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**LETTER TO THE EDITOR**

# Atomic-step rearrangement on Si(100) by interaction with antimony

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**Abstract.** Various domain structures of Sb:Si(100) surfaces with a miscut of 2° were observed, depending on the Sb coverage and substrate temperature. A single domain of $2 \times 1$ phase was observed after deposition of 0.5 ML of Sb at a substrate temperature of 375 K, and a single domain of $1 \times 2$ phase appears after annealing at 600 K the surface on which $\simeq$2–6 ML of Sb had been deposited at a substrate temperature of 375 K. A double domain of $1 \times 2$ and $2 \times 1$ phases appeared after deposition of 0.9 ML of Sb at high substrate temperatures (650–1000 K) or upon annealing the $1 \times 2$ single domain above 800 K. Also, a c($4 \times 4$) phase appeared via a $2 \times 2$ phase after annealing the $1 \times 2$ surface. Surface mixing, anisotropic stress, and the elimination of the reformed bonding in the $S_B$ step are expected to be the main causes of the observed domain structures and reconstructions.

Surfactants and the step on the surface of a substrate play important roles in epitaxial film growth [1–4]. The interactions of Si(100) step surfaces with surfactants such as As and Sb have attracted much attention due to their importance as regards epitaxial film quality, as they relate to the surface segregation of the surfactant and the growth mode [1–3]. It has been reported that the step structure of an initial surface and its changes upon interaction with surfactants during the initial stages of growth play important roles in determining the growth mode and interface mixing [1–4]. An interesting example is provided by stepped Si(100) surfaces covered with As [3–5]. As- and Sb-covered Si(100) surfaces (henceforth As:Si(100) and Sb:Si(100)) exhibited a $2 \times 1$ phase, and this phase has been explained as resulting from the dimerization of the top layer, irrespective of the surface mixing [5–7]. The step structures of Si(100) are well understood as a result of many experimental and theoretical studies [8–10]. On the basis of Chadi's notation for Si(100) step surfaces [10], a terrace in which the dimer rows are parallel to the step edge is termed an A terrace or a $1 \times 2$ phase and the step on the A terrace is called an $S_A$ step. A terrace in which the dimer rows are perpendicular to the step edge is termed a B terrace or a $2 \times 1$ phase and the step on the B terrace is called an $S_B$ step (for the notation for the Si(100) surface, see figure 1). Since As and Sb belong to the same group but to different periods in the periodic table, they will show both similarities and differences as regards their chemical and physical properties. Indeed, the two elements do show similar behaviour as surfactants in Ge/Si heteroepitaxy [1, 2]; and, on the other hand, they show different surface stresses due to their different covalent radii (As: 1.21 Å; Sb: 1.41 Å). It was found that the As:Si(100)

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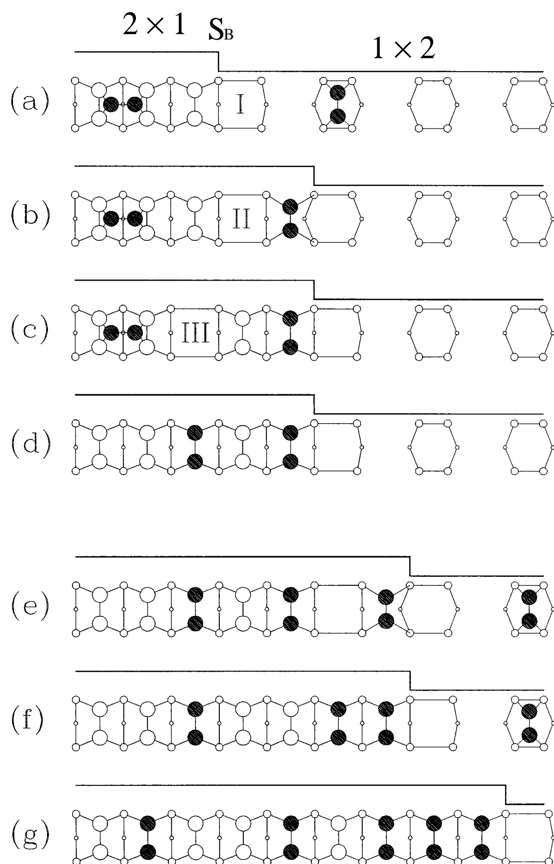


