Phase Transition from Asymmetric to Symmetric Dimer Structure on the Si(001) Surface at High Temperature

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The dimer configurations on the Si(001) surface at high temperatures have been investigated using the rocking curve of reflection high-energy electron diffraction. The Si(001) surface shows a displacive phase transition around 900 K, where a well-known asymmetric (tilted) dimer structure on the Si(001) at room temperature transforms to a symmetric dimer structure around 900 K. The metallic feature of the Si(001) surface above 900 K can be explained by the phase transition.

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The Si(001) surface is one of the most extensive studied surfaces because of its fundamental and technological importance. Recently, the Si(001) has been widely used as a substrate for fabricating the notable low-dimensional structure such as dot and wire (nanostructures). The detailed investigation of the Si(001) surface structure below room temperature (RT) has been carried out theoretically and experimentally by various surface techniques [1–8]. However, the understanding of the surface structure above RT still remains to be solved. The knowledge of detailed atomic structure on the surface in the high-temperature region is also important to make the nanostructures or oxide, because a slight change in atomic position on the substrate surface has a great influence on the growth of the nanostructure and the oxide.

It has been well known that the outermost atoms on the Si(001) form dimers in order to reduce the surface energy. Chadi has shown that dimers prefer to tilt instead of a parallel configuration to the surface theoretically [4]. It is also shown by scanning tunneling microscope observation [2] and the first-principles calculations [3,5] that the $c4 \times 2$ (or $p2 \times 2$) structure composed of tilted (asymmetric) dimers is very stable at low temperatures. When the temperature is higher than 200 K, the dimer atoms are thermally flipping in a double well potential separated by an energy barrier of 0.1 eV [6]. This means an order-disorder phase transition and the surface structure transforms from the $c4 \times 2$ to the 2×1 [1]. At higher temperature, it has been reported that the dimer structure breaks up at 1485 K [9,10], and the photoemission spectroscopy (PES) study suggests that the surface melting occurs at 1610 K [10].

It is interesting that the semiconductor-metal transition takes place around 900 K, which is much lower than the surface melting temperature of the Si(001) surface [11]. Gavioli, Betti, and Mariani suggested that the surface metallization was induced by the increase of the dimer flipping rate at finite temperature, i.e., an increase in the probability of instantaneous formation of a symmetric dimer structure [11]. Recently, Hwang *et al.* claimed that the surface metallization resulted from migrating adatoms on the surface where the surface dimer structure was kept to be asymmetric [12]. Then the origin of the surface metallization still remains controversial, in particular, the dimer configuration around 900 K seems to be open to further discussion.

In this Letter, we measured reflection high-energy electron diffraction (RHEED) intensities as a function of the glancing angle, i.e., a RHEED rocking curve, from the Si(001) surface in the wide temperature range from RT to 1660 K. By the analysis of the RHEED rocking curve using dynamical diffraction theory, we will show an evidence that the phase transition around 900 K corresponds to the transformation of the dimer structure from asymmetric to symmetric configuration. The result is completely different from the previous interpretation by the increase in the dimer flipping rate at finite temperature.

The measurement of the RHEED rocking curve was carried out in a homebuilt RHEED apparatus equipped with a magnetic deflector [13]. The glancing angle (θ) of the incident electrons accelerated at 10 kV was changed from 0.5° to 6° in 0.05° steps quickly. The incident azimuth was chosen at 23° away from the [110] direction (so-called one-beam condition [14]), where we can selectively obtain the information concerning the normal components of atomic positions to the surface.

The Si samples ($5 \times 25 \times 0.5$ mm^3) were cut from a mirror-polished commercial p-type Si(001) wafer (6–10 Ω cm). The clean surface was obtained by heating at 673 K for 24 h and flashing at 1473 K for 1 min by a direct current flow at pressures below 2×10^{-7} Pa. The surface temperature (T_s) was measured with an infrared radiation thermometer ($T_s < 1073$ K) and an optical pyrometer ($T_s > 1073$ K) within the experimental error of ± 20 K, which were compensated with the emissivity of 0.5.

