

Low-Energy Electron Diffraction Study of the Phase Transition of Si(001) Surface below 40 K

M. Matsumoto, K. Fukutani, and T. Okano

Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan

(Received 4 November 2002; published 12 March 2003)

The phase transition of Si(001) surface below 40 K was studied by low-energy electron diffraction (LEED). The temperature dependence of the intensities and widths of the quarter order diffraction spots and LEED intensity versus electron energy curves (I - V curves) were obtained in the temperature region from 20 to 300 K. While the spot intensities of the quarter order spots decrease and the widths broaden, the I - V curves do not change so much below 40 K. This clearly shows that a phase transition occurs from an ordered phase above 40 K to a disordered phase below 40 K.

DOI: 10.1103/PhysRevLett.90.106103

PACS numbers: 68.35.Rh, 61.14.Hg

The Si(001) surface has attracted a lot of attention due to its industrial importance and scientific interest. Many experimental [1–9] and theoretical [10–13] studies have been performed to elucidate its surface structure. The most widely accepted idea is that asymmetric buckled dimers construct an antiferromagnetically ordered $c(4 \times 2)$ structure [Fig. 1(e)]. This has been confirmed by the alternate zigzag rows in the image of scanning tunneling microscopy (STM) [1,2] and a $c(4 \times 2)$ low-energy electron diffraction (LEED) pattern [3,4] for the carefully prepared surface at temperatures around 100 K. At room temperature, a fast flip-flop motion is thermally activated, which shows symmetric dimer rows in the STM image [6] and a $p(2 \times 1)$ LEED pattern [3–5]. From the temperature dependence of LEED spot intensities [3,4] and a density functional theory calculation [12,13], an order-disorder phase transition has been confirmed to occur at about 200 K.

Recently, however, several groups reported a possibility of a phase transition at a low temperature by using STM. Yokoyama *et al.* [14] and Kondo *et al.* [15] observed symmetric dimer structure at 6 K and 20 K, respectively. Shigekawa *et al.* reported that the area which has $p(2 \times 2)$ symmetry increases below 50 K [16,17]. Since they all observed clear $c(4 \times 2)$ structure above 50 K, something should happen in this temperature region. These reports reopened the controversy over the structure of the Si(001) surface [18–23].

In the STM measurement, since the tip-surface interaction is very large, the observed image might differ from the real structure, and the information is restricted to a very narrow area [23]. On the contrary, the diffraction methods such as LEED and reflection high-energy electron diffraction (RHEED) have a much weaker interaction with the surface and enable us to get the average information of the surface order from a wider area. Furthermore, the LEED spot intensity versus an electron energy curve (I - V curve) or RHEED rocking curve is very sensitive to the local atomic structure. In this Letter we report a LEED investigation of Si(001) below 50 K. From the temperature dependence of the LEED spot

intensity, width and I - V curve, we found that an order-disorder phase transition occurs at about 40 K.

The LEED measurement was performed in an ultra-high vacuum chamber, whose base pressure is 5×10^{-9} Pa. The arsenic-doped n -type Si(001) sample (5×10 mm², $\rho = 0.003 \Omega$ cm) was heated by direct current

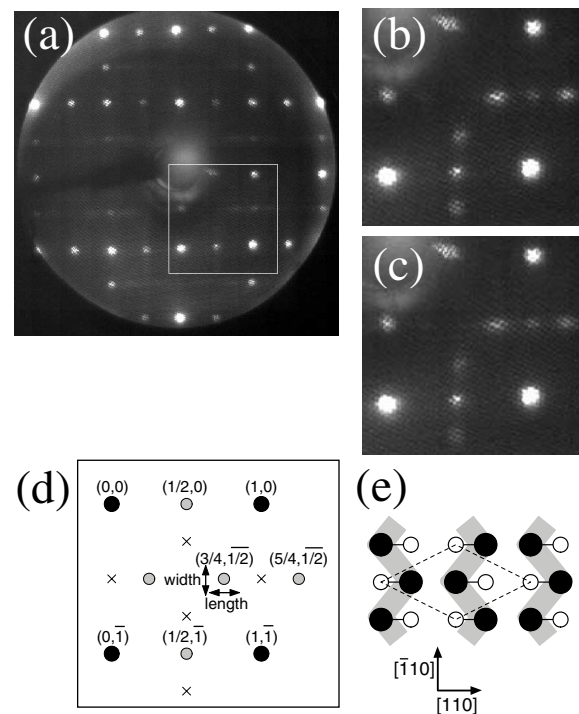


FIG. 1. LEED patterns observed at (a) 300 K, (b) 40 K, and (c) 25 K. Only the white square region in (a) is shown in (b) and (c). (d) Schematic LEED pattern for the white square region of (a). The gray dots show the quarter order diffraction spots from a domain which has dimer rows along $[\bar{1}10]$ direction, whose model is shown in (e). The crosses show the spots from another domain which has dimer rows along $[110]$. (e) Schematic of the buckled dimer model. A $c(4 \times 2)$ unit cell is shown by a dotted line. Large black dots show the upper Si atoms and small white dots show the lower atoms. The gray lines show the corresponding STM image.

