Structure of the metallic Si(001) surface at high temperatures: Synchrotron x-ray scattering measurements

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The structure of the metallic Si(001) surface above 900 K was investigated by synchrotron x-ray scattering. Above 900 K, the (2, 1) integer-order surface peak decreases anomalously while the (3/2, 0) reconstruction order peak increases. These results together with the behavior of the crystal truncation rod profile exclude the structural models of the metallic Si(001) surface based on the enhanced Debye-Waller factor and the transition to the symmetrical dimer. The experimental results are explained by the enhanced dynamic step-edge fluctuations induced by the adatom attachments and detachments above 900 K.

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The dimer structure of the Si(001) surface has attracted substantial attention since the observation of the metallic property of the Si(001) surface at high temperatures. Based on their high-resolution electron-energy-loss spectroscopy and ultraviolet photoemission spectroscopy results, Gavioli *et al.*[1] reported the surface metallicity of Si(001) surface above 900 K. Prior to this discovery of the semiconductor-metal transition on the Si(001) surface, Ha and Greene[2] had reported an anomalous decrease of the He atom scattering intensity around 930 K. They attributed this to a structural phase transition above which the Debye-Waller (DW) factor increases abnormally. Later Barbier and Lapujoulade[3] proposed the anharmonicity in surface atomic displacement rather than the DW factor as the reason for the anomalous decrease.

On the other hand, Fukaya and Shigeta[4] proposed that the transition to the symmetric 2×1 dimer structure is the origin of the semiconductor-metal transition. They claimed that the asymmetric dimer structure changes to a symmetric one at around 900 K based on their reflection high-energy electron-diffraction (RHEED) results. The RHEED intensity of the (004) reflection decreased less than the amount expected from the simple DW factor. This result was completely opposite to the Ha and Greene[2] result where the He atom scattering intensity decreased more than the DW factor.[3] The difference between the RHEED and the He scattering intensity remains to be explained, and the structural nature of the semiconductor-metal transition is still controversial.

In this study, we investigated the structure of the Si(001) surface around 900 K using surface x-ray scattering technique. The behavior of the specular crystal truncation rod (CTR), an integer-order surface peak, and a half-integer reconstruction peak was studied across the reported transition temperature. We found that the dimer structure remains to be asymmetrical even above the transition. The dynamic fluctuations of atomic step edges explain the observed behaviors consistently.

The x-ray scattering measurements were carried out at the BL13XU beamline at SPring-8 in Japan using an ultrahigh-vacuum (UHV) chamber equipped with x-ray scattering capability. The energy of the incident x-ray beam was fixed at 12.4 keV using a double bounce Si(111) monochromator. The sample was cut into a size of $5\times20\times0.3$ mm^3 from an *n*-type Si(001) wafer. To obtain a clean surface, the sample was degassed and flashed at 1473 K by flowing direct current through it in the UHV chamber with the base pressure of 3×10^{-10} torr. Detailed information for the surface x-ray scattering chamber is described in the Ref. 5.

We adopt the surface reciprocal-lattice coordinates to describe the scattering data which is related to the reciprocal lattice of the conventional cubic lattice unit cell by $\mathbf{b}_1=(110)_c$, $\mathbf{b}_2=(\bar{1}10)_c$, and $\mathbf{b}_3=(001)_c$. The momentum-transfer component in the surface plane $\mathbf{q}_{in}$ is indexed by (h,k) through $\mathbf{q}_{in}=h\mathbf{b}_1+k\mathbf{b}_2$. The normal component $\mathbf{q}_\perp$ is represented by $\mathbf{q}_\perp=l\mathbf{b}_3$. The temperature dependence of the integer-order (2, 1), the half-integer-order (3/2, 0) and (1/2, 0) peaks, and the CTR at (0, 0) were measured across the reported transition temperature.

In order to examine whether the dimer structure changes to the symmetric one as claimed by Fukaya and Shigeta, we measured the specular CTR, which is sensitive to the atomic positions in the surface-normal direction, at 725 K and at 970 K. Figure 1 shows the structure factors of the CTRs plotted as a function of l. There is no significant difference between the CTR measured at 725 K and that measured at 970 K.