**Figure 1.** Schematic drawings of the vacancy-mediated mixing mechanism. The open circles represent the Si atoms and the closed circles represent the Sb atoms. Chemical bonds are represented by thin solid lines, where a double thin solid line indicates a reformed bond. The terrace marked 2 × 1 corresponds to a B terrace and that marked 1 × 2 corresponds to an A terrace.

surface is under tensile stress in the directions parallel and perpendicular to the As dimer row, while the Sb:Si(100) surface is under tensile stress in the direction perpendicular to the Sb dimer row but under compressive stress in the parallel direction [5, 11]. The step structures of As:Si(100) surfaces have been extensively studied by varying the substrate temperature and As coverage, while the step structures of Sb:Si(100) have been studied comparatively rarely. For As:Si(100) surfaces the surface stress and the reformed bonding in the $S_B$ step were found to be important in determining the step structure and surface mixing [3–5]. The main purpose of this study is to observe the effects of anisotropic stress and the $S_B$ step on the relative population of 2 × 1 and 1 × 2 terraces on Sb:Si(100) surfaces. In this letter, the step distributions and reconstructions of Sb:Si(100) surfaces are studied under diverse experimental conditions, e.g. varying the substrate temperature and Sb coverage, and a model of vacancy-mediated mixing will be introduced.

The experiment was performed in an ultrahigh-vacuum chamber (base pressure $\approx 1 \times 10^{-10}$ Torr) equipped with conventional low-energy electron diffraction (LEED) optics and a double-pass cylindrical mirror analyser (CMA) for Auger electron spectroscopy (AES).

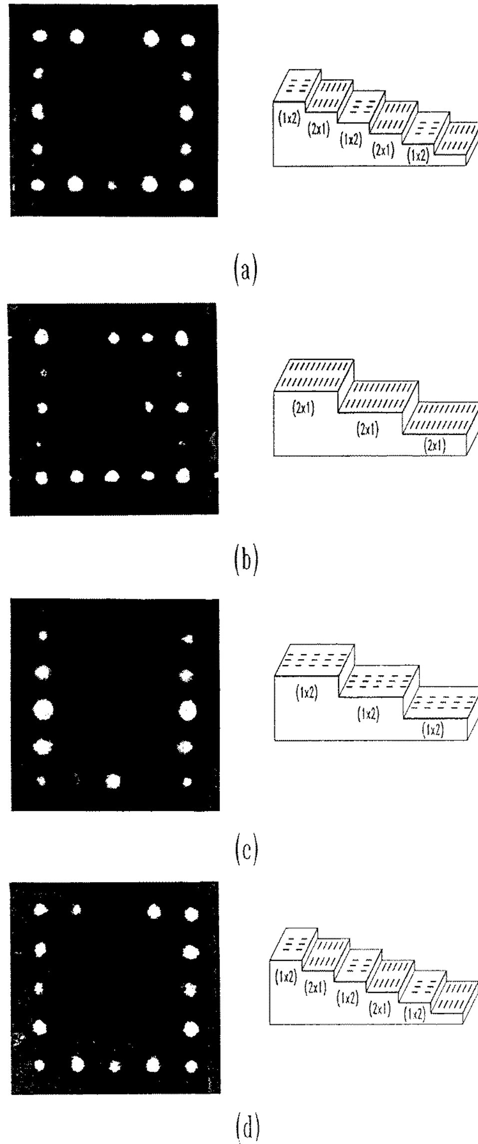


**Figure 2.** Photographs of LEED patterns and schematic diagrams of the step structures corresponding to the LEED patterns. (a) An asymmetric double domain from a clean surface. (b) A single-domain $2 \times 1$ pattern for 0.5 ML of Sb deposited at 375 K. (c) A single-domain $1 \times 2$ pattern for 1.4 ML of Sb deposited in a thick layer at 375 K and then annealed for 5 min at 600 K. (d) A symmetric double domain formed after deposition of 0.9 ML of Sb at 900 K.

