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Switching of the Dimer-Row direction through Sb-passivation on the vicinal Si(001)-4° off surface of a single domain

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ABSTRACT. We have investigated Sb interface on the single-domain vicinal Si(001) surface inclined by 4° toward [110] direction using scanning tunneling microscopy and high-resolution synchrotron photoelectron spectroscopy. This vicinal Si(100)-4° off surface is reconstructed to form nine-dimer-wide single-domain (001)-$p(2\times2)$ terraces separated by rebonded D_B double-layer steps, when the Si-dimer rows perpendicular to the steps. By 2ML Sb-deposition at RT and subsequent postannealing at 500°C, the Si surface has been covered by Sb-dimer rows whose direction is parallel to the steps composed of S_A and S_B (Sb rebounded atom) steps. And all the Si 2p components related to the clean surface have disappeared, while the Sb-Si interfacial component has been identified. Such a component is mainly due to charge transfer between Si and Sb atoms at the top layer. Based on these results, it has been concluded that Sb atoms passivate the vicinal Si(001)-4° off surface through forming 1ML Sb layers composed of Sb dimers and Sb rebonded atoms.

KEYWORDS. Sb interface, semiconductor crystal, Si surface

1. INTRODUCTION

The ideal truncation of an infinite semiconductor crystal creates half-filled dangling bonds at the surface inducing surface states within the fundamental gap. Due to these dangling bonds, the surface becomes highly reactive. When atoms like Sb belonging to group V are deposited on the clean Si surface, they saturate the dangling bonds through replacing surface Si atoms having a dangling bond, since the replacing atom belonging to group V bonds with the substrate and keeps one lone-pair orbital at the very surface [1]. Such passivation strongly reduces the free energy of the clean Si surface [2], making it more bulk-like. Therefore, Sb as a surfactant for creating high-quality heteroepitaxial films on Si surfaces through modifying the growth mode in systems with large lattice mismatch has been extensively studied [3-5].

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Until now, studies on reconstructed surfaces induced by Sb adsorption on the low- and high-index Si surfaces, such as Si(001), Si(110), Si(111), Si(112), and Si(113) surfaces, have been performed using scanning tunneling microscopy (STM), photoemission spectroscopy (PES), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and theoretical calculations [6-16]. From the STM study of the Sb-deposited Si(001)-2×1 surface, it was reported that Sb atoms form dimers oriented perpendicularly on the original Si dimers [6,7]. From the Sb/Si(113) system studied by STM and theoretical calculation, it was reported that topmost Si atoms are replaced by Sb atoms [15]. The core level photoemission studies of Sb-deposited (001), (110), (111), (112), and (113) surfaces have also shown that Sb atoms passivate the top layer through substituting and/or bonding to the surface Si atoms. Usually the clean Si surface is reconstructed as a result of the balance between dangling bond density and surface stress [15]. On the while, since Sb-passivated Si surfaces, free of partially-filled dangling bonds, are reordered mainly by surface stress [17], these systems are suitable for studies of surface phase transition induced by pure surface stress.

This work reports the results of STM and Si 2p core levels studies on the Si(001)-4° off surface deposited by 2-ML Sb at room temperature (RT) and postannealed 500°C. It also discusses stress balance and reconstruction of the clean and Sb-passivated Si(001)-4°off surface.

2. EXPERIMENTAL

A Si(001)-4° off substrate with a size of $9 \times 3 \times 0.25$ mm^3 was cut from an n-type (P doped) Si wafer and degreased with pure organic solvents. It was held with 0.025 mm Ta foils on a Cu holder and transferred to an ultrahigh vacuum (UHV) chamber with a base pressure of 7×10^{-11} Torr. The sample-holder assembly was outgassed at 600°C for 14 h. Then the surface was flashed at about 1150°C by resistive heating to remove the native-oxide layers and reconstructed by slow cooling from 900°C to 550°C at a rate of 10°C/min. Sb atoms were thermally evaporated from a tantalum foil on the clean vicinal Si(001)-4° off surface held at RT at a rate of 0.15 monolayer (ML) per minute. Then the sample was annealed between 500°C and 800°C for 10 min. STM images were acquired with W tips in constant current mode ($I_{tunneling} = 0.5$ nA) at RT with an RHK ATM 300 microscope controlled by an RHK SPM 100 system. Si 2p and Sb 4d core-level spectra were 2 obtained at RT at the 10D undulator beam line of Pohang Accelerator Laboratory (PAL) in Korea using a high-resolution electron analyzer, Scienta 3000, under UHV of a base pressure 2×10^{-10} Torr.

