New Phase and Surface Melting of Si(111) at High Temperature above the (7 × 7)-(1 × 1) Phase Transition

Y. Fukaya and Y. Shigeta*

Faculty of Science & Graduate School of Integrated Science, Yokohama City University, Seto 22-2, Kanazawa-ku, Yokohama 236-0027, Japan

(Received 1 May 2000)

The surface structure of Si(111) at high temperatures (950–1380 °C) has been studied with reflection high-energy electron diffraction. We have found three different surface structures: (1) A relaxed bulklike structure with adatoms of 0.25 monolayer (ML) is formed (950–1210 °C); (2) there is a new phase where the adatom coverage decreases to 0.20 ML (1250–1270 °C); (3) the surface melting occurs over 1290 °C. The crystalline structure below the melting layer can be explained by the vacancy model missing all adatoms and 0.45 ML of atoms in the first-double layer.

PACS numbers: 68.35.Rh, 61.14.Hg, 68.35.Bs

A Si(111) surface is fascinating because of the complexity of the surface structure and its property and has been widely studied by many researchers. At room temperature, the stable 7 × 7 structure, which is composed of the dimer-adatom-stacking fault layer (DAS) [1], is formed on the Si(111) surface. At temperatures higher than about 830 °C, the Si(111) surface structure is transformed from the (7 × 7)-DAS to the so-called "1 × 1" structure [2–5]. The 1 × 1 surface has been established to be a relaxed bulklike structure with random adatoms of 0.20–0.25 ML (1 ML = 7.8×10^{14} cm^{-2}) [6–9].

At high temperature near the bulk melting point (1410 °C), a phenomenon such as the incomplete surface melting resulting from the formation of a thin film of disordered atoms has been observed on the surface. In recent years, the surface melting on the Si(111) surface has been extensively studied experimentally [10–13] and theoretically [14]. The surface melting occurs at about 1200 °C by reflection high-energy electron diffraction (RHEED) [15], scanning electron microscope [11], and helium atom scattering [12]. Hibino *et al.* have estimated the number density of the disordered atoms at 0.8 ML and it is constant up to 1300 °C by using medium-energy ion scattering (MEIS) [13]. On the other hand, Vandré *et al.* have shown by core-level photoemission spectroscopy that some phase transition suggesting the formation of a liquidlike film occurs at 1277 °C [10]. However, the temperature leading to the surface melting on Si(111) surface currently calls for further discussion. Furthermore, the surface structure at temperatures near the bulk melting point still remains unresolved.

The RHEED is a very useful tool for the surface structure analysis over several layers below the surface. For example, during the growth of a molecular beam epitaxy, the intensity of a specular spot at a certain glancing angle shows regular oscillation with a period according to the deposition time of 1 ML [16–18]. Moreover, when we measure the glancing angle dependence of RHEED intensity (RHEED rocking curve) during growth, we can obtain some information regarding the continuous structural change in the growth [19,20] by comparing it with the calculated result based on the dynamical diffraction theory of RHEED developed by several authors [21–24].

In a previous study, we measured the accurate temperature dependence of RHEED rocking curves from clean Si(111) surface in the wide temperature range (20–800 °C) below the (7 × 7)-(1 × 1) phase transition, and we determined the effective surface Debye temperature [25]. In this Letter, we show RHEED rocking curves at high temperatures (950–1380 °C) to investigate the surface structure of the Si(111) above the transition temperature. From the analysis with the dynamical RHEED calculation, we also show an evidence of a new phase formation at temperature just below the surface melting point and propose the surface structure models corresponding to the new phase and the surface melting.

The Si bars ($5 \times 25 \times 0.4$ mm^3) cut from a mirror-polished commercial *n*-type Si(111) wafer (1.0–4.0 Ω cm) were used. The sample was heated up to 1200 °C for 3 h and flashed at 1200 °C for 10 min by a direct current flow at pressures below 2×10^{-7} Pa. The surface temperature (T_s) was measured with an optical pyrometer. The temperature was compensated with the emissivity of 0.5 and included the experimental error of ±20 °C.

We used a RHEED apparatus with a magnetic deflector to change the glancing angle of incident electrons in short time [26]. The accelerated voltage of incident electrons was 10 kV and the azimuthal angle was the direction rotated 7.5° from the $[11\bar{2}]$ direction. This diffraction condition is called "one-beam condition" [27]. Under the one-beam condition, we can selectively derive information regarding the atomic positions and the density of atoms normal to the surface because an effect of intense simultaneous reflection caused by the surface wave resonance is suppressed [28]. The integrated intensity of the specular reflection was plotted as a function of glancing angle (θ). We took the average of five measured curves at each

 0031-9007/00/85(24)/5150(4)$15.00

temperature. The pressure was less than 1×10^{-7} Pa during the measurement except for the cases above 1340 °C ($<1 \times 10^{-6}$ Pa).