The sample used in this experiment is a commercial mirror-polished Si(100) wafer with a miscut angle of 2° toward the [011] direction. Sb (purity 99.999%) was deposited from a W basket; during deposition the chamber pressure was less than $4 \times 10^{-10}$ Torr. The coverage was determined by the AES peak-to-peak ratio of Sb to Si referenced to that of the surface, which was obtained by deposition above 650 K. The saturation coverage of the

surface deposited above 650 K has been reported to be about 0.9 ML [6, 7], where 1 ML was defined as $6.78 \times 10^{14}$ atoms $cm^{-2}$.

After flashing the sample to 1500 K a few times and then annealing it at 1100 K, sharp integral-order and half-order LEED spots appeared. The half-order spot from the $2 \times 1$ domain is more intense than that of the $1 \times 2$ domain (figure 2(a)), which is consistent with previously reported data [8, 9]. A single-domain $2 \times 1$ phase appeared after deposition of 0.5 ML Sb at 375 K while a single-domain $1 \times 2$ phase appeared after annealing at 600 K for 5 min the surface on which 2–6 ML of Sb had been deposited at a substrate temperature of 375 K (figures 2(b) and 1(c)). The measured Sb coverage of the $1 \times 2$ surface was 1.4 ML. If the annealing temperature is below 500 K, the phase of the surface shows very diffuse double domains consisting of major $1 \times 2$ and minor $2 \times 1$ phases, and the coverage is above 1.6 ML. At higher substrate temperatures (>900 K), a double-domain surface with a symmetric domain population appeared (figure 2(d)), where the measured Sb coverage was 0.9 ML. Upon annealing the $1 \times 2$ surface covered by 1.4 ML above 800 K, the metastable single domain irreversibly changed to a stable double domain. The thermodynamically stable structure for a Sb:Si(100) surface is a double domain with a symmetric domain population, while the stable structure for As:Si(100) is the $2 \times 1$ single domain with a double step [3–5]. This difference will be discussed later.

It has been reported that a metastable $1 \times 2$ or $2 \times 1$ single-domain Si(100) surface with a double step can be obtained from the double-domain Si(100) with a single step by controlling the kinetics; here, the formation of single-domain surfaces has been explained as arising from anisotropic diffusion and sticking [12, 13]. A scanning tunnelling microscopy (STM) study showed that the diffusion of Sb atoms on Si(100) is faster in the direction perpendicular to the dimer row than in the dimer row direction and that the Sb atoms quickly form Sb dimers [14]. Unlike the diffusion of Sb atoms on Si(100) surfaces, Si or Ge atoms on a Si(100) surface preferentially diffuse along the dimer row [12, 13]. Considering only the anisotropic diffusion and sticking of adatoms, a double-domain structure rotated by 90° relative to the clean surface would be expected after deposition of a thick layer of Sb on a Si(100) single-step surface followed by an annealing at 600 K. In this case, the coverage would be about 1 ML because the Sb multilayer is desorbed above 600 K [6, 7]. Contrary to this expectation, which is based on the assumption that mixing processes do not occur in the surface layer, the observed step structure was a $1 \times 2$ single domain with a coverage of 1.4 ML. Since this result cannot be explained by just anisotropic diffusion and sticking of Sb adatoms, surface mixing of Sb and Si should be taken into account. In this case, the surface mixing process is different from the surface mixing observed in the case of As:Si(100). For As:Si(100) surfaces, displacive adsorption occurs not at a low substrate temperature but at a high temperature (about 1000 K), such that an As atom directly displaces a Si atom in the terrace [3–5, 15, 16].

