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Precise determination of surface Debye-temperature of Si(1 1 1)-7 × 7 surface by reflection high-energy positron diffraction

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Abstract

The surface Debye-temperature of the topmost surface of the Si(1 1 1)-7 × 7 has been determined by reflection high-energy positron diffraction. The positron diffraction intensity at the total reflection condition is altered by the thermal vibration amplitude of atoms only on the topmost surface because the incident positrons are not able to penetrate into the bulk in this condition. The intensity of totally reflected positrons was analyzed by means of the dynamical diffraction theory. The surface Debye-temperature was determined to be 310 ± 50 K, which is smaller than those determined in previous studies using electron diffraction. The vibration amplitude was estimated to be 0.13 Å at 293 K.
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1. Introduction

The thermal vibration of surface atoms is one of the most important issues to understand in detail aspects of the surface structure. In general, the surface atoms vibrate more intensely than the bulk atoms. The vibration amplitude becomes large with increasing temperature. The vibration amplitude plays an important role in the study on the surface phase transition. Therefore, it is very important to determine accurately the surface Debye-temperature, which is related to the thermal vibration of the surface atoms.

The bulk Debye-temperature is able to be determined by standard techniques such as X-ray diffraction [1]. On the other hand, the surface Debye-temperature can be estimated by electron diffraction techniques such as low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED) [2]. Using the electron diffraction, however, it is rather difficult to extract the surface Debye-temperature alone because the diffraction intensity is also affected by the bulk Debye-temperature.

Reflection high-energy positron diffraction (RHEPD) is a new powerful technique to study the surface structures and properties [3]. The experimental setup of the RHEPD resembles the RHEED method. Although it is very difficult to generate the

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high quality positron beam, the positron diffraction has a great advantage that is very sensitive to the topmost surface due to the occurrence of the total reflection below a critical angle [4]. The penetration depth of the incident positron in the total reflection region is extremely small, i.e., typically one to two monolayers. Therefore, the diffraction intensity gives knowledge of only the topmost surface. In 1998, we succeeded in fabricating the high-energy positron beam with an adequate quality to observe a diffraction pattern from the crystal surface [3]. Using the RHEPD apparatus, we have reported the surface structures of the SiC(0 0 0 1) [5] and hydrogen-terminated Si(1 1 1) [6]. Recently, we succeeded in the observation of the first-Laue zone spots and the fractional-order spots for the Si(1 1 1)-7 × 7 surface [7,8]. Then from the rocking curve analysis [8] and the RHEPD pattern [9] we have shown that the RHEPD is very useful to determine the adatom height accurately. It is proposed that using RHEPD the surface Debye-temperature can be determined accurately with a minimum influence from the bulk [4].

In this work, we measured the temperature dependence of the RHEPD intensity from a Si(1 1 1)-7 × 7 surface in the total reflection mode. Analyzing the measured intensities with the dynamical diffraction theory, we succeeded in determining the accurate surface Debye-temperature of the Si(1 1 1)-7 × 7 surface for the first time.

2. Experimental procedure

We used a mirror-polished n-type Si(1 1 1) wafer (1–10 Ω cm) as a sample (0.5 mm × 5 mm × 15 mm). The clean 7 × 7 reconstructed Si(1 1 1) surface was obtained by flashing the sample at 1250 °C for 30 s after the preheating at 400 °C for a few hours by passing a direct current in a UHV (<1 × 10^{-7} Pa) chamber. The clear 7 × 7 patterns were confirmed by the RHEED.

A 20 keV positron beam was generated with a ^{22}Na positron source and electrostatic lens system. The details of the experimental setup were described elsewhere [10,11]. Azimuthal angles of the incident beam were set at 1.5° and 7.5° away from the [1 1 $\bar{2}$] direction. The latter case is called the one-beam condition, where the RHEPD intensity is not sensitive to the

lateral coordinates of the atomic positions and hence depends on the surface normal component [12]. The RHEPD patterns enhanced by a micro channel plate were observed with a CCD camera. The integrated intensity was obtained from the RHEPD pattern stored in a personal computer. The glancing angle (θ) was adjusted by a pulse motor mounted to the sample manipulator. The sample temperature was calibrated with an infrared radiation thermometer.

3. Results and discussion

After the sample flashing, the RHEPD patterns exhibited the 7 × 7 reconstruction [8,9]. The (0 0) and (1 1) spot intensities from the Si(1 1 1)-7 × 7 surface in the temperature range from 293 to 1073 K at the glancing angles of 1.0° and 3.5° are shown in Fig. 1. Since the mean inner potential and the positron energies are 12 eV [12] and 20 keV, respectively, the critical angle for the total reflection is estimated to be 1.4° [4]. Thus, $\theta = 1.0°$ satisfies the total reflection condition. The latter glancing angle satisfies the
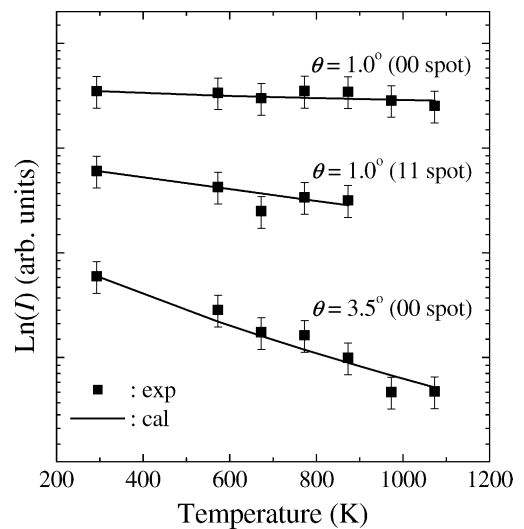

