Surface structure and phase transition of Ge(1 1 1)-3 × 3-Pb studied by reflection high-energy positron diffraction

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1. Introduction

It is known that Pb and Sn atoms occupy the T₄ site of Ge(1 1 1)-c2 × 8 surface and the super-structures with √3 × √3 periodicity appear at room temperature when the coverage is 1/3 monolayer (see Fig. 1). The Pb/Ge(1 1 1) and Sn/Ge(1 1 1) surfaces have been extensively studied experimentally and theoretically as a prototypical two-dimensional metal system [1–4]. These surfaces undergo the 3 × 3–√3 × √3 phase transition at around 200 K. Recently, it has been reported that on the Sn/Ge(1 1 1) surface new H₃/C₂H₃ structure, which is a Mott insulator, appears below 30 K [5]. Due to various phases on this surface, the Pb or Sn adsorbed Ge(1 1 1) surface system attracts much attention [6–19].

It has been reported that in the 3 × 3 phase, one adatom is located at the higher position compared to the other two adatoms [4,9–11]. This model is called one-up and two-down (1U2D) model (Fig. 1(b)). The 1U2D model is energetically favored from the density functional calculations [11]. In actual, the structure model has been supported by the experimental study [4]. However, the two-up and one-down, 2U1D, model has been reported as a 3 × 3 phase of the Sn/Ge(1 1 1) surface [8,18]. In the 2U1D model, the two adatoms are located at the higher position compared to another adatom (Fig. 1(c)). Thus, the atomic configurations of the 3 × 3 phase are still in debate [20]. Similarly, the mechanism of the phase transition is also still unknown [20]. In this study, we focus on the atomic configurations of the Pb-adsorbed Ge(1 1 1) surface at around 200 K.

Reflection high-energy positron diffraction (RHEPD) is a powerful tool to study the surface structures and properties. When the positron beam is incident on the surface at low glancing angle, the total reflection takes place [21,22].

The critical angle of the total reflection is estimated to be 2.2° using the Snell’s law when the accelerating voltage and the inner potential of the crystal are 10 kV and 14.3 V, respectively [21]. In the total reflection region, the incident positron beam is not able to penetrate the bulk. Therefore, the diffraction beam is very sensitive to the topmost surface. By means of the analyses of the total reflection intensity, we are able to investigate the adatom heights and the thermal vibrational amplitudes [23,24]. In this paper, we investigated the...
equipped with a positron source of 22Na and magnetic lenses. The electron diffraction observation. To obtain the Ge(1 1 1)-phase transitions of the Pb/Ge(1 1 1) surfaces using a reflection high-energy positron diffraction. Two independent heights of Pb atoms (denoted as \( z_1 \) (1/9 ML) and \( z_2 \) (2/9 ML)) and two heights of the first and second Ge layers (denoted as \( z_{Ge1} \) and \( z_{Ge2} \)) shown in Fig. 1(d) were varied so as to minimize the reliability factor (\( R \)) between the measured and calculated curves [24]. In the calculation, the thermal vibrational amplitudes of Pb and Ge atoms at 60 K were assumed to be 0.064 Å and 0.040 Å, respectively. The absorption potentials for the Pb and Ge layers were taken to be 0 V and 1.1 V, respectively [23,28].

The solid line in Fig. 3 shows the calculated rocking curve using the optimized atomic positions. In the lower glancing angle range including the total reflection, the calculated curve is in good agreement with the measured curve (\( R = 4.5\% \)). However, in the higher glancing angle region, the calculated curve slightly deviates from the measured one. This deviation indicates the relaxations with respects to the heights of deeper Ge layers. In the optimization, we obtained \( z_1 = 2.32 \) Å and \( z_2 = 1.81 \) Å at 60 K. Since \( z_1 \) is greater than \( z_2 \), the 1U2D structure is responsible for the Ge(1 1 1)-3 × 3-Pb surface. These values are compatible with the surface X-ray diffraction study [4], as shown in Table 1. The height

### Table 1

| Atomic heights of the Ge(1 1 1)-3 × 3-Pb surface |
|---------------|-------------|-----|-------|
| \( z_1 \) (Å)       | \( z_2 \) (Å)       | \( \Delta z \) (Å) | \( z_{Ge1} \) (Å) | \( z_{Ge2} \) (Å) |
| This study        | 2.32 ± 0.26   | 1.81 ± 0.09 | 0.51      | 3.06 ± 0.07 | 2.63 ± 0.09 |
| SXRD [4]         | 2.23         | 1.81       | 0.42      | 3.24        | 2.54        |

These parameters were defined in Fig. 1. For the comparison, the atomic heights determined by the surface X-ray diffraction (SXRD) are also listed.
difference between $z_1$ and $z_2$ is 0.51 Å. This is greater than that obtained for the Sn/Ge(1 1 1) surface (0.26 Å) [17]. The strong rippling may indicate that a charge transfer between the Pb and Ge atoms is significant as compared with the Sn/Ge(1 1 1) surface.

As shown in Fig. 3, the measured rocking curve at 293 K can also be reproduced by considering the 1U2D model. The black solid line at 293 K shows the calculated rocking curve using the optimized atomic positions. For a comparison, we also calculated the rocking curves using the 2U1D and the flat (the conventional $\sqrt{3} \times \sqrt{3}$) models. Since the shape of the curve for the flat model is similar to that for the 2U1D model, only the curve calculated using the 2U1D model is displayed. In this case, the additional peak distinctly appears at $\theta = 3.3°$, as shown in the gray solid line of Fig. 3. The measured curves are hardly reproduced by assuming the 2U1D ($R = 6.1\%$) and the flat models ($R = 5.0\%$). Therefore, the measured rocking curves from the $3 \times \sqrt{3}$ phases can be explained by considering the 1U2D model. In the $\sqrt{3} \times \sqrt{3}$ phases, the ratio of the occupation probability of the up-Pb and down-Pb atoms keeps 1:2. The Pb atoms on the Ge(1 1 1) surface thermally fluctuate between the up and down positions with keeping the ratio of the occupation probability, like a flip-flop motion of Si dimers on the clean Si(001)/C21 surface at room temperature [29]. The STM images taken at room temperature [14,15] are interpreted as the time-averaged ones of the thermally fluctuated $3 \times \sqrt{3}$ structures because the time scale in the STM observation is much larger than that in the fluctuation of the Pb atoms between the two different heights. Consequently, the phase transition of the $3 \times \sqrt{3}$ for the Pb/Ge(1 1 1) surface at 200 K is interpreted in terms of order–disorder transition. The 1U2D structure and the order–disorder type are common features in the Pb/Ge(1 1 1) and Sn/Ge(1 1 1) surfaces.

4. Summary

In summary, by means of the rocking curve analyses, we found that the 1U2D model is responsible for the Ge(1 1 1)-3 $\times \sqrt{3}$-Pb surface, in a similar way of the Sn-adsorbed Ge(1 1 1)-3 $\times \sqrt{3}$
surface. We also found that in the $\sqrt{3} \times \sqrt{3}$ phases above 200 K the equilibrium positions of the Pb atoms are the same as those in the $3 \times 3$ phases. Consequently, the phase transition of the Pb/Ge(1 1 1) surface at 200 K is responsible for the order–disorder type.

References