3. RESULTS AND DISCUSSION

3.1. **Atomic structure of the Si(001)-4° off surface.** Vicinal Si(001) surfaces oriented 4-19.5° off from (001) to (111) are composed of single-domain (001) terraces and double-layer (DL) steps [18]. In them, the Si(001)-4° off surface is located between (1 1 19) [9·(001) + DL, periodicity: 3.7 nm] and (1 1 21) [10·(001) + DL, periodicity: 4.0 nm], as shown in the bulk-terminated model viewed from the $[1\bar{1}0]$ direction of Fig 1. The filled- and empty-state STM images and the corresponding top- and side-view atomic structural models of the reconstructed clean Si(001)-4° off surface are shown in Fig 2. As shown in Fig 2(a), the Si(001)-4° off surface is composed of single-domain (001) terraces with an average period of 3.9 nm separated by a regular array of double-layer D_B steps. The Si dimer rows (perpendicular to the dimerization direction) are parallel to the [110] direction. As can be seen in Figs 2(b) and 2(c), the dimer rows on narrow (001) terraces are buckled with a $p(2\times2)$ periodicity, as marked by pairs of connected dots (small and large) and letter “D”. The upward atoms (marked large red dots) of dimer row appear bigger and brighter than the downward atoms (marked by small red dots) of dimer row, as shown in Fig 2(b).

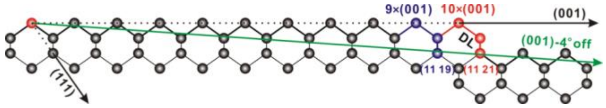

FIGURE 1. Cross-section of the Si crystal lattice viewed along the $[1\bar{1}0]$ direction. Letter DL indicates a double-layer step.

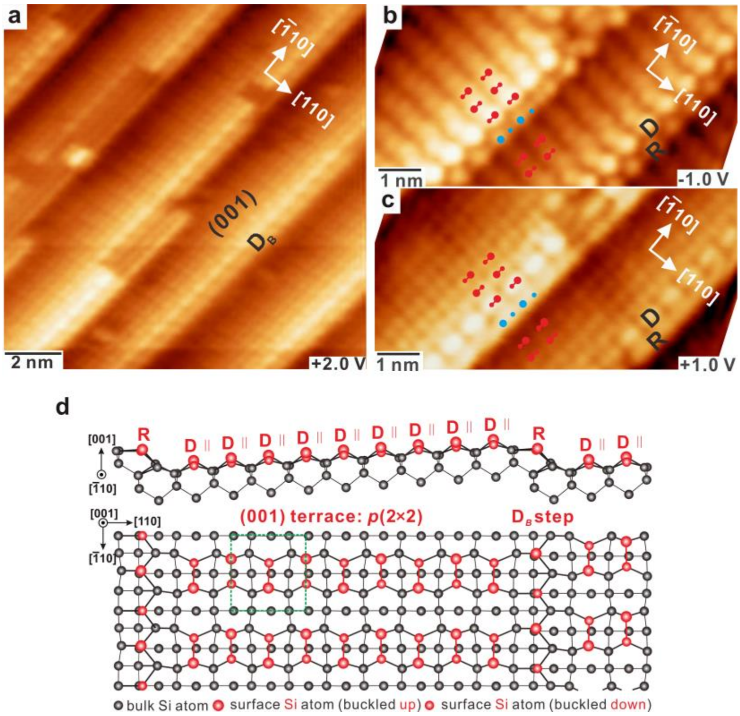

FIGURE 2. (a) Topographic empty state STM image (sample bias voltage: +2.0 V) of the clean Si(001)-4° off surface. (b) and (c): Topographic filled-state (sample bias voltage: -1.0 V) and empty-state (sample bias voltage: +1.0 V) STM images of the same area on the clean Si(001)-4° off surface. (d) Corresponding side- and top-view structural models. $D_{\parallel}$ and R indicate a Si dimer parallel with the DB steps and a Si rebonded atom, respectively.

