Controlling the surface chirality of Si(110)

Yoichi Yamada, Antoine Girard, Hidehito Asaoka, Hiroyuki Yamamoto, and Shin-ichi Shamoto

Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai, Naka, Ibaraki 319-1195, Japan

(Received 7 January 2008; revised manuscript received 9 March 2008; published 18 April 2008)

A widely well-defined homochiral surface is realized on Si(110), manipulating surface reconstruction by electromigration. Controlled switching of the surface handedness has also been demonstrated. In addition, by means of hydrogen passivation, the surface is sufficiently stabilized while surface chirality is conserved. These findings suggest the possible use of Si(110) as a heterogeneous catalyst for enantioselective chemical reactions.

Chirality is a common feature that is important in various fields such as biology, chemistry, and physics. Controlling the chirality of biological molecules is particularly important because the molecular functions often depend on the chirality of molecules. In the search for an effective heterogeneous catalyst for use in enantioselective molecular synthesis, a tremendous amount of effort has been devoted in introducing chirality to solid surfaces.[1] Surface chirality has thus been a major topic in condensed-matter physics. One straightforward way of realizing a chiral surface is to cover the surface with chiral molecules. A number of recent studies have revealed that enantioselectivity is in fact a property of such a molecule-covered surface.[2] Another possibility is to use the surface of naturally chiral bulk materials such as quartz or chiral steps with kinks mainly realized in high-index surfaces.[3] The enantioselectivity of such an atomic chiral structure has also been investigated well. In this Brief Report, we present another possibility for surface chirality on a low-index Si surface by the genuine surface reconstruction, which leads to a high-quality homochiral surface.

Si(110), which has recently attracted renewed interest[4] because of its promising applicability to next-generation complementary metal-oxide semiconductor devices,[5] has a unique quasi-one-dimensional surface reconstruction, 16×2, as depicted schematically in Fig. 1(a). The 16×2 reconstruction consists of two equivalent domains with straight rows of adatom units [pair of pentagons (PP)] running along two nonsymmetric directions, $\langle 1\bar{1}2 \rangle$ and $\langle \bar{1}12 \rangle$.[6–8] These two stripes are known to be mirror images about the mirror plane along $\langle 001 \rangle$.[6,7] Since they cannot be superimposed by translation and/or rotation, these domains are two-dimensional chiral. We term these domains as the *L* and *R* domains, respectively. (The PPs constructing the *L* and *R* domains are called *L*-PP and *R*-PP, respectively, according to Ref. 7.) In general, the 16×2 surface is achiral as a whole since it usually exhibits a double-domain structure with a random mixture of the *L* and *R* domains. However, surface homochirality could be realized in this system by altering the surface domain structure. Recently, we showed that the domain morphology of the 16×2 structure can be controlled by manipulating the adatoms by an external electric field and current (electromigration).[9] The controlled electromigration of adatoms along one reconstruction row resulted in a surface with only one type of stripe [a single domain of the 16×2 structure, Fig. 1(c)]. Note that the single domain of the 16×2 structure is homochiral. This implies that a single domain

with the other handedness can also be fabricated by electromigration along the other stripe, allowing controlled switching of the surface chirality. In the following, we show that this is indeed possible. The resulting surface exhibits widely well-defined homochirality with controllable handedness and remarkable stability, showing strong potential as a heterogeneous catalyst.

A $0.5-1.5 \, \Omega$ cm *n*-type Si(110) wafer was used as a specimen. Electromigration of surface atoms was performed by applying dc to the 1×7 mm^2 rectangular Si(110) sample in ultrahigh vacuum (UHV). The direction of electromigration can be controlled by selecting the orientation of the specimen.[9] In the present study, to selectively fabricate the *L* and *R* 16×2 single domains, electromigration in $\langle 1\bar{1}2 \rangle$ and $\langle \bar{1}12 \rangle$ was performed, i.e., two rectangular samples with $\langle 1\bar{1}2 \rangle$ and $\langle \bar{1}12 \rangle$ orientations were used. The surfaces were
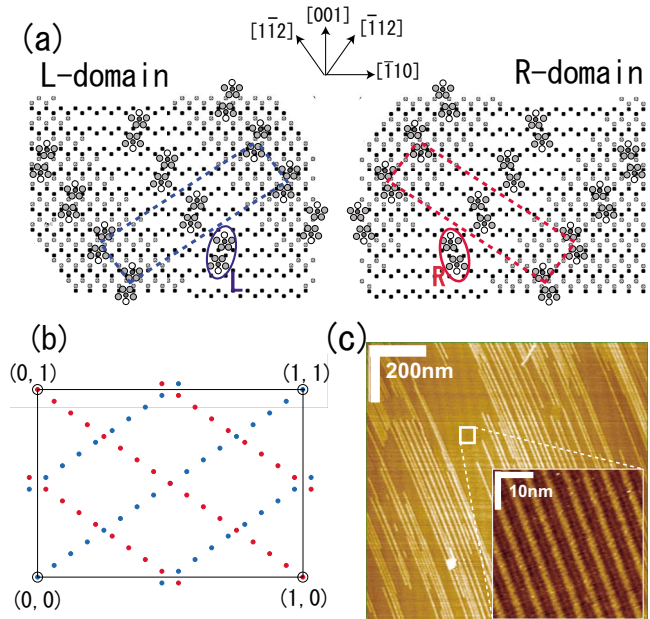