The two types of single-domain Sb:Si(100) surface were observed at a low substrate temperature of 375 K, while a double-domain surface appeared at high temperatures (figure 2). Although it has been reported that the As atom would directly displace the Si atom on a Si(100) surface at high temperature (about 1000 K), it is unreasonable to expect the Sb atom to directly displace the Si atom at 375 K because the temperature is too low. For the two types of single-domain surface which are formed not for thermodynamic conditions (high temperature) but for kinetic conditions (low temperature), the model of surface mixing should be based not on direct displacement, which requires a high substrate temperature, but on a new model, such as that of *'vacancy-mediated mixing'*, which would take place at low temperature. The processes of vacancy-mediated mixing are as follows. Since Sb atoms quickly form Sb dimers as soon as they are deposited on Si(100) surfaces, the Sb dimer is

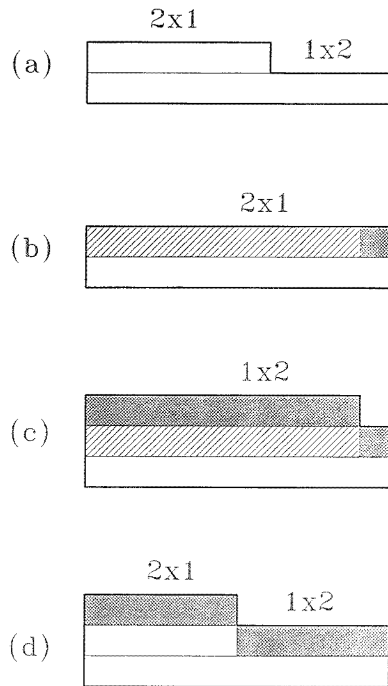


**Figure 3.** Schematic drawings of the step structures. (a) A clean Si(100) surface of a double domain with an asymmetric population. (b) A single domain of $2 \times 1$ phase. (c) An almost single domain of $1 \times 2$ phase. (d) A double domain with a symmetric population. Shaded layers represent the Sb layers, and hatched layers represent mixed layers of Sb and Si.

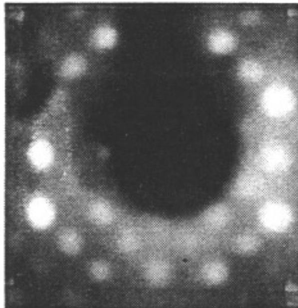

**Figure 4.** A photograph of the LEED pattern of a $c(4 \times 4)$ phase after desorption of Sb caused by annealing at 1200 K.

taken to be the basic unit in the vacancy-mediated mixing model. In the first stage (figure 1(a)) an Sb dimer moving across the dimer rows on an A terrace hops to near the reformed bond (marked I) in the $S_B$ step. In the second stage (figure 1(b)) the Sb dimer forms a bond with the dangling bond of the reformed bond, resulting in the generation of a new vacancy (marked II) and the regeneration of the reformed bond. The vacancy diffuses toward the B terrace in the third stage (figure 1(c)), and then this vacancy is annihilated by another Sb dimer on the B terrace in the final stage (figure 1(d)), which is a true mixing stage.

We call this entire process *'vacancy-mediated mixing'*, to distinguish it from the displacive adsorption or the site exchange of As:Si(100) surfaces. By repeating this process (figures 1(e), 1(f), 1(g)), a $2 \times 1$ single domain with a double step can be formed when 0.5 ML of Sb has been deposited. Also, embedded Sb dimers are formed on the Sb:Si(100) surface in the mixing model. The single-domain surface produced by this vacancy-mediated mixing process consists of a large mixed region and a small unmixed one (figure 3(b)). Once an Sb dimer forms a bond with the dangling bond of the reformed bond (marked I) and generates a vacancy (marked II), the strain energy increases due to the strong p-orbital character of the Sb atom. The driving force of the vacancy diffusion toward the B terrace is attributed to the relaxation of Sb-induced additional strain. That is, the vacancy in figure 1(c) (marked III) has a lower strain energy than the vacancy (marked II) in figure 1(b). Since the $2 \times 1$ phase produced by vacancy-mediated mixing is formed not under thermodynamic conditions but under kinetic conditions, the phase is not a thermodynamically stable state. Hence it changes to a stable double-domain surface upon annealing above 800 K. The $1 \times 2$ phase formation can be explained as follows: first the $2 \times 1$ surface is formed by vacancy-mediated mixing and then the $1 \times 2$ structure of the Sb adlayer is formed on the mixed surface (figure 3(c)). In the $1 \times 2$ single domain the pure Sb layer which is the first layer on the surface and the Sb dimers embedded in the second layer give rise to an Sb coverage of 1.4 ML in total. This explanation of the unexpected coverage of 1.4 ML is consistent with vacancy-mediated mixing. At high temperatures, an embedded Sb atom with one unpaired electron in the second layer would segregate to the surface and become a stable trivalent state with a lone pair of electrons. This energy gain arising from the change of the valence state from a tetravalent state to a trivalent one is ascribed to the driving force of the segregation of Sb from the second layer into the top layer. Thus the Sb coverage of the surface deposited at high temperature was about 0.9 ML (figure 2(d) and figure 3(d)).