In Figs 2(b) and 2(c), filled- and empty-state images of the same area, the end of the dimer rows appeared to brighter than the other terrace dimers [19]. It is due to the strong tensile surface stress induced by buckled Si rebonded atoms (marked by small and large blue dots) at the D_B steps, which determine the buckling of the upper-terrace dimers [20.21]. The buckled rebonded atoms (R) appear bright (upward atoms) and less bright (downward atoms) protrusions with a 2× periodicity along the $[\bar{1}10]$ direction between the (001) terraces in Figs 2(b) and 2(c). From these images, the side- and top-view structural models are constructed as in Fig 2(d). In here, $D_\parallel$ represents a Si dimer whose dimerisation direction is parallel with the D_B steps and R represents a Si rebonded atom.

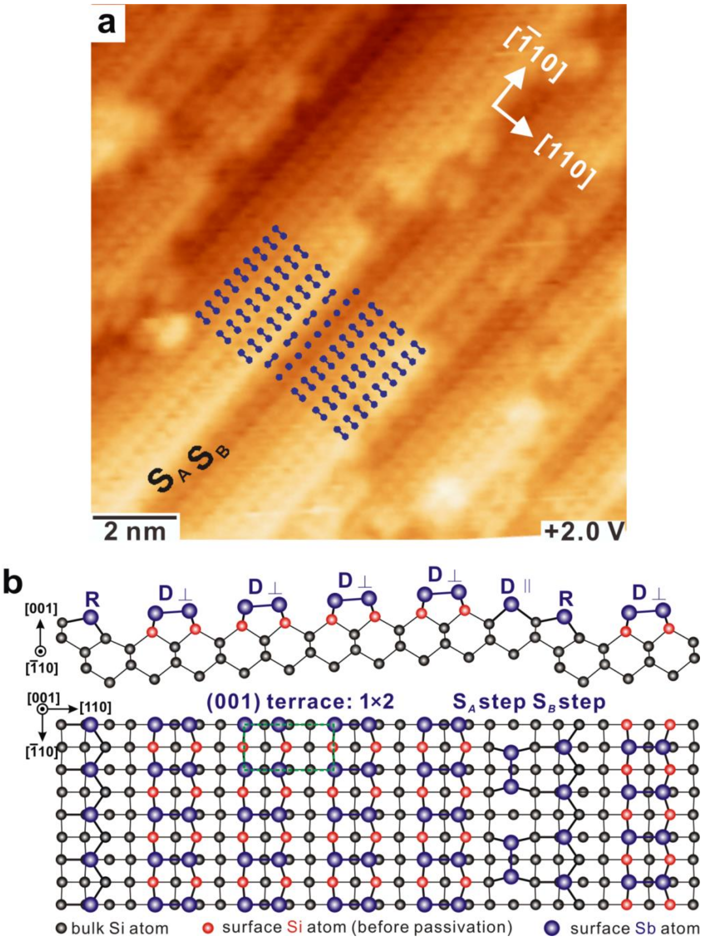

FIGURE 3. Passivation of the Si(001)-4° off surface through 2-ML Sb deposition at RT and postannealing at 500°C; (a) Empty-state STM image (sample bias voltage: +2.0 V), (b) Side and top-view structural models, where the whole surface are passivated by Sb atoms. Letters $D_\perp$ ($D_\parallel$), and R indicate a perpendicular (parallel) Sb dimer, and a Sb rebonded-atom, respectively.

3.2. **Sb covered Si(001)-4° off surface.** Figure 3(a) is an empty-state STM image obtained from the Si(001)-4° off surface deposited by 2-ML Sb at RT and postannealed 500°C for 10 minutes. As can be seen Fig 3(a), dimers without buckling on (001) terraces have been switched perpendicular to the step edge. Since Sb atoms have lone pair orbitals already, there is no partially-filled dangling bonds, no charge transfer, and no buckling. So, this fact suggests that all of the dangling bonds related to the Si atoms on the (001) terraces are removed by Sb atoms. Furthermore, symmetric Sb dimers ($D_\perp$s) are formed with a (1×2) periodicity, perpendicularly on the original Si dimers which have become bulk-like. On the other hand, the steps are broader than the D_B steps in Fig 2(a). The Si rebonded atoms under tensile stress in the D_B steps and its neighboring dimers ($D_\parallel$s) on the upside terrace are substituted easily by Sb atoms [15,22], since the covalent bond length of Sb, 0.139 nm, is longer than that of Si, 0.111 nm. As a result, the double layer D_B step on the clean Si(001)-4° off surface is converted to an single layer S_A step and an single layer S_B step with almost no buckling on its Sb-passivated surface. On the step edge, the compressive Sb $D_\parallel$ and tensile Sb R are stress balanced. Based on these facts, we built side- and top-view atomic structural models of the Sb-passivated Si(001)-4° off surface, as shown in Fig 3(b).