and cleaned by repeated cycles of flashing to 1150 °C under a pressure below 1×10^{-8} Pa [24]. After cleaning, a clear $c(4 \times 2)$ LEED pattern could be observed at about 80 K. The sample was cooled by a liquid He transfer-type cryostat (APD cryogenics, heli-tran). The lowest temperature was 20 K, which was measured by the Pt-PtRh(13%) thermocouple attached on the Ta sample holder. The temperature difference between the sample and the thermocouple position was corrected by putting a Si diode sensor on the sample after the experiment.

A conventional four-grid reverse view LEED optics (OCI, BDL600) was used and the LEED pattern on the phosphorous screen was captured by a high sensitive cooled CCD camera (Hamamatsu, C3140) [25]. The temperature dependences of the diffraction spots were obtained at constant incident electron energies of 110 and 52 eV. As no significant difference was observed between the two results, only the result at 110 eV is shown below. After cleaning and cooling, the sample was once heated above 300 K and variation of the LEED pattern was recorded in the cooling process. It took about 10 min to cool the sample from 400 to 25 K. The LEED I - V curves were obtained at a constant temperature. It took about 20 min to get the LEED patterns from 40 to 300 eV. The measurement time of 20 min is short enough to ignore the effect of electron irradiation and background gas. The area ratio of the two domains on the surface could not be controlled. Therefore, the $(\frac{3}{4}, \frac{1}{2})$ spot was much stronger than the $(\frac{1}{2}, \frac{3}{4})$ spot and the I - V curves for the $(1,0)$ and $(0,\bar{1})$ spots, which are equivalent for the perfect double domain surface, are largely different.

Typical LEED patterns measured in a cooling process are shown in Figs. 1(a)–1(c). The schematic LEED pattern and a buckled dimer model for a $c(4 \times 2)$ structure are shown in Figs. 1(d) and 1(e), respectively. At 300 K [Fig. 1(a)], only diffuse streaks can be seen around the quarter order spots. As the sample is cooled, the intensities of the quarter order spots increase rapidly. In the temperature region from 150 to 40 K, the quarter order spots are sharp and intense as shown in Fig. 1(b). At temperatures below 40 K, the quarter order spots become weak and streaky again. The quarter order spots at 25 K [Fig. 1(c)] are much weaker than those at 40 K [Fig. 1(b)].

The temperature dependence of the LEED spot intensities is plotted in a logarithmic scale in Fig. 2. The temperature dependence above 40 K is consistent with the previous LEED result [3]. While the intensities of the integer order [$(1, \bar{1})$ and $(0, \bar{1})$] and half order [$(\frac{1}{2}, \bar{1})$] diffraction spots follow the Debye-Waller law, the intensities of the quarter order spots [$(\frac{3}{4}, \frac{1}{2})$ and $(\frac{5}{4}, \frac{1}{2})$] largely deviate from the Debye-Waller law above 150 K which corresponds to the order-disorder phase transition between $c(4 \times 2)$ and $p(2 \times 1)$. In a low temperature region, the temperature dependence of each diffraction spot drastically changes at 40 K. The intensities of the quarter order spots deviate from the Debye-Waller law and decrease rapidly below 40 K. These results clearly

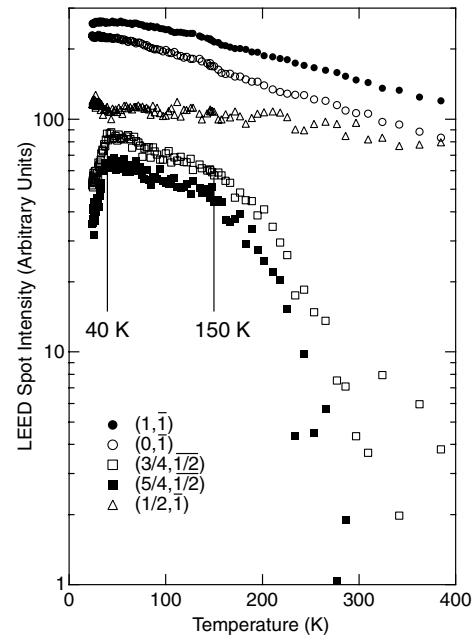


FIG. 2. The temperature dependence of the LEED spot intensities for the $(1, \bar{1})$, $(0, \bar{1})$, $(\frac{1}{2}, \bar{1})$, $(\frac{3}{4}, \frac{1}{2})$, and $(\frac{5}{4}, \frac{1}{2})$ spots. The intensities can not be compared because they are independently scaled in each spot.