The CTR data were fit to two models each assuming the asymmetrical dimer and the symmetrical dimer respectively using a reported fitting program.[6] In each model the positions of the near surface atoms given in Fukaya and Shigeta's[4] paper and references therein are used.[7] The surface roughness caused by the steps separating dimer domains was the only meaningful free parameter in the fitting. As shown in Fig. 1, the asymmetric dimer model fits the CTR much better

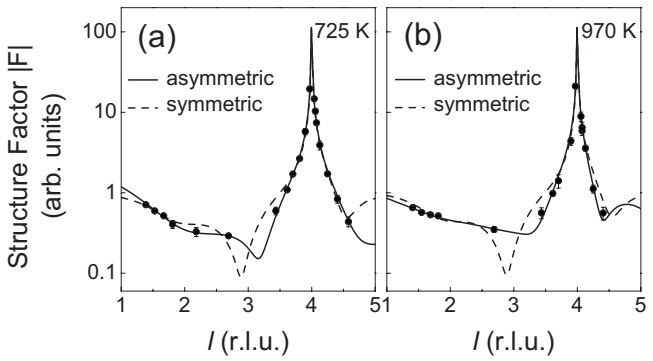

FIG. 1. Specular CTR profiles measured at 725 K (a) and 970 K (b). The solid lines are fits to the asymmetric dimer model and the dashed lines are fits to the symmetric dimer model.

than the symmetric model both at 725 K and at 970 K. At 725 K, the resultant χ^2 was 1.7, and the root-mean-square (rms) roughness σ is 1.6 ± 0.3 Å. The symmetric model results χ^2 of 5.9 and σ of 4.0 ± 0.2 Å. For the CTR measured at 970 K shown in Fig. 1(b), the asymmetric model (solid line) yields χ^2 of 3.1, and σ is 5.5 ± 0.2 Å. On the other hand, the χ^2 resulted by the symmetric model (dashed line) is as large as 15.0, with $\sigma = 3.6 \pm 0.2$ Å.

The fitting results illustrate that the dimer structure above the metallic transition remains to be asymmetric since the χ^2 of the symmetric model is about five times larger than that of the asymmetric model. This is in contrast to Fukaya and Shigeta's explanation of the surface structure in the high-temperature metallic phase based on the symmetric dimer structure. We also note that the surface became rougher at 970 K than at 725 K. This indicates that either there are more steps on the surface or the step height is increased at high temperatures.

To understand the behavior of the surface in-plane structure, we investigated the behavior of the (2, 1) surface integer-order reflection. The (2, 1) peak, which corresponds to the He atom scattering intensity, is sensitive to the surface in-plane structure. Figure 2(a) shows the transverse scan of the (2, 1) peak measured at $l=0.15$. Since the (2, 1) at $l=0$ with no momentum-transfer component in the normal direction lies exactly on the surface and x-rays cannot reach in and out of the surface, we adopted the grazing incident x-ray scattering geometry with a finite l.[8] The (2, 1) peak profile was fit to a Lorentzian curve, and the results are represented by the solid lines. The peak dwindles as the temperature increased from 725 to 1150 K, while there is no significant change in the peak width. From the half width at half maximum (HWHM) of the peak, the average terrace size is estimated to be about 1100 Å.

As illustrated in Fig. 2(b), the integrated intensity of the peak, the area under the peak, decreases as the temperature increases to around 800 K following the normal DW factor. Around 900 K, however, the integrated intensity decreases abruptly and deviates from the DW factor effect indicated by the dashed line. This behavior is similar to the reported He atom scattering results.[2,3] The diffraction intensity at the (2, 1) peak, which is in the middle of the bulk(131) and the $(13\bar{1})$ reflection, is quite sensitive to the presence of the step

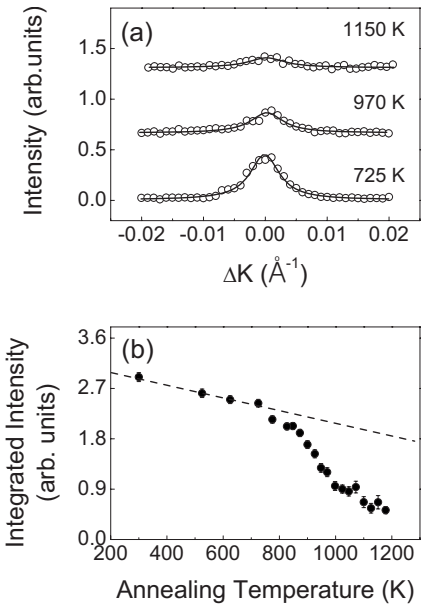

FIG. 2. (a) (2, 1) peak profiles at 1150, 970, and 725 K. The solid lines are the results of the fits to a Lorentzian curve. (b) Temperature dependence of the integrated intensity of the (2, 1) peak. The dashed lines are guide to eye for DW factor.