3.3. Photoemission spectra of the Sb-covered Si(001)-4° off surface. Angle-integrated valence band spectra obtained at normal emission using 65 eV photons from the clean Si(001)-4° off surface (A), and the Sb/Si(001)-4° off surface deposited with 2-ML Sb at RT and postannealed at 500°C (B) are shown in Fig 4(a). For a clear understanding, the difference of the Sb/Si(001)-4° off spectrum from the clean Si(001)-4° off spectrum is drawn as B-A in Fig 4(b). In these spectra, there are clear changes at two peaks, labeled S1, and S2, having binding energies of 0.8 eV, and 1.8 eV, respectively. For the clean Si(001)-4° off surface, the S1 peak is related to surface dangling bonds. After Sb deposition and postannealed at 500°C, one dominant Sb-related S2 peak appearing instead of the S1 peak originates from πg and πu orbital states of Sb lone pair in dimers and rebonded atoms [16,23-25]. This result reveals that the Si(001)-4° off surface is completely passivated by Sb atoms, as anticipated by the model shown in Fig 3(b).

In Figure 5, Si 2p core-level spectra was obtained at normal emission using 140 eV photons from (a) the clean Si(001)-4° off surface and (b) the Sb/Si(001)-4° off surface. The raw data designated by black circles were analyzed by standard least-squares fitting procedure using Voigt doublets with spin orbit splitting after subtracting the Shirley-type background. The fitting result was obtained using a Lorentian width of 0.09 eV, a Gaussian width of 0.34 eV (0.30 eV) for clean Si(001)-4° off surface (Sb passivated Si(001)-4° off surface), a spin-orbit splitting of 0.59 eV, and a branching ratio of 0.45. The corresponding fitting parameters and result are listed in Table 1. In Fig 5(a), the components of the clean Si(001)-4° off surface are denoted by surface related S1 and S2, subsurface SS, bulk B, and third-layer C [26]. The core level shifts of the SS, S1, C, and S2 components with respect to the bulk component B are +0.31 eV, +0.11 eV, -0.32 eV, and -0.51 eV, respectively. The two kinds of surface related components, S1 and S2, correspond to downward atoms and upward atoms of $D_\parallel$s and Rs composing the (001)-*p*(2×2) terraces and D_B step edges.

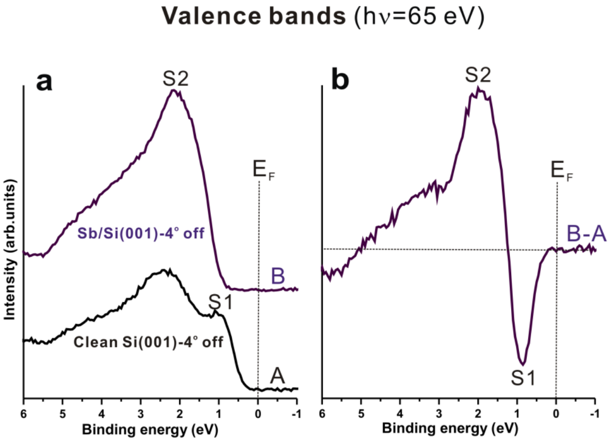

FIGURE 4. Valence bands spectra; (a) Si(001)-4° off (A), Sb/Si(001)-4° off (B) and (b) Differences (B-A).