Figure 1 shows the measured RHEED rocking curves in the temperature range from RT to 1660 K. We confirmed that the surface keeps the 2×1 structure up to 1440 K from the RHEED pattern. This indicates that the dimer structure is preserved up to 1440 K, which is consistent

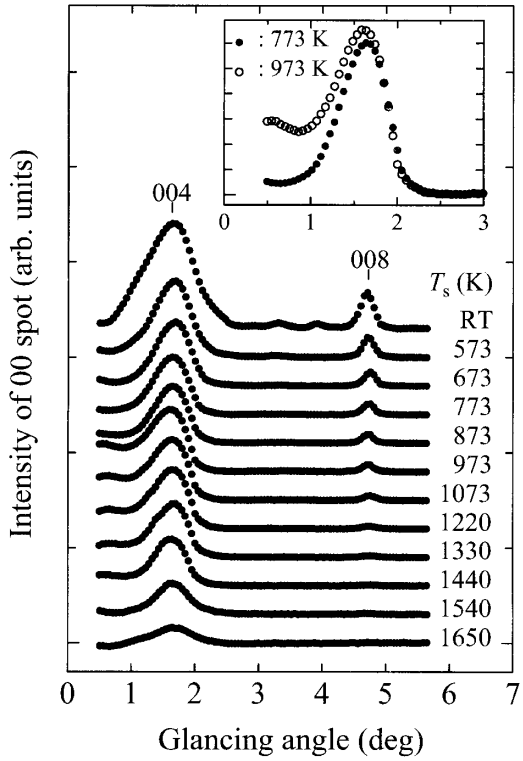


FIG. 1. RHEED rocking curves measured from clean Si(001) surface in the temperature range between room temperature (RT) and 1660 K. The surface temperature (T_s) is labeled on the right-hand side of the curve. Inset: The intensity changes below $\theta = 3°$ at 773 K (solid circles) and 973 K (open circles).

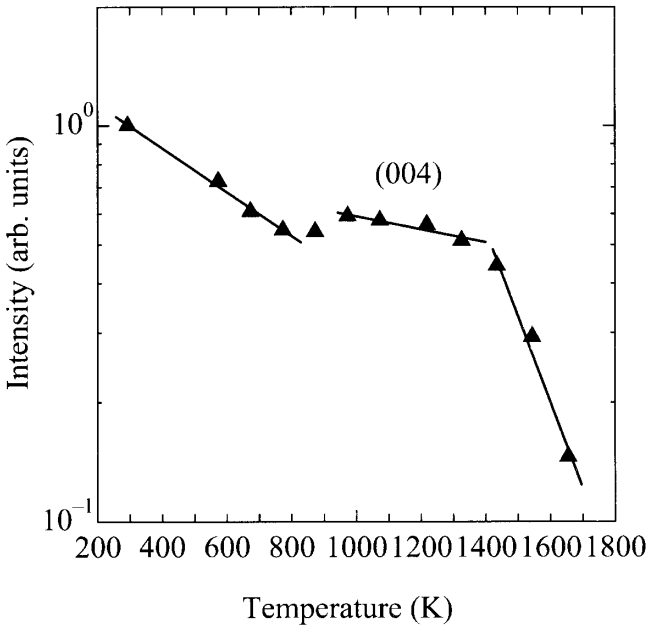


FIG. 2. Temperature dependence of the 004 Bragg peak intensity.

with observations by a reflection electron microscopy [9] and the PES [10]. The intensity in the rocking curves seems to decrease with the increase of temperature, gradually. However, around 900 K, the rocking curves show clear change as shown in the inset of Fig. 1. When the temperature is elevated from 773 to 973 K, the RHEED intensity at low glancing angle drastically increases.