We calculated the intensity based on the dynamical diffraction theory using the multislice method under the one-beam condition developed by Ichimiya [29]. We took account of imaginary potential resulting from the thermal diffuse scattering and electron excitation to estimate accurate temperature dependence of the intensity [26]. The reliability factor (R) was used to judge the goodness of fitting of a calculated curve to a measured one, as given in Refs. [20,25].

The dotted lines in Fig. 1 show the measured RHEED rocking curves from the Si(111) surface above 950 °C. These rocking curves at $T_s = 950-1160$ °C do not show any significant change except for the decrease of the intensities due to the enhancement of the thermal diffuse scattering. Therefore, it is considered that the surface structure is preserved in this temperature range. At 1270 °C, however, the intensities around 0.8° are much larger than those at 950−1160 °C, as indicated by an arrow. The change in curve at 1270 °C cannot be explained by the existence of the surface melting reported by Hibino *et al.* [13] because the intensity of the Bragg peaks (333, 444, and 555) does not show any drastic change. The increase of the intensities around 0.8° suggests an appearance of a new phase different from the surface melting.

Above 1290 °C, the intensities in the entire range of glancing angle ($0.5° < \theta < 6°$) drop abruptly compared with those at $T_s < 1270$ °C as shown in Fig. 2, where we plot the intensities of the 333 Bragg peak and the dip at $\theta = 0.8°$ as a function of T_s. This drastic decrease cannot be explained by the enhancement of the thermal diffuse scattering effect with elevated temperature. This result suggests that the surface melting occurs at 1290 °C. It is also supported by the fact that the peak position at $\theta = 1.3°$ observed at temperatures of 950−1270 °C also shifts to low angle at 1380 °C, as shown in Fig. 1.

In Fig. 2, the intensity of the 333 Bragg peak on the logarithmic scale decreases proportionally with an increase of T_s below 1270 °C. The abrupt decrease of Bragg peak intensity above 1290 °C suggests that the surface melting occurs at 1290 °C. Since the liquidlike phase has only short-range order, the liquidlike phase cannot have any influence on the electron diffraction essentially but leads to only attenuation of the intensity, in a similar way to the case of the noncrystalline phase. This temperature corresponds to the value (1277 °C) reported by Vandré *et al.* [10]. On the other hand, the intensity at dip ($\theta = 0.8°$) increases rapidly at temperature just below the surface melting point. Since the RHEED intensity at the lower angle is very sensitive to the outermost surface layer, this result means that the Si(111) surface shows a new surface phase in the narrow range of 1250−1270 °C. Outside this temperature range, the variation in the intensity at 0.8° is similar to that in the 333 Bragg peak.

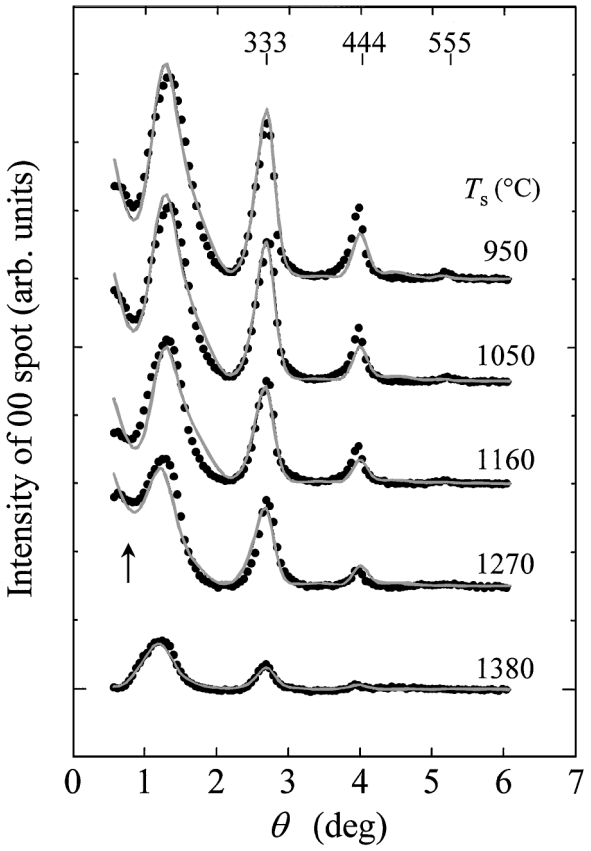


FIG. 1. RHEED rocking curves from Si(111) surface at temperature range between 950 and 1380 °C, where the surface temperature (T_s) is labeled on the right-hand side. The dotted lines show the measured curves, and the solid lines show the calculated curves determined from the optimum Debye temperature (510 K), atomic positions, and density of atoms at each position.