indicate that a phase transition occurs at 40 K. The intensity at 25 K is nearly half of that at 40 K for the $(\frac{5}{4}, \frac{1}{2})$ spot. The intensity of the $(\frac{1}{2}, \bar{1})$ spot slightly increases below 40 K. The intensities of the $(1, \bar{1})$ and $(0, \bar{1})$ spots slightly deviate from the exponential curves below 50 K, which may be because the Debye-Waller law deviates from the exponential relation to the temperature in a low temperature region. The reversibility and reproducibility of this temperature dependence were carefully checked. The intensities of the quarter order spots increase by heating the sample to 40 K and decrease by cooling again. The similar temperature dependence was obtained for several samples including a boron-doped p -type sample. At the measurement of Fig. 2, the LEED primary beam current was set constant at about 60 nA. While the temperature dependence was measured at several beam currents from 20 to 500 nA, no significant change was observed.

The width of a diffraction spot represents the degree of order of the corresponding structure; therefore, analysis of the spot profile gives us information about the nature of the phase transition. As the quarter order spot has an asymmetric shape, the spot profile was analyzed along the two directions. One is the direction along the streak (length) and the other is the direction perpendicular to it (width) as shown in Fig. 1(d). The length and width of a spot represent the ordering between the dimer rows and in a dimer row, respectively. The length is usually larger than the width, which shows that the ordering between the dimer rows is worse than the ordering in a dimer row. The spot profiles of the $(\frac{3}{4}, \frac{1}{2})$ spot in the length and width

directions are shown in Figs. 3(a) and 3(b), respectively. The spot profiles are obtained by integrating 25 lines to reduce the effect of shadowing by the LEED grid. Each profile was fitted to a Gaussian curve, which is shown by the solid line, and the full width at half maximum (FWHM) of a spot was estimated from the fitting parameter. The temperature dependences of FWHMs for the length and width are plotted as solid and open circles, respectively, in Fig. 3(c) for the temperature region from 25 to 220 K. As the spot intensity becomes very weak above 220 K, it is difficult to do the Gaussian curve fitting with a reasonable accuracy. Both length and width are constant from 40 to 150 K and increase above 150 K. This result is consistent with the previous results [3], which indicates that the ordering becomes worse at high temperatures. In the temperature region below 40 K, both length and width increase again. Therefore, the ordering becomes worse in both directions below 40 K.

In Fig. 4, the LEED I - V curves measured at 20 and 140 K are plotted as thin and solid lines, respectively. The I - V curves at 20 K look similar to those at 140 K. While the relative intensities are different, all peaks are present at both temperatures. Several peaks at 20 K shift to a few eV higher energy from those at 140 K. The reason for this small peak shift is suggested to be the insufficient normal incident condition because the shift amount does not depend on the beam energy but on the beam order. The difference between the two I - V curves can be estimated by the Pendry's R factor (R_p) [26]. In the previous dynamical LEED study, the theoretically calculated I - V curves were compared with the experimental I - V curves obtained at 120 K [5]. The R_p for the symmetric and buckled dimer models were 0.48 and 0.26, respectively.

Since the average of R_p for the two I - V curves in Fig. 4 is about 0.28 after the correction of the above mentioned small peak shift, it can be concluded that the structural change from buckled to symmetric dimer does not occur by cooling from 140 to 20 K. The I - V curves at 140 and 300 K were also compared for the integer and half order spots. The peak positions are identical and only the relative intensities are different, which is consistent with the previous result [3]. From these results, it is concluded that the local atomic arrangement is the same and the buckling of the dimer is conserved in the temperature region from 20 to 300 K.

As can be seen in Figs. 1(a)–1(c), the $(\frac{1}{2}, \frac{1}{2})$ spot, which originates from the $p(2 \times 2)$ symmetry, cannot be detected at any temperatures we measured. Therefore, it is considered that the $p(2 \times 2)$ structure, even if it is present, does not construct a large domain but exists only at the antiphase domain boundary.

