Structural phase transition and thermal vibration of surface atoms studied by reflection high-energy electron diffraction

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Abstract

We have developed a new system for reflection high-energy electron diffraction (RHEED) with two pairs of magnetic coils to measure rocking curves in a short time. Since the measurement time of the system is short and the intensity measurement is very accurate compared with mechanical angle adjustment systems currently in use, this system is the most suitable tool to determine structural phase transitions at high temperatures. For the Si(1 1 1) surface, we have discovered an additional phase just below the melting temperature, in which the thermal vibration of surface atoms is strongly enhanced. For the Si(0 0 1) surface, the asymmetric dimer structure, which is believed to be the most stable at low temperature, transforms into the symmetric dimer structure, as confirmed by comparison with a rocking curve from a hydrogen-terminated Si(0 0 1) 2 × 1 surface.

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1. Introduction

Reflection high-energy electron diffraction (RHEED) is widely used to determine atomic scale surface structures. A scanning tunneling microscope (STM) is also very useful to study the surface structures, but the STM only yields information on the uppermost surface layers. On the other hand, RHEED provides the details of surface structure within a few layers, although the information is the mean value in the electron beam spot.

When we observe the specular spot at a certain glancing angle during epitaxial growth, the intensity shows an oscillation, whose periodicity corresponds to the growth time of one layer. The RHEED intensity oscillation is widely used to monitor thin film growth [1–6]. When we measure the intensity of each spot as a function of glancing angle (θ), we can obtain detailed information about the atomic position up to a few layers underneath the surface [7–10]. The intensity change with θ is called “RHEED rocking-curve (RC)” and widely used to determine surface structure.
To determine dynamical structure changes, we used a RHEED system with two pairs of magnetic coils to measure the rocking curves on short time scales. By using the system, we succeeded in the study of dynamic structure change during epitaxial growth of Si/Si(1 1 1) [11]. This system is also useful to study surface structure under extreme conditions such as a high temperature near the melting point, because of the short measurement times. To analyze the surface structure at high temperature, we should include the temperature dependence of the scattering potential for high-energy electrons [12]. In this way the temperature dependence of the RHEED intensity for Si(1 1 1) surface has been determined [13,14].

In this paper, we describe the imaginary potential due to thermal diffuse scattering and two examples applied to study structural phase transitions: (1) On the Si(1 1 1) surface, we observed an additional surface phase just below the surface melting point [15], where the thermal vibration amplitude parallel to the surface is strongly enhanced [16]. (2) On the Si(0 0 1) surface, we observed a structural phase transition from the asymmetric dimer into the symmetric dimer structure, which causes a metallic behavior above 900 K [17]. In addition to these two examples, we will provide evidence of the phase transition by comparison with results for the hydrogen-terminated Si(0 0 1) 2 × 1 surface, on which the symmetric dimers are formed.

2. RHEED apparatus with magnetic deflector

For a rapid observation of rocking curves, we built a RHEED apparatus with a magnetic deflector composed of two pairs of magnetic coils, as sketched in Fig. 1. We can change the glancing angle, θ, of the high-energy electrons within an accuracy of 0.01° by computer control of the currents flowing through these magnetic coils. We obtained a well-focused electron beam in the glancing angle range 0°–6°. This range is enough to observe the rocking curve from the Si(1 1 1) surface, because the 333, 444, and 555 Bragg reflections of the Si(1 1 1) plane can be covered [13,14].

We accelerated the incident electron at 10 kV (E = 10 keV) and the angle θ was increased from 0.5° to 6° at steps of 0.05°. The RHEED pattern was measured by a TV camera and recorded on a laser video disk at each step by the computer control system. The recording time of a whole RHEED pattern (1 1 0 images) is about 18 s because the recording time of the laser videodisk for one image is 1/6 s. After the measurement, the integrated intensity of the specular reflection within the angle region of ±0.5° at each glancing

![Fig. 1. Schematic drawing of RHEED apparatus with a magnetic deflector composed of two pairs of magnetic coils. The glancing angle is controlled within an accuracy of 0.01°.](image-url)
angle was obtained from the recorded patterns through a frame memory.

