

## Order-disorder phase transition of Sn/Ge(111) surface studied by reflection high-energy positron diffraction \*

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We investigated the phase transition from a  $3 \times 3$  to  $\sqrt{3} \times \sqrt{3}$  structure on the Sn/Ge(111) surface at 220 K using a reflection high-energy positron diffraction. We measured the rocking curves at 110 K and 293 K under the one-beam condition and along the  $[11\bar{2}]$  and  $[10\bar{1}]$  directions. There are no significant changes in the rocking curves at any conditions according to the phase transition. The curves at both temperatures can be explained by 'one-up and two-down' model for Sn atoms. The result clearly indicates the order-disorder phase transition. [DOI: 10.1380/ejsnt.2006.435]

Keywords: order-disorder phase transition; reflection high-energy positron diffraction; Tin; Germanium

### I. INTRODUCTION

When 1/3 monolayer (ML) of Sn atoms are deposited on a clean Ge(111)- $c2 \times 8$  surface at around 500 K, the Sn atoms are adsorbed at  $T_4$  site on the bulk-truncated Ge(111) surface (see Fig. 1). Below 220 K, the surface shows a  $3 \times 3$  periodicity [1, 2]. Two different models have been reported for the  $3 \times 3$  structure. One is that one Sn atom is higher than the other two atoms in an unit cell (so-called 'one-up and two-down', 1U2D), as shown in Fig. 1(b) [3]. The other is that two atoms is higher than one atom (so-called 'two-up and one-down', 2U1D), as shown in Fig. 1(c) [4]. Recently, we found that the 1U2D model is responsible for the Sn/Ge(111)- $3 \times 3$  at 110 K [5]. The 1U2D model was supported by density functional theory (DFT) calculations [6].

The Sn/Ge(111) surface undergoes the phase transition from the  $3 \times 3$  to  $\sqrt{3} \times \sqrt{3}$  structure [1, 2]. The surface structure of the  $\sqrt{3} \times \sqrt{3}$  phase is still controversial. At room temperature, two different models, i.e., the thermally fluctuated rippled structure (Fig. 1(d)) [7] and the flat structure where Sn atoms do not rumple (Fig. 1(e)) [8], are tentatively considered. Thus, if the model (d) is the structure at room temperature, the phase transition is described as an order-disorder type [7, 9–11]. In the case of model (e), the phase transition is a displacive type [3, 8].

In this study, we used a reflection high-energy positron diffraction (RHEPD) to investigate the surface structures and phase transition for the Sn/Ge(111) surface. The RHEPD technique is appropriate for the study of the top-most surface structures and thermal vibrations because

the total reflection occurs below a critical angle [12, 13]. At the total reflection condition, the incident positrons are not able to penetrate into the bulk region and hence the

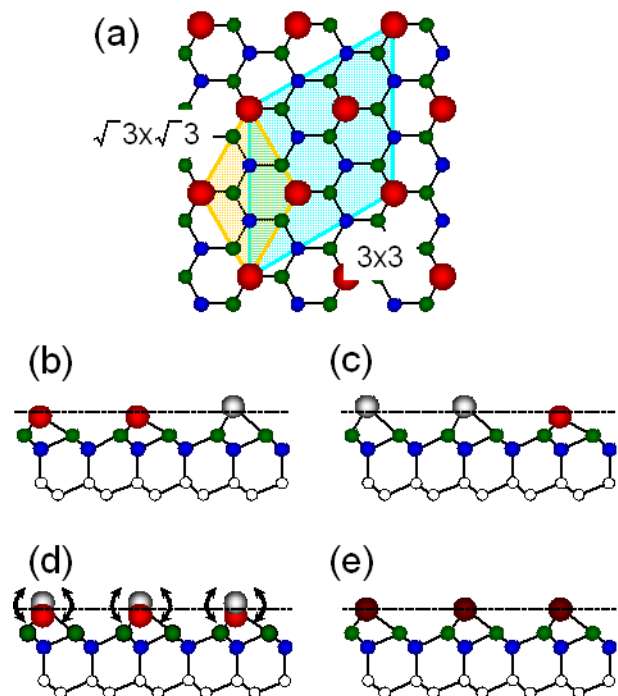


FIG. 1: (a) Plane view of the structure models of Sn/Ge(111) surface. Sn atoms denoted as large red circles are situated at  $T_4$  sites. Blue and yellow regions indicate unit cells of the  $3 \times 3$  and  $\sqrt{3} \times \sqrt{3}$  structures, respectively. Cross-sectional view of proposed models for the  $3 \times 3$  and  $\sqrt{3} \times \sqrt{3}$  phases; (b) one Sn atom is higher than the others ('one-up and two-down', 1U2D model), (c) two Sn atoms are higher than the other ('two-up and one-down', 2U1D model), (d) the Sn atoms thermally fluctuate between two different positions within 1U2D or 2U1D model (thermal fluctuation model), and (e) the heights of all the Sn atoms are the same (flat model).