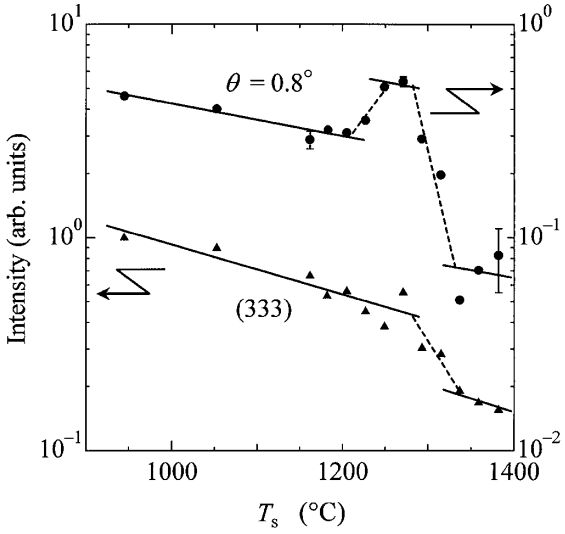


FIG. 2. Temperature dependence of the RHEED intensity. The circles and triangles indicate the intensities at the dip ($\theta = 0.8°$) and 333 Bragg peak, respectively. The error bars show the root mean square deviation.

In the dynamical calculation of RHEED intensity, first, we determined the atomic positions minimizing the R factor of the calculated curve to the measured curve at $T_s = 950$ °C by using the standard nonlinear minimization scheme [30,31]. For the surface structure at $T_s = 950$ °C, we assumed that the surface was composed of the 1×1 lattice and random adatoms, and the adatom coverage was 0.25 ML as reported by Kohmoto and Ichimiya [6]. Since the RHEED intensity under the one-beam condition is not sensitive to the atomic coordinates parallel to the surface [28], the difference in the adatom configurations between T_4 and H_3 sites does not have influence on the intensity under the condition. Therefore, we assumed that all adatoms were situated at the T_4 site. We classified the atomic positions into seven groups (Z_{1-7}) according to their situations (see Table I). The atomic coordinates below Z_7 were assumed to be the same as those of the bulk.

In the optimization of the atomic coordinates, we used the seven atomic positions for the random adatom model [6] as the initial values, although the structure model was slightly different from our model in the density (ρ) of atoms. The other fitting parameters were the effective surface Debye temperature (Θ_D) and the imaginary part of the crystal potential (U_{el}) caused by the plasmon excitation. The optimum values of these parameters were obtained following the procedure outlined in Ref. [25] and are given in Table I. The optimized value of Θ_D (510 K) is consistent with the value (440 ± 70 K) obtained below 800 °C [25]. The values of Θ_D and U_{el} optimized for the curve at 950 °C were used in the calculation for the curves throughout the whole temperature range in this study.

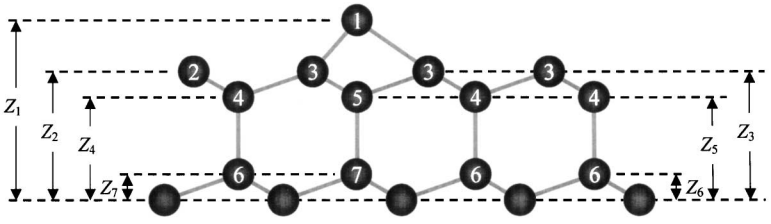
The solid lines for 950, 1050, and 1160 °C in Fig. 1 show the calculated curves using the atomic positions Z_{1-7}, optimized at 950 °C. The calculated curves coincide with the measured curves in the temperature range between 950 and 1160 °C. The temperature dependence of the experimental rocking curves is almost reproduced, and the R factors are less than 3.3%. Therefore, we conclude that the surface structure is the relaxed 1×1 lattice structure with adatoms of 0.25 ML, as shown in Table I, and is preserved in this temperature range.