3. RHEED RC under the one beam condition

Before a detailed description of the temperature dependence, we define a diffraction condition of RHEED. Fig. 2(a) shows RHEED RCs of the specular beam at the [1 1 2] azimuth of the Si(1 1 1) 7 x 7 surface, where the dotted line shows a measured curve and solid lines are calculated curves based on many-beam dynamical theory [8]. The number of beams used in the dynamical calculation is shown on the right-hand side. The positions of the 3 3 3, 4 4 4, and 5 5 5 Bragg peaks expected by the kinematical calculation are $\theta = 2.7^\circ$, $4.0^\circ$, and $5.2^\circ$, as indicated at the top of this figure.

The Bragg peaks calculated by using one-beam appears at those Bragg positions. However, under this condition along the [1 1 2] azimuth, where the electron beam excites some intense diffracted beams simultaneously, the position of each peak in the measured RC does not coincide with that of the Bragg peak predicted by the kinematical calculation. We can reproduce the peak shift in the calculated curve by two additional beams, as indicated by three-beams in Fig. 2(a). With the increase in the number of beams in the calculation, the calculated curve reproduces a more detailed structure in the measured curve: The calculated curve for 29 beams shows an additional weak structure in $\theta = 4^\circ$–$5^\circ$, which appears in the measured curve. Therefore the effect of simultaneous reflection can be simulated by the many-beam calculation, with great precision.

Fig. 2(b) shows RHEED RCs, when the azimuth angle of the incident beam was set at 7.5$^\circ$ rotated from the [1 1 2] toward [1 0 0]. Under this asymmetric condition, the simultaneous reflections are suppressed and the measured curve (dotted line) is sufficiently described by a calculated curve using only one-beam. Therefore, this condition is called “one-beam condition” and the RHEED RC reflects the information about the normal component ($Z_i$) of atomic positions and the number density ($\rho$) of atoms at $Z_i$ [18]. In this paper, we will describe the experimental results under the one-beam condition with corresponding results by the one-beam calculation.

To perform a quantitative evaluation, we define the reliability-factor ($R$) to compare between the measured and calculated curves as follows:

$$R = \sqrt{\frac{\sum_\theta (\alpha I_{\theta}^{\text{cal}} - I_{\theta}^{\text{exp}})^2}{\sum_\theta I_{\theta}^{\text{exp}}} \times 100 \%},$$

where $I_{\theta}^{\text{exp}}$ and $I_{\theta}^{\text{cal}}$ denote the measured and calculated intensities at the glancing angle ($\theta$), respectively.

4. Imaginary potential including an anisotropy in the thermal vibration

When we use the RHEED rocking curve to analyze the structures on a surface at different temperatures,
we need to clarify the temperature dependence of the RHEED RC from the surface caused by the thermal vibration of surface atoms. The effect of the thermal vibration will be included in the real and imaginary part of the crystal potential [12], where the Fourier component of the imaginary part of the crystal potential arising from the thermal motion (the so-called TDS scattering) is represented by five Gaussian exponential terms.

According to the method proposed by Dudarev et al. [12], if the amplitude of the Debye parameter \(B\) at a temperature \(T\) is given, the Fourier components of the real and imaginary potential at \(T\) can be represented by a set of Gaussian exponential terms which is a similar representation of the real part of the crystal potential tabulated by Doyle and Turner [19]. The crystal potential \(U(r)\), including the isotropic thermal vibration, is expressed by

\[
U(r) = -\frac{2\pi \hbar^2}{m_0} \sum_a \sum_{n=1}^N a_n^{(\text{Re})} \left( \frac{4\pi}{b_n^{(\text{Re})} + B} \right)^{3/2} \exp \left[ -4\pi^2 \frac{(r - R_a)^2}{(b_n^{(\text{Re})} + B)} \right]
\]

\[
+ i \frac{2\pi \hbar^2}{m_0} \sum_a \sum_{n=1}^N a_n^{(\text{TDS})} \left( \frac{4\pi}{b_n^{(\text{TDS})} + (B/2)} \right)^{3/2} \exp \left[ -4\pi^2 \frac{(r - R_a)^2}{(b_n^{(\text{TDS})} + (B/2))} \right],
\]

where \(\hbar\) is Planck’s constant, \(m_0\) is the electron rest mass and \(R_a\) denotes the equilibrium position of the \(a\)-th atom. The coefficients of \(\{a_n\}, \{b_n\}, \{a_n^{(\text{TDS})}\}\) and \(\{b_n^{(\text{TDS})}\}\) are numerically obtained from the amount of \(B\) and the form factor for elastic scattering \(f^e_s(s)\) of the \(a\)-th atom.