FIG. 1. (Color online) (a) Schematic drawing of the chiral domains with 16×2 structure (based on Ref. 7). The dotted square represents the unit cell for 16×2, and the solid circle indicates the PP. (b) Reciprocal scheme of 16×2 structure. The blue and red spots represent the reciprocal lattice points of *L* and *R* single domains. (c) $1 \times 1 \, \mu$m^2 and 40×40 nm^2 STM images of the clean *L* single domain. Tunneling current=1 nA and sample bias voltage =1 V.

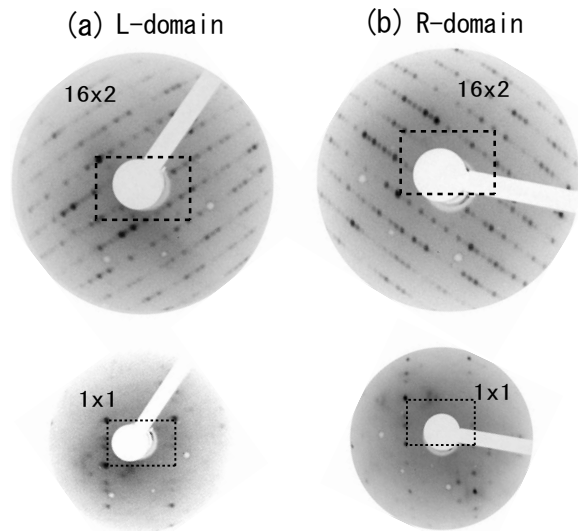FIG. 2. LEED image of L and R 16×2 single domains, which were obtained with beam energy of 70 eV. The dotted square represents the 1×1 unit mesh determined from the LEED image with 1×1 phase (bottom).

prepared by resistive heating in UHV. After flash heatings at around 1200 °C, the surface was annealed at 650 °C for 30 min, during which simultaneous thermal annealing and electromigration of surface atoms occurred. The current and voltage during the annealing were approximately 0.1 A and 7 V, respectively, corresponding to a current density of 0.7 A/mm^2 and an electric field of 1.75 kV/m. After annealing, the surfaces were quenched down to room temperature. According to Ref. 9, this treatment results in a 16×2 single domain with high reproducibility. Surface electromigration is a well-known phenomenon of metal and semiconductor surfaces particularly for its ability to manipulate the step morphology of vicinal surfaces.[10] Since the surface reconstruction of Si(110) contains atomic steps,[6–8] electromigration works quite well, resulting in an excellent ordering of the reconstructed surface. After electromigration treatment, the surfaces were characterized by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

The selective growth of the R and L single domains by controlled electromigration is demonstrated in Fig. 2. Figures 2(a) and 2(b) show the LEED patterns of the surfaces after the electromigration treatment along $\langle1\bar{1}2\rangle$ and $\langle\bar{1}12\rangle$, respectively. Note that both LEED patterns exhibit parallel streaklike fine fractional spots, which indicate the formation of a one-dimensional single domain with 16×2 structure [also see the reciprocal scheme in Fig. 1(b)]. Since the 1×1 spots are difficult to recognize in the crowded 16×2 pattern, the 1×1 phase (with metastable five times ordering[11]) was also fabricated on the same samples by quenching the surface from the high-temperature 1×1 phase.[9] The 1×1 unit mesh is then determined based on the LEED image obtained in the same condition, as shown in the bottom of Fig. 2. It is now clear that the orientation of the diagonal fractional spots with respect to the 1×1 unit mesh differs between Figs. 2(a) and 2(b). This clearly confirms the selective growth of the chiral L and R 16×2 single domains.
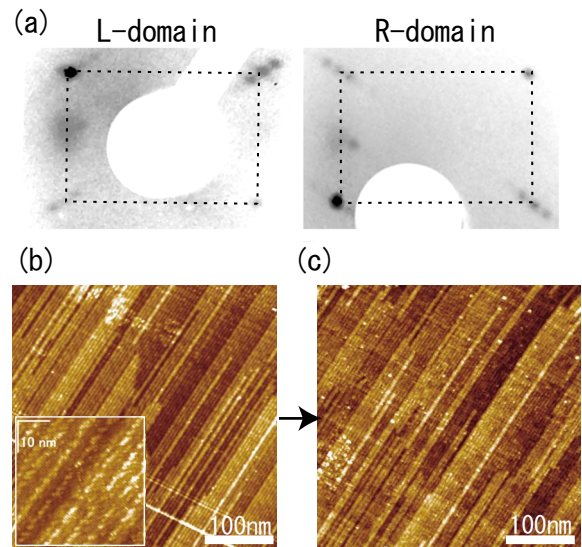