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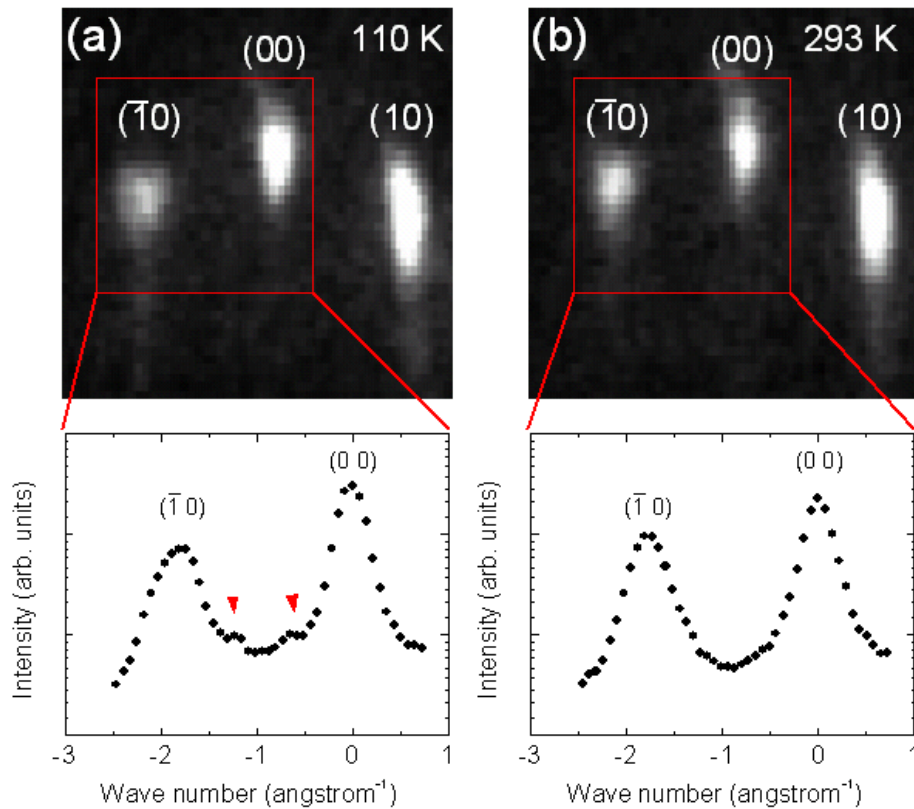


FIG. 2: RHEPD patterns from the Sn/Ge(111) surface (a) at 110 K and (b) at 293 K (upper panels). The incident azimuth corresponds to the  $[10\bar{1}]$  direction. The glancing angle is  $3.5^\circ$ . The line scans integrated over the region denoted as red square were plotted (lower panels). Red arrowheads indicate the  $3 \times 3$  spots.

diffracted intensities are very sensitive to the coordinates and vibration amplitudes of the topmost atoms [14, 15]. To study the change in the atomic positions according to the phase transitions at 220 K, we measured the rocking curves of the RHEPD intensities at 110 K and 293 K. We also performed the intensity simulations based on the dynamical diffraction theory. We will show an experimental evidence of the order-disorder phase transition.

## II. EXPERIMENTAL PROCEDURE

Samples ( $15 \times 5 \times 0.5 \text{ mm}^3$ ) were cut from a *n*-type mirror-polished Ge(111) wafer ( $\sim 35 \text{ } \Omega\text{cm}$ ). They were cleaned by several cycles of  $\text{Ar}^+$  sputtering and annealing at 1000 K in 10 min until a sharp  $c2 \times 8$  pattern appears in a reflection high-energy electron diffraction (RHEED). Keeping the temperature at 500 K,  $1/3$  ML of Sn atoms were deposited on the Ge(111)- $c2 \times 8$  surface. Amount of 1 ML corresponds to  $7.2 \times 10^{14} \text{ cm}^{-2}$ . RHEPD experiments were carried out in an ultra-high vacuum chamber equipped with a positron beam apparatus [16]. The energy of the incident positron beam was set at 10 keV. The glancing angle ( $\theta$ ) was varied up to  $6^\circ$  at a step of  $0.1^\circ$  by rotating the sample holder. The incident azimuths were set at  $7.5^\circ$  away from the  $[11\bar{2}]$  direction, the  $[11\bar{2}]$ , and the  $[10\bar{1}]$  directions. The first is called one-beam condition [17], under which the diffraction intensities depend on only the surface-normal components of atomic positions.