Such an intensity change is also observed at the 004 Bragg spot around 900 K, as shown in Fig. 2. The RHEED intensity drastically decreases with the increase of temperature up to 773 K. However, the RHEED intensity increases in the temperature range from 773 to 973 K, which indicates a structural phase transition. The slope of the intensity change above 973 K is smaller than that below 773 K. The drastic decrease in the intensity over 1440 K clearly shows an evidence of the surface melting [10].

Since the slope of the intensity change for the Bragg spot relates to the surface Debye temperature (Θ_D), the gentle slope in the temperature range from 973 to 1440 K means high Θ_D, which is comparable to the evaluated value for the Si(111) surface (420 K) [15], and the steep slope below 773 K corresponds to low Θ_D. Therefore, the thermal vibration shows a tendency to be suppressed above 900 K. The tendency is contrary to a mechanism of the phase transition around 900 K recognized to be induced by the increase in the dimer flipping rate at high temperature [11], because the increase of the dimer flipping rate leads to the enhancement in the thermal vibrational amplitude, i.e., the large attenuation of the RHEED intensity.

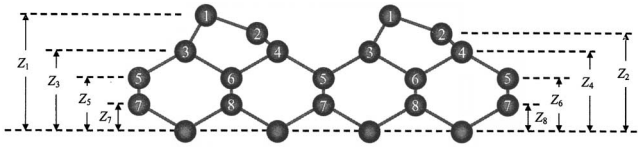
We also observed streaks near the RHEED spots by diffuse scattering around 900 K. The intensity of the diffuse scattering rapidly increased as the temperature approached to 900 K, and the intensity came to disappear rapidly over 900 K. The change suggests that the phase transition is continuous and related to a softening of some vibration mode at the phase transition temperature.

In order to investigate the detailed surface structures above and below the phase transition temperature (900 K), we tried to determine the atomic positions on the Si(001) surface near the 900 K by optimizing the calculated curve to the measured one using the Marquardt algorithm [16,17]. The RHEED rocking curves were calculated based on the dynamical diffraction theory developed by Ichimiya [18] and the details of the optimization were described in Refs. [19,20]. For the optimization, we used the atomic positions obtained from the first-principles calculations for the asymmetric dimer model as the initial values [5]. We classified the atomic positions into eight groups according to their situations (see Table I). The surface Debye temperature was taken as 420 K.

The optimized curves are plotted by the solid lines in Fig. 3. The calculated rocking curves at low and high temperatures are in good agreement with the measured curves, in particular, at low glancing angle. Although the

TABLE I. Atomic coordinates (Z_i) obtained by optimization (in units of Å). Schematic drawing of surface structure for Si(001) is also shown in the lower part. Each number labeled in atom corresponds to a classified group.

No.	Si(001)-(2 × 1) Z_i (Å) (Ref. [5])	T_s = 773 K Z_i (Å) (this work)	T_s = 973 K Z_i (Å) (this work)
1	5.27	5.24	5.29
2	4.96	4.99	5.29
3	4.02	4.15	4.00
4	4.09	4.15	3.99
5	2.52	2.73	2.59
6	2.85	2.73	2.60
7	1.22	1.35	1.19
8	1.46	1.34	1.19



intensity of the 008 Bragg peak shows some difference, the R factors defined in Ref. [21] for the rocking curves at 773 and 973 K are 3.4% and 2.3%, respectively. The intensity in the low glancing angle region is very important to determine the surface structure, because the difference between the rocking curves caused by the different dimer configurations (see Table I) can be seen below the glancing angle of the 004 Bragg peak and the intensity of the 004 Bragg peak is much larger than that of the 008 Bragg peak.