FIG. 3. (Color online) (a) LEED images of hydrogen-terminated L and R 16×2 single domains. The incident beam energy=70 eV. (b) 400×400 nm^2 and 40×40 nm^2 STM image of the hydrogen-terminated R single domain. Tunneling current=1 nA, sample bias=2.5 V. (c) 400×400 nm^2 STM image of the hydrogen-terminated surface after the exposure to air for 10 min. Tunneling current=1 nA, sample bias=2.5 V

Almost all the measured region (about 1×4 mm^2) of the sample exhibits the same diffraction pattern, suggesting the formation of a huge homochiral domain up to the millimeter scale. Only the small portions near the electrodes at both ends of the specimen show deviation from the single-domain structure, which is possibly due to a significant temperature gradient during heating.

These observations demonstrate the macroscopic homochirality with controlled handedness on the common low-indexed Si surface. Since this homochirality uses genuine surface reconstruction, the resultant structure is essentially well defined over a macroscopic distance. However, the mechanism by which electromigration forms the single domain is not yet clearly understood in detail since the surface atomic structure of the 16×2 reconstruction has not been fully clarified. Nevertheless, we can assume that the same mechanism is at work here as in the case of vicinal surfaces[10] because of the similarity of the system.[9]

The homochirality of this structure emerges both from the atomic arrangement inside the stripe [L-PP and R-PP, as shown in fig. 1(a)] and from the symmetry of the stripe's orientation with respect to the substrate ($\langle1\bar{1}2\rangle$ and $\langle\bar{1}12\rangle$). The former chirality might not be as useful as typical molecule-covered systems since the presence of the highly reactive dangling bonds at the adatoms sometimes prevents the molecular self-assembly, which is problematic from the viewpoint of the asymmetric molecular synthesis on the surface. Therefore, it is important to investigate how the passivation of the adatoms affects the chirality of the surface.

In the following, we discuss the geometry of the hydrogen-passivated surfaces. Hydrogen passivation of the adatoms was performed with atomic hydrogen generated by a hot tungsten filament in a backfilled hydrogen ambient of

5×10^{-4} Pa, maintaining the surface temperature at 200 °C. Figure 3 displays the LEED images of the hydrogen-terminated L and R single domains. The LEED pattern reveals almost 1×1 diffraction for both cases. Around the 1×1 peaks, a few satellite spots can be observed. The LEED pattern and its beam-energy dependence agree well with a previous study.[11] The satellite peaks around the 1×1 spots indicate the presence of the striped structure with 16×2 reconstruction in the passivated surface.[12,13] Note that the arrangement of the satellite peaks differs between the L and R domains, reflecting the different orientations of the surface stripes. The conservation of the striped structures with their original orientation ensures that surface chirality is also rigidly maintained even after the hydrogen passivation of adatoms. The STM image of the hydrogen-terminated surface (R domain) provided in Fig. 3(b) directly confirms the presence of striped reconstruction throughout the surface. It is clear that the surface morphology with straight stripes is maintained without a significant change from that of the clean surface. Extensive scanning confirms that the domain size is also unchanged from the clean surface. On the other hand, the atomic structure of the PP is hardly resolved in the smaller scans [inset in Fig. 3(b)] because hydrogen saturates the dangling bonds. More detailed studies are required to clarify the atomic nature of the hydrogen-passivated surface.

The hydrogen termination provides remarkable stability to the homochiral structures. To investigate the stability, we moved the specimen from the UHV system to the atmosphere, left it expose to air for 10 min, and checked the structure again in UHV. Figure 3(c) shows the STM image just after the air exposure, without any surface cleaning. Even after such a violent treatment, the STM measurements reveal that the surface remains almost unchanged. The LEED image (not shown) also shows no noticeable alteration upon exposure to air, confirming that the macroscopic structure is also unaffected. This demonstrates a very stable homochiral surface, which should be suitable for a realistic catalyst.