## III. RESULTS AND DISCUSSION

Figure 2(a) and 2(b) show RHEPD patterns from the Sn/Ge(111) surface at 110 K and 293 K. The incident azimuth corresponds to the  $[10\bar{1}]$  direction. In the RHEPD pattern, the integer-order spots of (00), (10), and  $(\bar{1}0)$  are clearly seen. As shown in the lower panels of Fig. 2, at 110 K, the fractional-order spots resulting from the formation of the  $3 \times 3$  phase are observable although the intensities are very weak as compared with the (00) spot intensity. The intensity ratio in the observation was confirmed by the intensity calculation. At 293 K, however, the fractional-order spots disappear. These fractional-order spots were also confirmed by the RHEED observations. When the temperature is higher than about 220 K, the  $3 \times 3$  spots disappear. The change in the pattern clearly indicates that a certain kind of the phase transition from the  $3 \times 3$  and  $\sqrt{3} \times \sqrt{3}$  structure takes place.

Figure 3(a) shows the rocking curves under the one-beam condition at 110 K and 293 K, respectively. In the total reflection region of  $\theta < 2.2^\circ$  [18], the specular intensity is high and a dip is clearly observed. The position of the dip and the curve shape are dominated by the atomic position and the potential regarding topmost adatoms [5]. These do not change from 110 K to 293 K. Similarly, the other peak positions and heights are also almost the same at both temperatures. Thus, although the diffraction patterns are different from each other, the rocking curves are almost the same. This indicates that the equilibrium po-

sitions of Sn surface atoms do not change according to the temperature variance. Moreover, this result also suggests that the ratio of the occupation probabilities of up- to down-Sn atoms is close to 1 to 2 above the phase transition temperature. That is, Sn atoms surrounding an up-Sn atom show a tendency to be situated at down-site. The suggestion is supported by molecular-dynamics simulations [9]. It should be noted that the configuration of the up-Sn atoms does not have a long range order of the  $3 \times 3$  periodicity above the phase transition temperature. Thus, it is considered that in the relatively wide region the ratio becomes almost 1:2. The rocking curves along the  $[11\bar{2}]$  and  $[10\bar{1}]$  azimuths also do not change with temperature. As shown in Fig. 3(b), the curves do not show any drastic changes not only for the integer-order spots but also for the fractional-order spots such as  $(\bar{1}/3 \ \bar{1}/3)$  and  $(1/3 \ 1/3)$  due to the phase transition. Furthermore, the rocking curves do not show any significant changes not only for the specular spot but also for the integer-order spots such as  $(\bar{1}0)$  and  $(10)$  according to the temperature, as shown in Fig. 3(c). Therefore, it is concluded that there are also no changes in the surface-parallel components of the atomic positions above and below the phase transition temperature. The phase transition is order-disorder type and the surface structures at low and high temperatures are in the ordered and disordered states, respectively.

To investigate the effect of the disordering of the Sn atoms on the RHEPD intensities, we calculated the rocking curves based on the dynamical diffraction theory [15, 19]. For the ordered state the surface structure used in the calculation was single 1U2D model. On the other hand, for the disordered state, the ratio of the occupation probabilities of up- to down-atom for each Sn height was 1 to 2. The detail of the calculation was described in the previous paper [20]. The root mean square amplitudes of the thermal vibration for Sn and Ge atoms were assumed to be 0.048 Å and 0.045 Å in the ordered state and 0.074 Å and 0.066 Å in the disordered state, respectively [5]. The absorption potential resulting from the electronic excitations for topmost Sn atoms was set at 0 V because the effect on the RHEPD intensity is very weak [14]. The absorption potential for inner Ge atoms was assumed to be 1.1 V [21]. The solid lines in Figs. 3(d), 3(e), and 3(f) display a demonstration of the RHEPD intensity calculations from the ordered and disordered states. Under the one-beam condition, the calculated curves from the both states are almost the same. For a comparison, the rocking curves from the 2U1D and the flat model were also calculated. Since the curve for the flat model is similar to that for the 2D1U model, only the curve for the 2D1U model is plotted. In the case of the 2D1U and the flat models, the positions of the dip and the (111) Bragg peak shift to lower angle. Furthermore, the additional shoulder around  $3.5^\circ$  appears. These characteristics are not consistent with the measured ones. Consequently, the measured curve can be explained by the 1U2D model. The detail of the determination of the atomic positions will be reported elsewhere [5]. At the  $[11\bar{2}]$  and  $[10\bar{1}]$  directions, only the slight changes can be seen between these states. The calculated curves well reproduce the characteristics of the measured ones at each state. Therefore, the equilibrium positions of the Sn atoms do not change due to the phase transition.