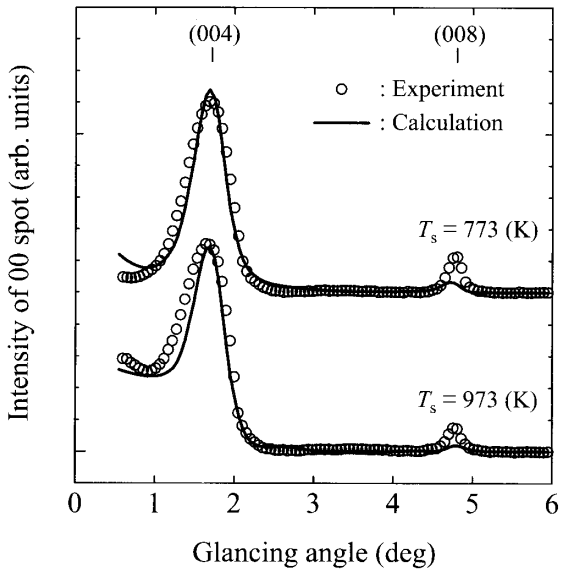


FIG. 3. RHEED rocking curves from clean Si(001)-(2 × 1) surface at 773 and 973 K. The open circles show the measured curves, and the solid lines show the calculated curves determined by the optimization of atomic configuration at each temperature.

Table I shows the atomic positions obtained by the optimization at each temperature. At 773 K, the dimer atoms show different heights and the surface structure still remains the asymmetric dimer structure. On the other hand, at 973 K, the dimer atoms show the same height and become symmetric. Therefore, the surface structure below 900 K is composed of the asymmetric dimer and the dimer is thermally flipping [2,6]. However, the surface structure above 900 K is transformed into the symmetric dimer structure.

Next, we consider the temperature dependence of the RHEED intensity in Fig. 2. The drastic change in the slope of the 004 Bragg spot intensity above and below 900 K can be well explained by the framework of the displacive phase transition described above. Since the dimers are asymmetric below 900 K, the steep slope of the intensity change with temperature results from the anharmonic effect in a double well potential with a very low activation barrier for the asymmetric dimer model. On the other hand, above 900 K, the surface potential is transformed into a single well potential forming the symmetric dimer. Therefore, the flip-flop motion does not occur above 900 K. The gentle slope of the 004 Bragg spot above 900 K can be explained by the disappearance of the anharmonicity in the potential. The change in the slope due to the structure transformation is also supported by the theoretical calculation. Tütüncü *et al.* reported by using the *ab initio* pseudopotential method that the tilt of the dimer gives rise to the reduction of the zone-edge surface phonon energy [22]. This result indicates that the surface Debye temperature for the asymmetric dimer geometry is lowered in comparison with that for symmetric dimer geometry.

For the surface metallization over 900 K [11], the dispersive phase transition is also consistent. The first-principle calculations show that the symmetric dimer structure has the metallic feature whereas the asymmetric dimer structure is semiconducting [7]. The surface metallization is not mainly induced by the instantaneous formation of the symmetric dimer structure due to dynamic thermal flipping of asymmetric dimer atoms [11] but by the static formation of the symmetric dimer structure around 900 K. Recently, Hwang *et al.* suggested that the existence of migrating Si adatoms on the asymmetric dimer structure leads to the surface metallization [12]. They considered the fact that the adatoms act as a donor as well as the case of the high-temperature Si(111) surface [23]. We also calculated the RHEED rocking curves from the Si(001) surface composed of the asymmetric dimers and adatoms. However, such a structure model cannot explain the drastic increase of the RHEED intensity at the low glancing angle we observed. Therefore, we can rule out the mechanism of the metallization due to the adatoms.

In summary, we investigated the surface structures of Si(001) at high temperatures by using RHEED. When the temperature is elevated up to 1440 K, the Bragg peak intensity abruptly increases around 900 K, and gradually decreases with temperature. Meanwhile, the 2×1 structure is preserved. From the intensity analysis of the RHEED rocking curve, we found that the asymmetric dimer structure transforms to the symmetric dimer structure around 900 K. This phase transition leads to the hardening of the surface layer and metallization. Then, we have to consider the phase transition, which has a great influence on the surface diffusion and the film growth on the surface.

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