edges. Considering the diamond structure of silicon, the phase of the x rays reflected from every other (001) atomic planes changes by π, and the scattered x rays from atomic planes separated by a step edge can interfere destructively. Therefore, the decrease of the peak indicates that the surface becomes rougher as the temperature increases above 900 K. This roughening can result from the step proliferation or the step-edge fluctuations. Since the average terrace size does not change much as indicated from the behavior of the peak width, it is likely that the meandering fluctuations of the step edges be the major contribution to the roughening. The enhanced dynamic step-edge meandering at elevated temperatures have been reported by scanning tunneling microscopy and low energy electron microscopy.[9–12] In the reference, the meandering of the S_B type of step becomes so large that adjacent step edges occasionally collide to create steps of double-atomic layer above 900 K.[12] If we make a crude approximation that the integrated intensity shown in Fig. 2(b) corresponds roughly the scattering intensity from the step-free region of a terrace, the integrated intensity might be related to the step meandering width W by $(1-\frac{W}{L})^2$, where L is the typical terrace width as schematically illustrated in Fig. 3.

Interestingly, the half-integer order from the 2×1 reconstruction increases as the temperature increases. Figure 4(a) shows the profiles of the (3/2, 0) reconstruction peak at 1150, 970, and 725 K, respectively. All the diffraction profile is obtained with l fixed at 0.5 (r.l.u.). Compared to the (2, 1) integer-order peak, the (3/2, 0) peak is much sharper. The width obtained by fitting the peak to a Lorentzian is 8.5×10^{-4} Å^{-1}, which is about 6.5 times smaller than the width of the integer-order peak. The instrumental resolution in this direction is estimated to be 1.9×10^{-4} Å^{-1}. The sharp peak indicates that the 2×1 order is correlated over large length

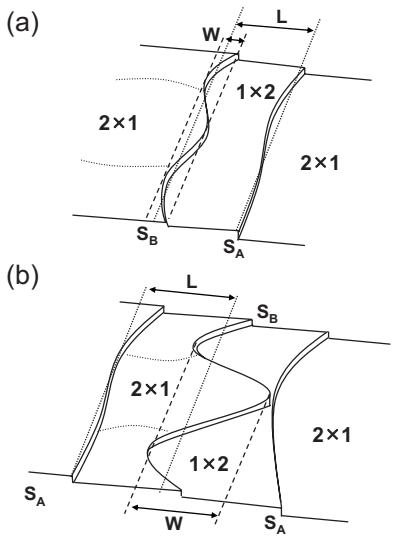

FIG. 3. Schematic diagrams of surface domains with step fluctuations (a) below and (b) above 900 K (L is typical terrace width and W is step meandering width).

in the direction of the scan, the {110} direction, parallel to the typical step-edge direction. The 2×1 order is well correlated on a single terrace. The peak intensity at 1150 K is significantly larger than the peak measured at 970 K. Similar behavior is also observed at the (1/2, 0) fractional-order peak.

The temperature dependence of the integrated intensity of the (3/2, 0) and the (1/2, 0) is shown in Fig. 4(b). The increase of the fractional-order peak at high temperatures excludes the models based on the enhanced DW factor. If the DW factor is enhanced anomalously at high temperatures as proposed in Refs. 3 and 13–15, the fractional-order peaks as well as the integer-order peak should decrease.

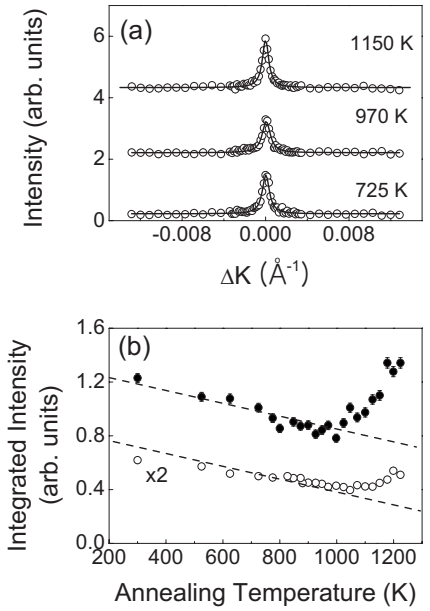

FIG. 4. (a) (3/2, 0) peak profiles at 1150, 970, and 725 K (the solid lines are fitted by a Lorentzian curve). (b) Temperature dependence of the integrated intensity (1/2, 0) (○) and (3/2, 0) (●) at $l=0.5$ (the dashed lines are guide to eye for DW factor).

