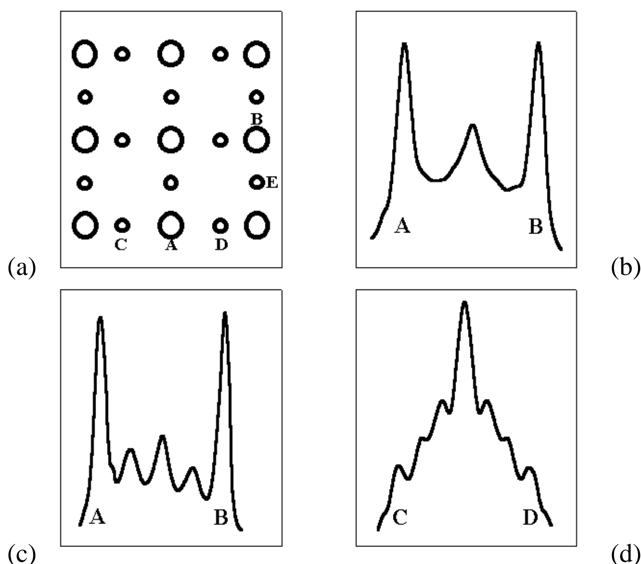

Figure 2. The line profiles of LEED patterns for reconstructed surfaces. (a) A schematic drawing to represent the direction of line profile. (b) (2×2). (c) c(4×4) (d) (2×7).

among Bi dimers in the c(4×4) is longer than that in the (2×2). The increased distance among Bi dimers will lower the repulsion among them. It is expected that the preference of the c(4×4) reconstruction to the (2×2) at the low coverage is due to the full relaxation of the residual strain in the (2×2) reconstruction owing to the increased substrate temperature. It can be concluded that the surface energy of c(4×4) is lower than that of the (2×2) phase.

For the Si(001) surface saturated with Bi, a (2×1) LEED pattern was observed below 400 K during deposition while a high order reconstruction appeared at 500–800 K. The line profile for the high-order reconstruction clearly shows that the phase is a (2×7) reconstruction (figure 2(d)). In order to explain the observed (2×1) and (2×7) phases at the saturation coverage, the effect of defects on the Bi:Si(001) surface should be considered. It was revealed that the Bi:Si(001) surface has many defects due to the large size of Bi as compared to Si [22–25]. These defects are believed to be ordered or disordered depending on the substrate temperature during deposition. At low temperatures ($\leqslant$400 K), the defects are disordered due to the limited diffusion of Bi dimers and this results in the diffuse (2×1) phase. The disordered defects arrangement in the (2×1) phase is supported by the line profile of the beam intensity in which the width of half-order spots of the Bi:Si(001)-(2×1) surface is broader than that of the clean surface (see figure 3). At high temperatures (500–800 K), the defects or Bi dimers can diffuse at a long enough distance to form a long-ranged seventh ordering to relax an additional strain energy caused by the Bi overlayer. The Bi dimers are continuously missed along the dimerization direction and the missing Bi dimer lines occur every seventh period in the direction perpendicular to the dimerization direction, which relaxes the strain induced by the Bi overlayer. The observed (2×7) phase is consistent with the STM results [25] and can be ascribed to an ordered-defect arrangement. From the ordered-defect arrangement of (2×7), it is expected that the Bi coverage on the saturated Bi:Si(001) surface will be 6/7 ML. The temperature of 400 K is high enough to form the c(4×4) phase, while it is not high enough to form the (2×7) phase which requires a large amount of mass transportation and a longer diffusion length compared to the c(4×4) phase.

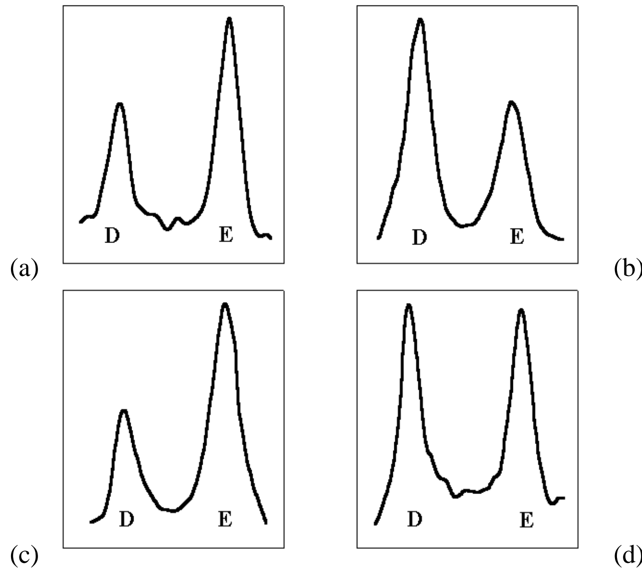

Figure 3. The line profiles of half-order spots. The directions of line profiles are represented in figure 2 (a). (a) Clean surface with $R = 0.5$. (b) Bi:Si(001) with $R = 2$. (c) Bi:Si(001) with $R = 0.5$. (d) The transient surface observed during desorbing the Bi atoms on the Bi:Si(001) with $R = 0.5$.