Since \(B\) is proportional to the mean square of the amplitude of the thermal vibration \((B = 8\pi^2 \langle u^2 \rangle)\), we applied the Einstein model [20] to express the temperature dependence of \(B\),

\[
B = \frac{8\pi^2 \hbar^2}{k_B M_a \Theta_E} \left\{ \frac{1}{\exp(\Theta_E/T) - 1} + \frac{1}{2} \right\},
\]

where \(k_B\) is Boltzmann’s constant, \(M_a\) is the mass of the \(a\)-th atom and \(\Theta_E\) is the Einstein temperature which relates to the Debye temperature (\(\Theta_D\), \(\Theta_E = \Theta_D \sqrt{3}\)).

For the anisotropic thermal vibration, we assumed that there is no coupling between the parallel and normal components of the thermal vibration to the surface and the parallel component is isotropic in the surface plane. Then, the Debye–Waller factor may be approximate by:

\[
W(s) = \exp[-(B || s^2 + B \perp s^\perp)],
\]

where \(B || = 8\pi^2 \langle u^2 \rangle \) and \(B \perp = 8\pi^2 \langle u^\perp \rangle\). \(\langle u^2 \rangle\) and \(\langle u^\perp \rangle\) are the parallel and normal components of the mean square displacement of the thermal vibration amplitude, respectively. \(s ||\) and \(s \perp\) are the parallel and normal components of the scattering vector. Then the crystal potential \(U(r)\) including the anisotropic thermal vibration is also expressed in a similar way [16], which includes \(B ||\) and \(B \perp\) as parameters. Using this formulation, we can analyze the data showing anisotropic thermal vibration behavior.

5. Application of the RHEED RC to study of phase transition

5.1. Phase transition and surface melting on Si(1 1 1) at high temperature [15, 16]

At temperatures higher than about 900 °C, the Si(1 1 1) surface structure is transformed from the 7 × 7-DAS to the so-called “1 × 1” structure [21–24]. The “1 × 1” surface has been established to be a relaxed bulk-like structure with random adatoms of 0.20–0.25 ML (1 ML = 7.8 × 10^14 cm^-2) evaluated by using RHEED [25], ellipsometry [26], STM [27], and optical second-harmonic generation (SHG) [28].

The dotted lines in Fig. 3 show the measured RHEED RC from the Si(1 1 1) surface above 950 °C under the one-beam condition [15, 16]. These rocking curves at \(T = 950–1160\) °C do not show any significant change except for the decrease in intensity due to the enhancement of thermal diffuse scattering. Therefore, it is considered that surface structure is preserved in this temperature range. These RHEED RCs can be represented by the one-beam calculation drawn by solid lines, where we assume that (1) the optimized value of \(\Theta_D\) is 240 °C, (2) the surface is composed of the 1 × 1 lattice and random adatoms, and (3) the adatom coverage (\(\rho_{ad}\)) is 0.25 ML as
reported by Kohmoto and Ichimiya [25]. The optimized value of \( Q_D (240 \pm 8^\circ C) \) is consistent with the value \( (170 \pm 8^\circ C) \) obtained below the \( 7 \times 7 \rightarrow 1 \times 1 \) phase transition [14].

At \( 1270^\circ C \), however, the intensity around 0.8\(^\circ\) is much larger than that at 950–1160 \(^\circ\)C, as indicated by an arrow. The intensity changes at \( \theta = 0.8^\circ \) and 3 3 3 Bragg peak are plotted, as a function of \( T \), in Fig. 4. The intensity at \( \theta = 0.8^\circ \) jumps up at 1270 \(^\circ\)C. The change cannot be explained by the existence of the surface melting because the intensity of the Bragg peaks (3 3 3, 4 4 4, and 5 5 5) does not show any drastic change. The increase of the intensities at \( \theta = 0.8^\circ \) is associated with the appearance of a new phase different from the surface melting. The surface structure of the additional phase is explained in terms of a decrease of adatom coverage. The calculated curve for \( \rho_{ad} = 0.20 \) ML is in very good agreement with the measured curve \( (R = 3.0\%) \), as plotted by a solid line in Fig. 3. The additional phase with adatom coverage of 0.20 \( \pm 0.01 \) ML is formed at \( T_s = 1250–1280^\circ \)C.