For the c$(4 \times 4)$ phase appearing via a $2 \times 2$ phase after annealing of the $1 \times 2$ surface at 1200 K, the measured AES signal showed no trace of elemental Sb within the detection limit. From this observation, together with the fact that the formation temperature of the c$(4 \times 4)$ structure is higher than the temperature required for desorption of Sb from Si(100), it seems likely that the c$(4 \times 4)$ phase is due to an Sb-induced substrate reconstruction rather than the ordered Sb overlayer. It is expected that the Sb dimers embedded in the second layer will segregate and desorb, leading to the generation of missing-dimer vacancies. These missing-dimer vacancies are expected to form a vacancy island or to be ordered to reduce the local strain. Tromp *et al* observed vacancy islands during the desorption of As on an As:Si(100) surface by low-energy electron microscopy [16]. Thus it is reasonable for the c$(4 \times 4)$ phase to be attributed to an ordered defect arrangement, which is consistent with previous results [16, 17].

The appearance of the double domain and the symmetric domain population of the Sb:Si(100) surface can be explained by the elasticity theory of stress and strain. Alerhand *et al* showed that a crystal surface with degenerate phases and an anisotropic surface stress tensor can lower its energy compared to that of a uniform one-domain surface by forming an ordered alternative domain configuration [8]. The reduction in energy comes from a long-range elastic or strain relaxation. The asymmetric domain population in the clean surface (figure 2(a)) is due to the coupling between the local strain fields in the reformed bond in the $S_B$ step and its neighbouring $S_A$ step [8, 9]. It is interesting that at high temperatures the $2 \times 1$ single-domain surface with a double step has been observed in the case of As:Si(100) surfaces [3–5], while the double-domain structure of $1 \times 2$ and $2 \times 1$ phases with symmetric domain populations was observed in our experiment. This difference between As:Si(100) and Sb:Si(100) surfaces can be explained by the difference of the surface stress. There is

no elastic strain relaxation in either the single- or the double-domain surface of As:Si(100) due to tensile stress in the directions parallel and perpendicular to the As dimer row, so a double-step structure with lower step density is more favoured than the single step. In contrast to the case for the As:Si(100) surface, the Sb:Si(100) surface is under tensile stress in the direction perpendicular to the Sb dimer row but under compressive stress in the parallel direction [5, 11]. Thus the Sb:Si(100) surface can lower its surface free energy by taking up an alternative domain configuration of the $1 \times 2$ and $2 \times 1$ domains. It is expected that the energy gain from the strain relaxation caused by the formation of a double-domain surface with a single step will exceed the energy cost from the higher step density when compared with that of the single domain of the double step. Also, there is a difference between Sb:Si(100) and clean Si(100) as regards the domain population of $1 \times 2$ and $2 \times 1$ phases; that is, a symmetric population was observed for Sb:Si(100) (figure 2(d) and figure 3(d)) while an asymmetric population was observed for clean Si(100) (figure 2(a) and figure 3(d)). This can be attributed to the difference in local structure in the $S_B$ step. An Sb atom exchanges with a strained Si atom in a tetravalent state in the reformed bond in the $S_B$ step to reduce the local strain, as does As in As:Si(100) surfaces [5]. Thus, the reformed bonding at the $S_B$ step is eliminated, which results in a decoupling of the local strain fields in the $S_B$ step and the $S_A$ step. On one hand, the anisotropic stress of the Sb:Si(100) surface gives rise to the alternative domain configuration of $1 \times 2$ and $2 \times 1$ phases via strain relaxation, and, on the other hand, the elimination of the reformed bonding in the $S_B$ step leads to the symmetric domain population.