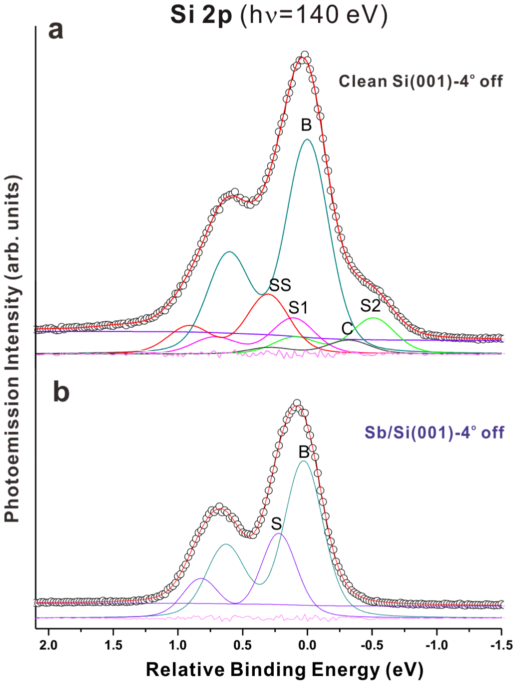

FIGURE 5. Si 2p core-level photoemission spectra obtained at normal emission angle with 140 eV photons. (a) Clean Si(001)-4° off (A), (b) Sb/S(001)-4° off (B) surfaces. Detailed fitting result are listed in Table 1.

TABLE 1. Fitting results and parameters of surface core-level shifts (SCLSs) for the Si 2p spectra shown in Fig 5. The SCLSs are referred to the bulk species (B) in kinetic energy (KE). The intensity is defined by the ratio relative to that of the bulk species of the clean surface. Lorentzian width: 0.09 eV, spin-orbit splitting: 0.59 eV and branching ratio: 0.45:

Spectrum	Gaussian width (eV)	Species	B (KE)	S1	S2	SS	C	S
(a) Clean Si(001)- 4° off	0.34	SCLS (eV)	38.4	+0.11	-0.51	+0.31	-0.32	
		Intensity	1	0.17	0.17	0.28	0.06	
(b) Sb/Si(001)- 4° off	0.3	SCLS (eV)	38.37					+0.19
		Intensity	1					0.53

This Si 2p core-level spectrum is somewhat different from the spectrum of the clean Si(001) surface, since rebonded atoms in D_B double-layer steps of Si(001)-4° off surface are induce strong and uneven tensile stress an the (001) terraces.

On the Sb passivated Si(001)-4° off surface as shown in Fig 5(b), its Si 2p core level spectrum, instead of all of the surface-related and the subsurface-related Si 2p core-level components, only one dominant Sb-Si interfacial component S appears at a higher binding energy of +0.19 eV relative to the bulk one. It revealed that Sb is saturates all the dangling bonds of the Si surface atoms on the $p(2\times2)$ terraces and D_B step edges. The observed binding-energy-shift is determined by different electronegativity of two kinds of atoms. Since the electronegativity of Sb (2.05) is larger than that of Si (1.90), charge transfers from Si to Sb[26]. The binding-energy shift of the Sb-Si interfacial component is similar to the value of Sb/Si(001)-2×1, +0.20 eV [8-11,13], and to the value of Sb/Si(113)-1×1,+0.17 eV [16].

After Sb passivation, bulk component B shifted to a higher binding energy by 0.03 eV compared to that of the clean surface shown in Fig 5(a). This indicates that the Sb passivation removes the gap states due to Si dangling bonds and a surface state is newly located at 0.03 eV above the original Fermi level of the clean surface, resulting in such a band flattening.

4. CONCLUSION

The atomic and electronic structure of the clean Si(001)-4° off surface and Sb-covered Si(001)-4° off interface were investigated by STM and high-resolution PES. The clean Si(001)-4° off surface is reconstructed to single domain (001)-$p(2\times2)$ terraces separated by rebonded double-layer (D_B) steps. When 2-ML of Sb is deposited at RT and postannealed at 500°C, the Sb-passivated Si(001)-4° off surface is reconstructed to (001)-(1×2) terraces with symmetric Sb dimers separated by double-layer (S_A and S_B) steps, minimizing surface stress. At this postannealing temperature, the Si 2p core-level spectra show that one dominant Sb-Si interfacial component, indicating charge transfer from Si to Sb atoms on top layer, appears at the disappearance of the surface- and subsurface-related species of the clean surface. In the valence bands it has also been observed that the states related to dangling bonds disappear as the state related to Sb lone-pair orbital appears, which confirms the deduction that the vicinal Si(001)-4° off surface is fully passivated by Sb atoms.

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