Above 1290 \(^\circ\)C, the intensities in the entire range of glancing angle \( (0.5^\circ < \theta < 6^\circ) \) drop abruptly compared with those at temperatures below 1270 K 1270 \(^\circ\)C, as shown in Fig. 3. The intensity of the 3 3 3 Bragg peak on a logarithmic scale decreases proportionally with an increase in \( T \) below 1280 \(^\circ\)C as shown in Fig. 4. The abrupt decrease of the Bragg peak intensity above 1290 \(^\circ\)C shows that the surface melting occurs at 1290 \(^\circ\)C, because this drastic decrease cannot be explained by the enhancement of the thermal diffuse scattering effect with elevated temperature.

In the additional phase, we also found an abnormal enhancement of thermal vibration amplitudes [16] in addition to the decrease of adatom coverage. Fig. 5 shows the mean square amplitude of the thermal vibration of the adatoms and the first-double layer atoms as a function of temperature. The parallel and normal components of the amplitudes to the surface are evaluated from measurements of RHEED RCs for the [1 1 2] and [1 1 0] azimuths, in which the temperature dependencies in two azimuths are completely different, reflecting the anisotropic feature of thermal vibration. The parallel component is about three times larger than the normal component, and both components are enhanced with the phase transition. The enhancement of the thermal vibration is directly related to the decrease of adatom density, because the adatom binds with three surface atoms in the first layer.

5.2. Transition from asymmetric to symmetric dimer structure on the Si(0 0 1) surface at high temperature

It is now well known that the outermost atoms on Si(0 0 1) form dimers in order to reduce the surface
energy. The dimers theoretically prefer to tilt instead of adopting a parallel configuration to the surface [29]. At low temperatures, the c4 × 2 (or p2 × 2) structure composed of tilted (asymmetric) dimers is very stable [30–33]. When the temperature is higher than −70 °C, the dimer atoms are thermally flipping in a double potential well separated by an energy barrier of 0.1 eV [34]. At higher temperature, it has been reported that the dimer structure breaks up at 1210 °C [35,36], and photoemission spectroscopy (PES) studies suggest that the surface melting occurs at 1340 °C [36].

We measured the RHEED RCs in the temperature range from RT to 1390 °C. The intensity in the RC seems to decrease with the increase in temperature, gradually. However, around 600 °C, the RCs show clear changes as shown in Fig. 6, where the RHEED intensity at low glancing angle drastically increases [17]. Such an intensity change is also observed at the 0 0 4 Bragg spot around 600 °C as shown in Fig. 7. The Bragg peak drastically decreases with the increase in temperature up to 500 °C. However, the Bragg peak increases in the temperature range from 500 °C to 700 °C, which indicates a structural phase transition. The slope of the intensity change above 700 °C is smaller than that below 500 °C. The gentle slope from 700 °C to 1060 °C means high ΘD compared with the steep slope below 500 °C (low ΘD). The drastic decrease in the intensity over 1170 °C clearly shows an evidence of surface melting [36].

To determine the structure change around 600 °C, we optimized the surface structure by comparison between calculated and measured RHEED RCs. The optimized atomic coordinates (Z) are shown in Table 1, and the calculated RCs for the 500 °C and 700 °C are plotted in Fig. 6 by dotted and solid lines, respectively. From the atomic coordinates, we can judge that the dimer structure at 500 °C is asymmetric but the structure shifts to the symmetric dimer at 700 °C.
To confirm this transition, we also measured the hydrogen terminated Si(0 0 1) 2 × 1 surface, on which the symmetric dimer is formed [37]. Fig. 8 shows the RHEED RCs for the Si(0 0 1) 2 × 1-H and the clean Si(0 0 1) 2 × 1 surfaces at 500 °C. The intensity below

1° has increased for the Si(0 0 1) 2 × 1-H composed of symmetric dimmers, which corresponds to the change in the RCs from 500 °C and 700 °C on the clean surfaces. The fact is also confirmed by the atomic coordinates for the Si(0 0 1) 2 × 1-H determined by using X-ray diffraction [37] as shown in Table 1. The atomic coordinates for the Si(0 0 1) 2 × 1-H coincide with that for the clean surface at 700 °C forming symmetric dimer structure.

The change in the 0 0 4 Bragg peak above 700 °C showing high ΘD originates from the structure transition, because the flip-flop vibration of dimer atoms in the double-well potential (asymmetric dimer) transforms into a vibration in the single well potential (symmetric dimer), which reduces the thermal vibration amplitudes of the dimer atoms.

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