At 1270 °C, the intensity enhancement at $\theta = 0.8°$ cannot be explained by the random adatom model with the coverage (ρ_{ad}) of 0.25 ML. There are two possible cases to explain it: the shift of the adatom height and the change of the adatom coverage. We calculated the curves taking account of both cases and confirmed that the effect of the adatom coverage is dominant. Figure 3 shows the variation in rocking curves with change of adatom coverage for $Z_1 = 5.36$ Å. The calculated curve for $\rho_{\mathrm{ad}} = 0.20$ ML is in very good agreement with the measured curve ($R = 3.0\%$), and the curve is also plotted by a solid line in Fig. 1. Therefore, the new phase with adatom coverage of 0.20 ± 0.01 ML is formed at $T_s = 1250-1270$ °C. The uncertainty, 0.01 ML, of the adatom coverage is estimated from the error bar in Fig. 2.

Above 1340 °C, we considered that the adatoms and the first-double layer (first- and second-layer) atoms became disordered, because the intensity dropped dramatically. Then, the RHEED intensity should give information regarding the crystalline structure below the liquidlike phase. For the curve at 1380 °C, we varied the coverages and the heights of the adatoms and the first-double layer atoms in the intensity calculation. The calculated curves for vacancy models, in which all adatoms, 20%–55% of the first-layer atoms and 0%–25% of the second-layer atoms are missing, were in good agreement with the measured one. The best agreement ($R = 3.1\%$) is obtained for the vacancy model, in which 0.65 ML of atoms in the first layer and 0.90 ML of atoms in the second layer are still ordered (see Table I).

TABLE I. Atomic coordinates (Z_i) in units of Å and the density of atoms (ρ) classified into seven groups. A schematic drawing of Si(111) surface structure at high temperature is shown in the lower part. Each number labeled in each atom corresponds to each classified group.

Layer	No. i	Situation	$T_s = 950-1160$ °C Z_i (Å)	ρ (ML)	$T_s = 1270$ °C Z_i (Å)	ρ (ML)	$T_s = 1380$ °C Z_i (Å)	ρ (ML)
Adatom layer	1	Adatoms	5.30	0.25	5.36	0.20		0.00
First layer	2	Rest atoms	4.50	0.25	4.50	0.40	3.80	0.65
	3	Atoms bounded with adatoms	3.93	0.75	3.93	0.60		0.00
Second layer	4	Atoms bounded with rest atoms	3.16	0.75	3.16	0.80	3.26	0.90
	5	Atoms just below adatoms	2.75	0.25	2.75	0.20		0.00
Third layer	6	Atoms just below atoms of $i = 4$	0.95	0.75	0.95	0.80	0.95	1.00
	7	Atoms just below atoms of $i = 5$	0.93	0.25	0.93	0.20		0.00



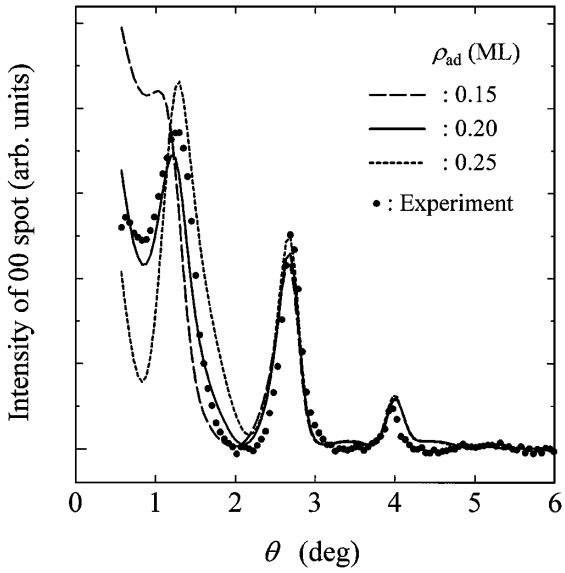


FIG. 3. Calculated rocking curves for Si(111) at 1270 °C for various adatom coverages ρ_{ad}.

The calculated curve at 1380 °C in Fig. 1 is multiplied by a factor of 0.2 because of the attenuation by the liquidlike layer. If the number density of surface atoms is kept constant in the temperature range between 1270 and 1380 °C, the density of atoms in the liquidlike layer is estimated to be about 0.65 ML (0.20 + 0.35 + 0.10 ML). This density is close to the value of 0.8 ML reported by Hibino *et al.* using MEIS [13]. It should be noted that in this case the atomic densities of No. 1, 3, 5, and 7 in Table I become zero because there is no adatom at temperature near the bulk melting point. As the surface begins to melt, the crystalline structure is replaced with vacancies and disordered atoms in a liquidlike state.