Fig. 1. Temperature dependence of the RHEPD intensities (I) from a Si(1 1 1)-7 × 7 surface. Filled squares indicate the measured intensities of (0 0) spots at $\theta = 1.0°$ (upper) and 3.5° (lower) and (1 1) spot at $\theta = 1.0°$ (middle). The (0 0) spot intensities were measured under the one-beam condition. The (1 1) spot intensity was measured at 1.5° away from the [1 1 $\bar{2}$] direction. Solid lines show the calculated intensities using the optimum Debye-temperatures ($\Theta_S = 310$ K and $\Theta_B = 630$ K).

(4 4 4) Bragg reflection. Both the (0 0) and (1 1) spot intensities at $\theta = 1.0°$ gradually decrease with increasing temperature. On the other hand, the (0 0) spot intensity at $\theta = 3.5°$, which is outside the total reflection region, drastically decreases with increasing temperature in comparison with the intensities at $\theta = 1.0°$.

The attenuation of the RHEPD intensity due to the increase in the temperature results from the thermal vibration of the atoms. The slope of the intensity change becomes large with increasing θ because the magnitude of the scattering vector in the Debye–Waller factor increases. The thermal vibration gives rise to the temperature dependence of the diffraction intensity through the Debye-temperature. The Debye-temperature (Θ) is composed of the terms from the surface (Θ_S) and the bulk (Θ_B). In general, the Θ_S is smaller than the Θ_B because the thermal vibration amplitude of the surface atoms is larger than that of the bulk atoms. Since the incident positron in the total reflection region hardly penetrates into the bulk, the temperature dependence of the RHEPD intensity at $\theta = 1.0°$ may be closely related to the thermal vibration of the topmost atoms. On the other hand, when the glancing angle is beyond the critical angle of the total reflection, the effect of the thermal vibration of the topmost surface atoms on the RHEPD intensity trends toward diminishing since the incident positron penetrates into the bulk. Therefore, the temperature variation of the RHEPD intensity at high glancing angles gives the bulk Debye-temperature.

To determine the Debye-temperature from the temperature dependent RHEPD intensity, we calculated the RHEPD intensities at various temperatures based on the dynamical diffraction theory.[1] The calculated RHEPD intensities of the (0 0) spots and the (1 1) spot from the Si(1 1 1)-7 × 7 surface as a function of temperature are shown in Fig. 2. The surface Debye-temperature was fixed at 300 K. The bulk Debye-temperature was changed from 300 to
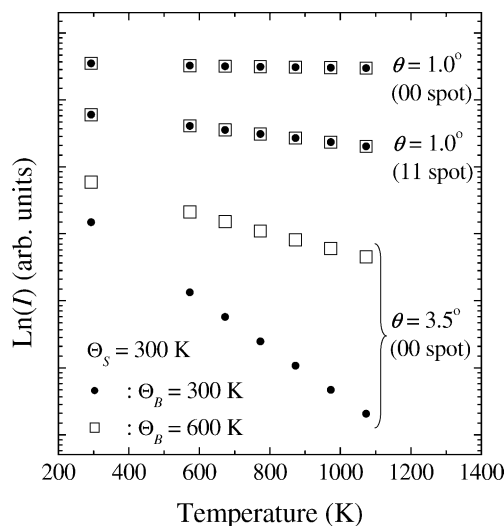

Fig. 2. Typical example of the calculated RHEPD intensities (*I*) of (0 0) and (1 1) spots from the Si(1 1 1)-7 × 7 surface as a function of temperature. The incident condition used in the calculation was the same as the experimental one in Fig. 1. Filled circles and open squares indicate the calculated intensities using the bulk Debye-temperature of 300 and 600 K, respectively, with fixing the surface Debye-temperature to be 300 K.

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600 K. It should be noted that in the total reflection region the calculated temperature dependence of the (0 0) and (1 1) spot intensities at $\theta = 1.0°$ are not affected by the bulk Debye-temperature [4]. This means that the incident positrons are not able to penetrate into the bulk. On the contrary, the temperature dependence, i.e., the slope, of the (0 0) spot intensity at $\theta = 3.5°$ dramatically changes when the bulk Debye-temperature was varied from 300 to 600 K. This is because of the relatively deep penetration of positrons at high glancing angles. Thus, the bulk Debye-temperature can be determined from the temperature dependence of the RHEPD intensity over the total reflection region.