It should be noted that the transition temperature of 40 K was sample dependent and sometimes increased to 70 K. In such a case, the LEED spot intensity changes were less sharp than those in Fig. 2 in both temperature regions below 70 K and above 150 K. It has been shown that the broad transition range above 150 K is caused by the presence of an appreciable amount of defects on the surface [12,13]. Therefore, it is suggested that the presence of defects on the surface causes the transition temperature shift and a broad transition range below 70 K. Since the intensity changes in Fig. 2 are sharper than the previous LEED results [3], we believe that the defect density is appreciably low in this study.

The LEED experimental results below 40 K can be summarized as follows: (i) The intensities of the quarter

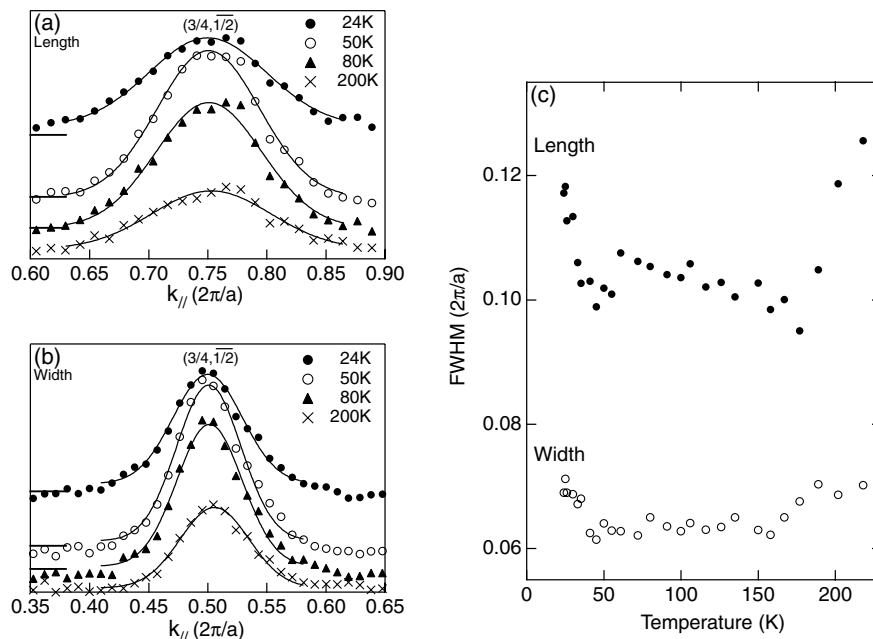


FIG. 3. The LEED spot profiles of the $(\frac{3}{4}, \frac{1}{2})$ spot along the (a) length and (b) width directions for several temperatures from 24 to 200 K. (c) The temperature dependence of the length and the width of the $(\frac{3}{4}, \frac{1}{2})$ spot.

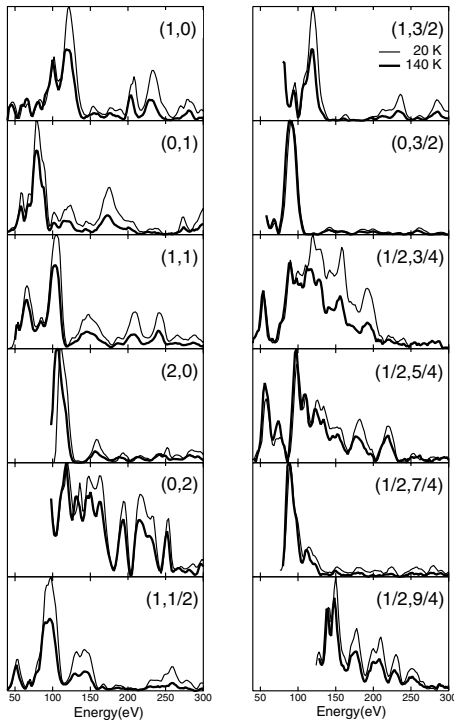


FIG. 4. The LEED I - V curves at 20 and 140 K. The thin and thick lines show the I - V curves at 20 and 140 K, respectively.

order spots decrease largely. (ii) Both length and width of the quarter order spots increase. (iii) The LEED I - V curves are basically invariant in the temperature region from 20 to 300 K. (iv) The diffraction spots which are characteristic of the $p(2 \times 2)$ symmetry cannot be detected. From these results, it can be concluded that an order-disorder phase transition occurs at 40 K. The symmetric dimer or $p(2 \times 2)$ structure observed in the previous STM papers [14–17] is considered to be caused by a frequent flip-flop motion of the dimer reactivated at a low temperature.