In conclusion, by manipulating the genuine surface reconstruction by controlled electromigration, widely well-defined homochirality was realized on a Si(110) surface. This methodology also enables us to select the surface handedness. In addition, the hydrogen-passivated surface shows remarkable stability with the chirality originating from the striped surface structure rigidly maintained. The superior properties of the fabricated homochiral surface suggest its possible use as a heterogeneous catalyst for enantioselective molecular synthesis. These findings provide a new topic for research on Si(110), calling for further investigations.

[1] A. Baiker and H. U. Blaser, in *Handbook of Heterogeneous Catalysis*, edited by G. Ertl, H. Knözinger, and J. Weitkamp (VCH, Weinheim, 1997), Vol. 5, p. 2422; D. Rampulla and A. J. Gellman, in *Dekker Encyclopedia of Nanoscience and Nanotechnology*, edited by J. A. Schwarz, C. I. Contescu, and K. Putyera (Marcel, New York, 2004), pp. 1113–1123.

[2] For example, B. Ohtani, A. Shintani, and K. Uosaki, J. Am. Chem. Soc. **121**, 6515 (1999); J. Weckesser, A. De Vita, J. V. Barth, C. Cai, and K. Kern, Phys. Rev. Lett. **87**, 096101 (2001); M. O. Lorenzo, C. J. Baddeley, C. Muryn, and R. Ravel, Nature (London) **404**, 376 (2000); R. Fasel, M. Parschau, and F.-H. Ernst, *ibid.* **439**, 449 (2006).

[3] For example, C. A. Orme, A. Noy, A. Wierzbicki, M. T. McBride, M. Grantham, H. H. Teng, P. M. Dove, and J. J. DeYoreo, Nature (London) **411**, 775 (2001); J. D. Horvath and A. J. Gellman, Top. Catal. **25**, 9 (2003); R. M. Hazen and D. S. Sholl, Nat. Mater. **2**, 367 (2003); J. I. Pascual, J. V. Bath, G. Ceballos, G. Trimarchi, A. De Vita, K. Kern, and H.-P. Rust, J. Chem. Phys. **120**, 11367 (2004).

[4] M. Yang, V. W. C. Chang, K. K. Chan, L. Shi, D. M. Fried, J. H. Stathis, A. I. Chou, E. Gusev, J. A. Ott, L. E. Burns, M. V. Fischetti, and M. Ieong, IEEE Trans. Electron Devices **58**, 965 (2006).

[5] S. Liang, R. Islam, David J. Smith, P. A. Bennett, J. R. O'Brien, and B. Taylor, Appl. Phys. Lett. **88**, 113111 (2006); N. D. Kim, Y. K. Kim, C.-Y. Park, H. W. Yeom, H. Koh, E. Rotenberg, and J. R. Ahn, Phys. Rev. B **75**, 125309 (2007); M. Suemitsu, A. Kato, H. Togashi, A. Konno, Y. Yamamoto, Y. Teraoka, A. Yoshigoe, Y. Narita, and Y. Enta, Jpn. J. Appl. Phys., Part 1 **46**, 1888 (2007).

[6] W. E. Packard and J. D. Dow, Phys. Rev. B **55**, 15643 (1997).

[7] T. An, M. Yoshimura, I. Ono, and K. Ueda, Phys. Rev. B **61**, 3006 (2000).

[8] A. A. Stekolnikov, J. Furthmuller, and F. Bechstedt, Phys. Rev. Lett. **93**, 136104 (2004).

[9] Y. Yamada, A. Girard, H. Asaoka, H. Yamamoto, and S. I. Shamoto, Phys. Rev. B **76**, 153309 (2007).

[10] For example, Y.-N. Yang, E. S. Fu, and E. D. Williams, Surf. Sci. **356**, 101 (1996); A. Kirakosian, R. Bennewitz, J. N. Crain, Th. Fauster, J.-L. Lin, D. Y. Petrovykh, and F. J. Himpsel, Appl. Phys. Lett. **79**, 1608 (2001); S. Yoshida, T. Sekiguchi, and K. Ito, *ibid.* **87**, 031903 (2005).

[11] Y. Ohira, M. Yoshimura, and K. Ueda, Jpn. J. Appl. Phys., Part 1 **46**, 5652 (2007).

[12] H. Ampo, S. Miura, K. Kato, Y. Ohkawa, and A. Tamura, Phys. Rev. B **34**, 2329 (1986).

[13] M. Yoshimura, M. Odawara, and K. Ueda, Mater. Sci. Eng., B **91-92**, 120 (2001).