For step distributions (figure 3 and 4), it was quantified by the ratio $R = I_A/I_B$, where I_A represents the intensity of half-order spots resulting from A terraces and I_B that from B terraces, respectively. A clean surface showed the asymmetric terrace population of $R = 0.5$ with a majority of the B terrace (figure 3(a) and figure 4(a)). For the surface saturated with Bi, the terrace populations depend on the substrate temperatures during deposition as do the reconstructions on terraces. In the case of low temperatures ($\leqslant$400 K), the surface showed the asymmetric terrace population of $R = 2$ (figure 3(b) and figure 4(b)), the ratio of which is inverted to that of the clean surface. At high temperatures (500–800 K), the surface with asymmetric terrace population also appeared but the ratio is $R = 0.5$ (figure 3 (c) and figure 4 (c)) which is the same as that of the clean surface. After desorbing Bi overlayers above 800 K on the Bi:Si(001) surface of $R = 0.5$, the symmetric terrace population of $R = 1$ was observed (figure 3 (d) and figure 4 (d)). The surface of $R = 1$ in which the Bi coverage is below 0.1 ML is not a stable but meta-stable state observed during the transformation of the Bi:Si(001) surface of $R = 0.5$ to the original clean surface of $R = 0.5$.

Group V atoms form dimer rows rotated by 90° referenced to the Si dimer rows on a clean Si(001), that is, the adsorption of the group V element rotates the A terrace of the clean surface to the B terrace of group V:Si(001) and *vice versa* [17–19]. Thus, the inverted domain population of $R = 2$ is easily explained by the rotated Bi dimer rows without a step movement (figure 3(a), (b), figure 4(a), and (b)). The surface with the inverted domain population of $R = 2$ has been frequently reported, whereas the surface with the same domain population of $R = 0.5$ as the clean Si(001) has not been reported on the surfaces of group V:Si(001) [17–19]. The observation of the Bi:Si(001) surface with an asymmetric domain population of $R = 0.5$ is very interesting. The formation of the Bi:Si(001) surface of $R = 0.5$ formed at an elevated temperature should rely on the movement of steps on the original clean surface, which is represented in figure 4 (c) and (d).

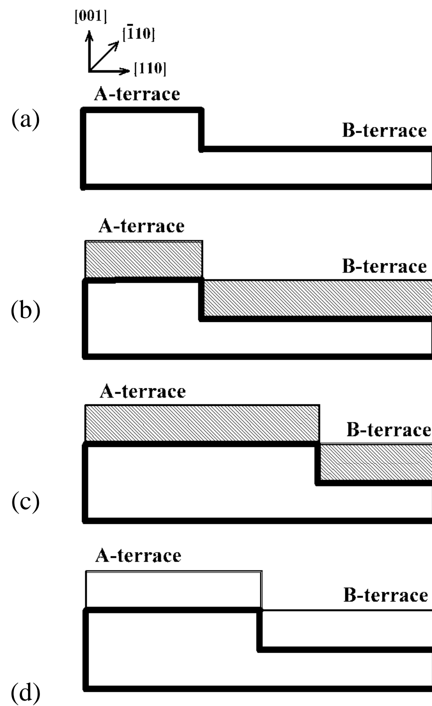

Figure 4. Schematic drawings of the terrace distributions of two types of A and B terraces. The dark-hatched layer represents the Bi layer. (a) Clean surface with $R = 0.5$. (b) Bi:Si(001) with $R = 2$. (c) Bi:Si(001) with $R = 0.5$. (d) The transient surface observed during desorbing the Bi atoms on the Bi:Si(001) with $R = 0.5$.

The alternative distribution of A and B terraces of the Bi:Si(001) of $R = 0.5$ with single layered step height which appears at high temperature (500–800 K) can be understood based on the elasticity theory and the local step structure. Contrary to the case of the As:Si(001), the Bi:Si(001) and the Sb:Si(001) can lower their surface free energy by taking up an alternative domain configuration of the A and B terraces because the Bi:Si(001) and Sb:Si(001) surfaces are under tensile stress in the direction perpendicular to the Bi dimer row but under compressive stress in the parallel direction. It is expected that the energy gain from the strain relaxation caused by the formation of an alternative double domain surface will exceed the energy cost from the higher step density as compared with that of the single domain of A terraces or B terraces. Although the surfaces of both Sb:Si(001) and Bi:Si(001) exhibit the alternative terrace distribution with single layered step height due to the anisotropic stress tensors, the domain populations of the A and B terrace are different. One is symmetric ($R = 1$) for the Sb:Si(001) [17] and the other is asymmetric for the Bi:Si(001) ($R = 0.5$). This can be attributed to the difference in the local structure in the S_B step [5–7]. Three types of local structures are possible at the S_B step of the group V:Si(001) surface as shown in figure 5. The first is a *non-rebonded edge* (NRBE) structure without a reformed bond and the second and third are a *rebonded edge* (RBE) structure with a reformed bond. The reformed bond at the rebonded edge of group V:Si(001) can consist of a Si atom and group V atom (figure 5(b)) or Si atoms (figure 5 (c)). For the Sb:Si(001) surface, Lee *et al* suggest, based on the symmetric domain population of the A and B terraces, that the Sb:Si(001) surfaces prefer the NRBE to the RBE [17]. In the Sb:Si(001) surfaces, an Sb atom exchanges with the strained Si atom of a tetravalent state in