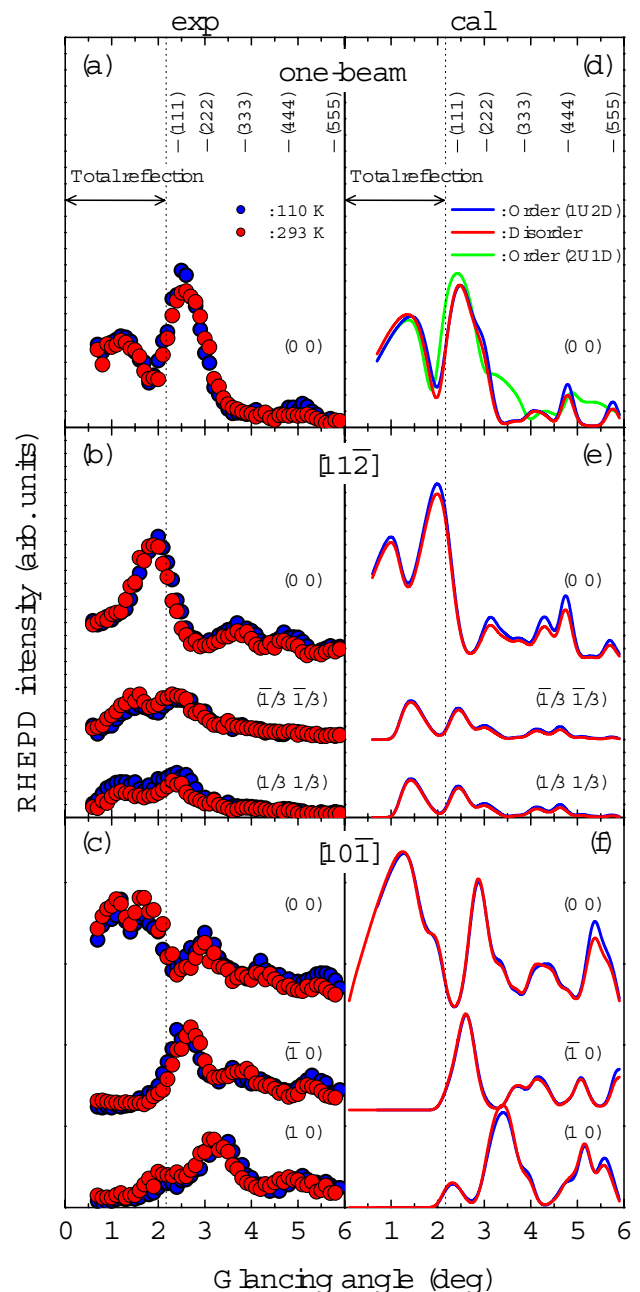


FIG. 3: RHEPD rocking curves from the Sn/Ge(111) surface under the one-beam condition ((a) and (d)), along the  $[11\bar{2}]$  azimuth ((b) and (e)) and  $[10\bar{1}]$  azimuth ((c) and (f)). Blue and red dots indicate the measured rocking curves at 110 K and 293 K, respectively. Blue and red solid lines show the curves calculated from the ordered and disordered 1U2D structures, respectively. Calculated curve for the 2D1U model is denoted as green line. The corresponding Bragg reflections are labeled on the top of the figure.

The RHEPD study shows the order-disorder phase transition for the system of the Sn/Ge(111). This result is consistent with the photoemission spectroscopy (PES) [7] and recent x-ray standing wave method [11]. The ground state of the surface structure is 1U2D. When the temperature is higher than 220 K, the Sn atoms fluctuate between two different vertical positions. From the rocking curve analysis, the occupation probabilities of the up-

and down-site do not significantly change above 220 K. Consequently, the 1U2D model is kept for the  $\sqrt{3} \times \sqrt{3}$  phase. In the scanning tunneling microscopy (STM) observation, two kinds of protrusions are measured at low temperature. At room temperature, only the single type is seen. The STM images from the  $\sqrt{3} \times \sqrt{3}$  phase are thermally averaged ones between two different states in the atomic height for the Sn atoms, like a flip-flop motion of dimers on a clean Si(001) surface [22]. On the other hand, in the cases of the RHEPD and PES, the components for the two different states at a moment can be resolved. As a result, it is concluded that the phase transition is interpreted as the order-disorder one.

#### IV. SUMMARY

In summary, the rocking curves for the RHEPD spots at various conditions were measured from the  $3 \times 3$  and  $\sqrt{3} \times \sqrt{3}$  phases on the Sn/Ge(111) surface. All the rocking curves do not show notable changes depending on the phase transition. Therefore, the equilibrium positions of the Sn atoms are almost the same for the  $3 \times 3$  and  $\sqrt{3} \times \sqrt{3}$  phases. The  $\sqrt{3} \times \sqrt{3}$  phase is composed of the 1U2D structure in a similar way of the  $3 \times 3$  phase. The experimental result suggests that the order-disorder phase transition takes place at 220 K.

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