At $\theta = 1.0°$, the temperature dependences of the spot intensities were calculated with varying Θ_S and fixing Θ_B to be 580 K [1] so as to reproduce the experimental results in Fig. 1. The variation of the reliability factor (*R*) depending on Θ_S is shown in Fig. 3(a). There is a minimum of the *R* for the (0 0) spot at $\theta = 1.0°$ around 300 K although the change in the *R* is very small in comparison with the (1 1) spot intensity. This is because the magnitude of the scattering vector in the Debye–Waller factor for

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[1] We calculated the RHEPD intensity based on the dynamical diffraction theory developed by Ichimiya [13] taking account of the absorptions due to the electronic excitation [14] and thermal diffuse scattering [15]. We used the atomic positions of the Si(1 1 1)-7 × 7 surface determined from a theoretical calculation of Brommer et al. [16].
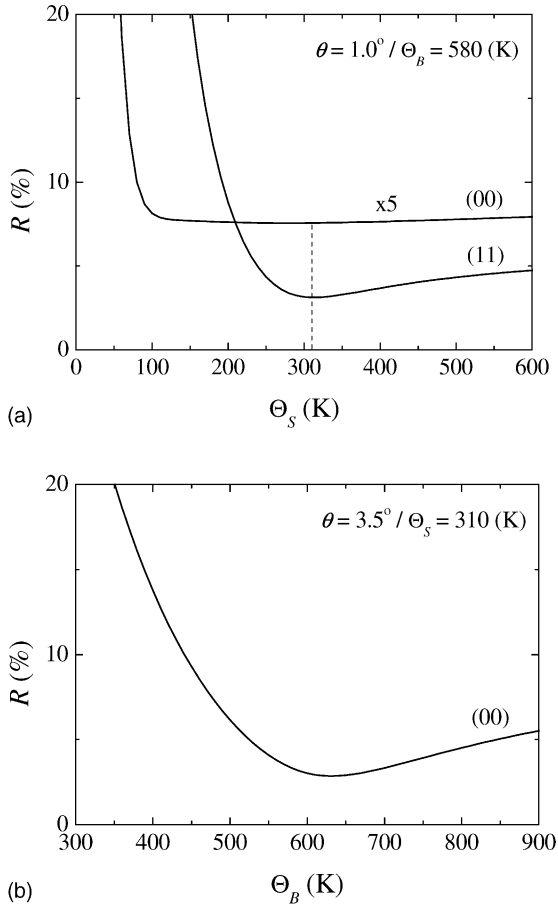
Fig. 3. (a) Reliability factor (R) as a function of the surface Debye-temperature (Θ_S). The R defined in Ref. [2] was calculated from the (0 0) and (1 1) spot intensities at $\theta = 1.0°$, (b) the R, which was calculated from the (0 0) spot intensity at $\theta = 3.5°$, as a function of the bulk Debye-temperature (Θ_B).

the (0 0) spot at $\theta = 1.0°$ is small. From the minimum of the R, we obtain $\Theta_S = 310 \pm 50$ K. Similar to the above, at $\theta = 3.5°$, the temperature dependences of the spot intensity was calculated with varying Θ_B and fixing Θ_S to be 310 K. Then, we obtain $\Theta_B = 630$ K, as shown in Fig. 3(b). The solid lines in Fig. 1 (denoted as cal) well reproduce the experimental result.

The surface Debye-temperature of 310 K is much smaller than the bulk Debye-temperature. The vibrational amplitude ($=\sqrt{\langle u^2 \rangle}$) is calculated to be 0.13 Å at room temperature. For the Si(1 1 1)-7 × 7 surface, the adatom is situated at the topmost surface [17]. The

RHEPD mainly detects the thermal vibration of the adatoms, as mentioned above. In previous RHEED studies, the surface Debye-temperature was determined to be 420 K and hence $\sqrt{\langle u^2 \rangle} = 0.10$ Å [2]. This is probably the intermediate value between the surface Debye-temperature (310 K) and the bulk Debye-temperature (630 K) determined above. This means that the incident electrons see some extent of the surface region and the intensity change of the electron diffraction provides the averaged information about the thermal vibration amplitude of the surface atoms. On the contrary, in the RHEPD experiment, the surface Debye-temperature of the topmost atoms is well-separated from the bulk Debye-temperature. Consequently, the surface Debye-temperature of adatoms on the Si(1 1 1)-7 × 7 surface determined above is more accurate than that evaluated by the electron diffraction. The adatoms on the Si(1 1 1)-7 × 7 surface vibrate more intensely than expected before, i.e., the real vibration amplitude of adatoms is 30% greater than that predicted before [2]. The Debye-temperature of 630 K is compatible with that of the bulk (505–658 K) [1]. This agreement also assures the reliability of the determination of the surface Debye-temperature with the RHEPD.

4. Summary

In summary, we have studied the temperature dependence of the RHEPD intensity from the Si(1 1 1)-7 × 7 surface. We determined the surface Debye-temperature associated with the adatoms to be 310 K without any contributions from the bulk, for the first time. It is pointed out that the real surface Debye-temperature is lower than that estimated by the electron diffraction. That is, the topmost surface atoms vibrate more intensely than that expected before. The RHEPD enables us to determine the topmost surface Debye-temperature accurately.

Acknowledgements

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