Two possibilities have been discussed previously. One is the dynamical flipping caused by reduction in the barrier height for the dimer flipping, which originates in the anharmonic potential effect induced by the negative thermal expansion [14]. A recent theoretical study suggests that the energy difference between symmetric and buckled dimer arrangements decreases by the negative thermal expansion [21]. Another is that the quantum fluctuation rate becomes high at a low temperature [19], which was derived on the analogy of the hopping rate of muon [27]. It is considered that the quantum fluctuation is activated at a low temperature because the quantum coherence between the two energetically degenerate buckled state of Si dimer becomes better. While it is difficult to conclude which possibility is correct from our results, the quantum fluctuation is probable because the negative thermal expansion would cause the structural change. A LEED dynamical analysis would be useful to get a more definite conclusion.

In summary, it is confirmed by LEED that a phase transition occurs from an ordered phase above 40 K to a disordered phase below 40 K on the Si(001) surface. It is suggested that the disordered phase is responsible for the anomalous STM images observed below 50 K. The quantum fluctuation activated by the quantum coherence at a low temperature is the most probable cause for this phase transition.

This work was supported by a grant-in-aid for COE Research from the Ministry of Education, Science, Sports and Culture of Japan.

-
- [1] R. A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).
 - [2] H. Tochiyama, T. Amakusa, and M. Iwatsuki, Phys. Rev. B **50**, 12 262 (1994).
 - [3] T. Tabata, T. Aruga, and Y. Murata, Surf. Sci. **179**, L63 (1987).
 - [4] M. Kubota and Y. Murata, Phys. Rev. B **49**, 4810 (1994).
 - [5] H. Over *et al.*, Phys. Rev. B, **55**, 4731 (1997).
 - [6] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).
 - [7] F. J. Himpsel and D. E. Eastman, J. Vac. Sci. Technol. **16**, 1297 (1979).
 - [8] E. Landemark, C. J. Karlsson, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. Lett. **69**, 1588 (1992).
 - [9] M. Aono, Y. Hou, C. Oshima, and Y. Ishizawa, Phys. Rev. Lett. **49**, 567 (1982).
 - [10] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).
 - [11] J. E. Northrup, Phys. Rev. B **47**, 10 032 (1993).
 - [12] K. Inoue, Y. Morikawa, K. Terakura, and M. Nakayama, Phys. Rev. B **49**, 14 774 (1994).
 - [13] K. Terakura, T. Yamasaki, and Y. Morikawa, Phase Transit. **53**, 143 (1995).
 - [14] T. Yokoyama and K. Takayanagi, Phys. Rev. B **61**, R5078 (2000).
 - [15] Y. Kondo, T. Amakusa, M. Iwatsuki, and H. Tokumoto, Surf. Sci. **453**, L318 (2000).
 - [16] H. Shigekawa *et al.*, Jpn. J. Appl. Phys. **35**, L1081 (1996).
 - [17] K. Hata, S. Yoshida, and H. Shigekawa, Phys. Rev. Lett. **89**, 286104 (2002).
 - [18] S. B. Healy, C. Filippi, P. Kratzer, E. Penev, and M. Scheffler, Phys. Rev. Lett. **87**, 016105 (2001).
 - [19] Y. Yoshimoto and M. Tsukada, in *Proceedings of the 25th International Conference on the Physics of Semiconductors, Osaka, Japan, 2000* (Springer, Berlin, New York, 2001).
 - [20] T. Uozumi, Y. Tomiyoshi, N. Suehira, Y. Sugawara, and S. Morita, Appl. Surf. Sci. **188**, 279 (2002).
 - [21] P. Bokes, I. Stich, and L. Mitas, Chem. Phys. Lett. **362**, 559 (2002).
 - [22] G. Le Lay *et al.*, Phys. Rev. B **66**, 153317 (2002).
 - [23] T. Mitsui and K. Takayanagi, Phys. Rev. B, **62**, R16251 (2000).
 - [24] K. Hata, T. Kimura, S. Ozawa, and H. Shigekawa, J. Vac. Sci. Technol. A **18**, 1933 (2000).
 - [25] M. Matsumoto, N. Tatsumi, K. Fukutani, and T. Okano, Surf. Sci. **513**, 485 (2002).
 - [26] J. B. Pendry, J. Phys. C **13**, 937 (1980).
 - [27] R. Kadono *et al.*, Phys. Rev. B **39**, 23 (1989).