TABLE I. Calculated structure factors ($|F|$) at (1/2, 0) $l=0.5$, (3/2, 0) $l=0.5$, and (2, 1) $l=0.15$ for asymmetrical and symmetrical dimer models (f_{Si} is atomic form factor of Si).

	$\|F\|_{(1/2,0)l=0.5}$	$\|F\|_{(3/2,0)l=0.5}$	$\|F\|_{(2,1)l=0.15}$
asymmetrical	1.29 f_{Si}	2.15 f_{Si}	3.62 f_{Si}
symmetrical	1.47 f_{Si}	2.00 f_{Si}	3.63 f_{Si}

The model based on the transition from the asymmetrical dimer to the symmetrical dimer is also excluded. Table I shows the structure factors at the three reciprocal space positions calculated from the asymmetrical and the symmetrical dimer models using the atomic positions reported by Fukaya and Shigeta's result. The structure factor is calculated in a unit cell constructed by the (110), $\frac{1}{2}(\bar{1}10)$, and (001) unit vectors in real space. At (3/2, 0), the symmetrical dimer results in a smaller structure factor than the asymmetrical dimer contracting the experimental result. At the (1/2, 0), the structure factor of the symmetric dimer is larger than that of the asymmetric dimer by about 12%, which is not enough to explain the observed data. Both models produce a similar value of structure factor at the integer-order (2, 1) peak, while the experimental value diminishingly small at high temperature.

We attribute the increase of the fractional-order peaks to the increase of the correlation in the 2×1 order. As shown in Fig. 3 schematically, the reconstruction order changes from the 2×1 dimer to the 1×2 dimer across a step edge, which changes back to 2×1 dimer at the following step edge. There are two possible configurations forming the 2×1 reconstruction out of the bulk terminated 1×1 surface. On a single terrace, two possible 2×1 domains separated by domain boundary coexist. The 2×1 order on two terraces separated by a terrace of 1×2 dimer are not correlated typically. At high temperatures, the adatoms are quite mobile as evidenced by reported increase in the mobility of the step edges.[12] The increase in the (3/2, 0) peak indicates that the 2×1 order propagate across the 1×2 terrace as the step edge collides frequently at high temperatures. Figure 5 shows the behavior of the full width at half maximum (FWHM) of the (3/2, 0) peak. The width decreases slightly indicating that the 2×1 domain size along the step-edge direction increases, although it is difficult to extract quantitative value since the width is already close to the instrumen-

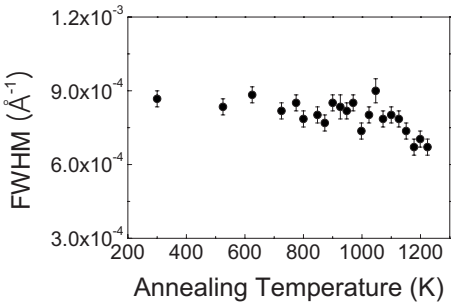

FIG. 5. FWHMs of (3/2, 0) peak profiles as a function of annealing temperature.

tal resolution. The 2×1 domain size inside a terrace increases at high temperatures. In summary, we have observed that the integer-order reflection decreases anomalously while the fractional-order reconstruction peak increases on a Si(001) surface at temperatures above 900 K. Our results exclude the models based on the enhanced Debye-Waller factor and the transition of the asymmetrical to symmetrical dimer in describing the high-temperature metallic Si(001) surface. The specular CTR data were fit well to a surface of the asymmetrical dimer structure with enhanced surface roughness. The observed experimental results are explained by the dynamic step-edge fluctuations caused by the adatom detachment and attachment. The observed structural information of the Si(001) surface might cast clue in understanding the metallic properties of Si(001) surface at high temperatures.

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