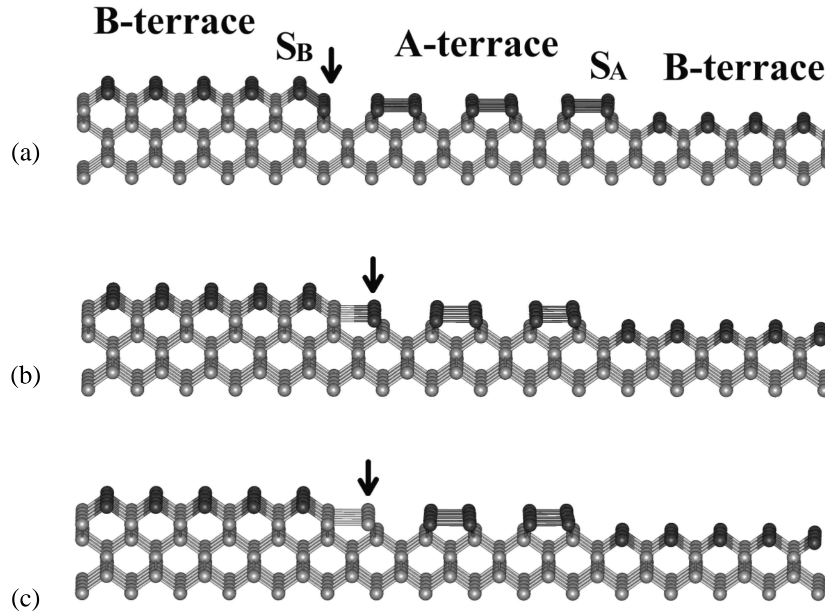

Figure 5. Schematic drawing of Sb:Si(001) and Bi:Si(001) surface with single layered step height, where two types of terraces of A terrace and B terrace and two types of steps S_A and S_B are shown. Dark atoms represent Sb or Bi atoms. (a) The Sb:Si(001) surface of non-rebonded edge structure without dangling bonds. The position of Sb atom marked by arrow is originally the one of Si atom. (b) The Bi:Si(001) surface of rebonded edge structure with a reformed bond which is formed between Si and Bi. (c) The Bi:Si(001) surface of rebonded edge structure, where dangle bonds exist at reformed bonds which are formed between Si and Si.

the reformed bond as does As in As:Si(001) [13, 17]. The displacement of the Si atom with Sb at the S_B step breaks the reformed bond at which the force dipole is originated. Thus, there is no coupling of the force dipole and force monopole, which results in the formation of the symmetric population of the A and B terraces. The driving force of the replacement of the Si atom by Sb in the step edge is the elimination of the dangling bonds of edge atoms and the relaxation of the local strain by breaking the reformed bond.

Contrary to the Sb:Si(001) surface, the Bi:Si(001) surface gives an asymmetric domain population with the B terrace as major domain as does the clean Si(001) surface, which means that the coupling of the force dipole and force monopole should exist. We think that the local structure of the S_B step edge would be one of RBE structures with a reformed bond. Such possible RBE structures are represented in figure 5(b) and (c). It is expected that the step structure without a dangling bond at the reformed bond of figure 5(b) will be more stable than the one with a dangling bond on the Si atom of the reformed bond of figure 5 (c). From the asymmetric terrace population with B terraces as the major domain, we conclude that the Bi:Si(001) surface should have the RBE without a dangling bond at the S_B step as shown in figure 5(b). In order to form the NRBE, the Bi atom must displace the Si atom in the reformed bond, but the Bi atom is too large to displace the Si atom. On one hand, the anisotropic stress of the Bi:Si(001) surface gives rise to the alternative domain configuration of A and B terraces via a long-range elastic relaxation, and, on the other hand, the reformed bond at the S_B step gives the asymmetric domain population.

The various reconstructions and the step structures on Bi:Si(001) are observed depending on the substrate temperatures and Bi coverages. At low coverages, (2×2) and c(4×4) phases

are observed below 350 K and at about 400 K, respectively. For the saturated surfaces, (2×1) and a high order (2×7) phase are observed below 400 K and at 500–800 K, respectively. Comparing the formation temperatures for each phase, it can be concluded that the c(4×4) structure has energy lower than the (2×2) at low coverages and the (2×7) has energy lower than the (2×1). For the step distributions, the asymmetric domain population of A and B terraces is observed at 500–800 K, which is the same as that of the clean surface. From the observed asymmetric domain population, the rebonded edge structure is suggested as a local structure of the S_B step on the Bi:Si(001).

Acknowledgments

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