In conclusion, for the Si(111) surface, the adatom coverage on the relaxed 1×1 structure is 0.25 ML in the temperature range between 950 and 1160 °C. Around 1250 °C, the surface structure transforms to the new phase, in which the adatom coverage decreases to 0.20 ML. At 1290 °C, the further phase transition occurs on the surface, and the surface melting layers of 0.65 ML are formed above 1340 °C. The crystalline structure below the liquidlike phase is the vacancy structure, in which all adatoms, 35% of the first-layer atoms, and 10% of the second-layer atoms, are missing.

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 12650031) from Japan Society for the Promotion of Science, Takahashi Industrial and Economic Research Foundation, and the Grants in Support of the Promotion of Research at Yokohama City University.

*Corresponding author.
Electronic address: shigeta@yokohama-cu.ac.jp

[1] K. Takayanagi *et al.,* Surf. Sci. **164**, 367 (1985).
[2] J. J. Lander, Surf. Sci. **1**, 125 (1964).
[3] S. Ino, Jpn. J. Appl. Phys. **16**, 891 (1977).
[4] P. A. Bennett and M. W. Webb, Surf. Sci. **104**, 74 (1981).
[5] N. Osakabe *et al.,* Surf. Sci. **109**, 353 (1981).
[6] S. Kohmoto and A. Ichimiya, Surf. Sci. **223**, 400 (1989).
[7] A. V. Latyshev *et al.,* Surf. Sci. **254**, 90 (1991).
[8] Y.-N. Yang and E. D. Williams, Phys. Rev. Lett. **72**, 1862 (1994).
[9] U. Höfer *et al.,* Phys. Rev. B **52**, 5264 (1995).
[10] S. Vandré *et al.,* Surf. Sci. **377–379**, 283 (1997).
[11] Y. Homma *et al.,* Phys. Rev. B **55**, 10 237 (1997).
[12] G. Lange *et al.,* Phys. Rev. B **56**, 4642 (1997).
[13] H. Hibino *et al.,* Phys. Rev. B **58**, 12 587 (1998).
[14] A. Natori, T. Suzuki, and H. Yasunaga, Surf. Sci. **367**, 56 (1996).
[15] A. Ishizaka and T. Doi, Philos. Mag. Lett. **65**, 95 (1992).
[16] J. J. Harris, B. A. Joyce, and P. J. Dobson, Surf. Sci. **103**, L90 (1981).
[17] T. Sakamoto *et al.,* Appl. Phys. Lett. **47**, 617 (1985).
[18] J. Aarts and P. K. Larsen, Surf. Sci. **188**, 391 (1987).
[19] Y. Shigeta *et al.,* Surf. Sci. **402–404**, 313 (1998).
[20] Y. Fukaya, Y. Shigeta, and K. Maki, Phys. Rev. B **61**, 13 000 (2000).
[21] P. A. Maksym and J. L. Beeby, Surf. Sci. **110**, 423 (1981).
[22] A. Ichimiya, Jpn. J. Appl. Phys., Part 1 **22**, 176 (1983).
[23] T. C. Zhao, H. C. Poon, and S. Y. Tong, Phys. Rev. B **38**, 1172 (1988).
[24] G. Meyer-Ehmsen, Surf. Sci. **219**, 177 (1989).
[25] Y. Fukaya, K. Nakamura, and Y. Shigeta, J. Vac. Sci. Technol. A **18**, 968 (2000).
[26] K. Yamaguchi, H. Mitsui, and Y. Shigeta, J. Vac. Sci. Technol. A **15**, 2569 (1997); **17**, 3530 (1999).
[27] A. Ichimiya, Surf. Sci. Lett. **192**, L893 (1987).
[28] In the many beam calculation based on the dynamical theory, the rocking curve using 29 beams under the one-beam condition, under which the azimuthal angle is chosen at 7.5° from the $[11\bar{2}]$ direction, coincides with the curve using one beam. The difference is 2% in the R factor.
[29] A. Ichimiya, *The Structure of Surfaces III,* Springer Series in Surface Sciences Vol. 24 (Springer, Berlin, 1991), p. 162.
[30] D. W. Marquardt, J. Soc. Ind. Appl. Math. **11**, 431 (1963).
[31] M. R. Osborne, J. Aust. Math. Soc. B, Appl. Math. **19**, 343 (1976).