In conclusion, we have observed various surface structures by controlling the kinetics and the thermodynamics. In the kinetic regime, at 375 K, a $2 \times 1$ single domain or a $1 \times 2$ one was observed, depending on the Sb coverage, while in the thermodynamic regime, above 900 K, a double domain with a symmetric domain population was observed. Also, the $1 \times 2$ surface underwent successive structural phase transitions from a $2 \times 1$ to a $2 \times 2$ phase and from a $2 \times 2$ to a c$(4 \times 4)$ phase as the $1 \times 2$ surface was annealed at 1200 K. These successive structural phase transitions are irreversible. The single-domain formation was explained using the vacancy-mediated mixing model, which can explain the unexpected coverage of 1.4 ML of $1 \times 2$ single domain at low temperature and the c$(4 \times 4)$ reconstruction consistently. The symmetric double-domain structure was discussed on the basis of an anisotropic stress tensor and the elimination of reformed bonding by replacing Si atoms with Sb in the $S_B$ step.

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## References

[1] Horn-von Hoegen M, Müller B H and Al-Falou A 1994 *Phys. Rev.* B **50** 11 640
[2] Copel M, Reuter M C, Horn-von Hoegen M and Tromp R M 1990 *Phys. Rev.* B **42** 11 682
[3] Ide T 1995 *Phys. Rev.* B **51** 1722
[4] Bringans R D, Biegelsen D K and Swartz L-E 1991 *Phys. Rev.* B **44** 3054
[5] Alerhand O L, Wang J, Joannopoulos J D, Kaxiras E and Becker R S 1991 *Phys. Rev.* B **44** 6534
[6] Richter M, Woicik J C, Nogami J, Pianetta P, Miyano K E, Baski A A, Kendelewicz T, Bouldin C E, Spicer W E, Quate C F and Lindau I 1990 *Phys. Rev. Lett.* **65** 3417
[7] Nogami J, Baski A A and Quate C F 1991 *Appl. Phys. Lett.* **58** 475
[8] Alerhand O L, Vanderbilt D, Meade R D and Joannopoulos J D 1988 *Phys. Rev. Lett.* **61** 1973
[9] Swartzentruber B S, Kitamura N, Lagally M G and Webb M B 1993 *Phys. Rev.* B **47** 13 432
Tong X and Bennett P A 1991 *Phys. Rev. Lett.* **67** 101
[10] Chadi D J 1987 *Phys. Rev. Lett.* **59** 1691

[11] Schnell-Sorokin A J and Tromp R M 1990 *Phys. Rev. Lett.* **64** 1039
[12] Hoeven A J, Lenssinck J M, Dijkkamp D, van Loenen E J and Dieleman J 1989 *Phys. Rev. Lett.* **63** 1830
[13] Bedrossian P and Klitsner T 1992 *Phys. Rev. Lett.* **68** 646
[14] Mo Y W 1993 *Phys. Rev. Lett.* **71** 2923
[15] Yu B D and Oshiyama A 1993 *Phys. Rev. Lett.* **71** 585
[16] Tromp R M, Denier van der Gon A W and Reuter M C 1992 *Phys. Rev. Lett.* **68** 2313
[17] Moriarty P, Koenders L and Hughes G 1993 *Phys. Rev.* B **47** 15 950
Ide T and Mizutani T 1992 *Phys. Rev.* B **45** 1447