

## Atomic Scale Study of Surface Structures and Phase Transitions with Reflection High-Energy Positron Diffraction

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**Abstract.** In this work, we studied a few surfaces, of which the structures have not yet been revealed, using reflection high-energy positron diffraction (RHEPD). We studied the Ge(111)/Pb and Ge(111)/Sn surfaces that exhibit the phase transition from  $3\times 3$  to  $\sqrt{3}\times\sqrt{3}$  periodicities at around 200K. We found that in both phases the equilibrium positions of Pb and Sn adatoms are conserved. That is, in the unit-cell, one of three adatoms is located upper position and two of them are located lower positions (one-up-two-down). The phase transition is interpreted in terms of an order-disorder type. We furthermore studied the quasi-one dimensional Si(111)/In surface which exhibits the metal-insulator transition at around 120K. The high temperature phase is well explained as the zigzag chain structure. We found that a dynamic atomic displacement which leads to the formation of hexagon structure occur below 120 K. We confirmed the appearance of the band gap using the surface structure determined from the RHEPD rocking curves.

### Introduction

Reflection high-energy positron diffraction (RHEPD) is well suited to study surface structures in an atomic scale. Well-collimated highly parallel positrons are totally reflected at the first surface layer when small enough glancing angles because of the positive crystal potential for positrons [1,2]. Diffraction intensity versus glancing angle plot (rocking curve) is very sensitive to the structure of the first surface layer. The total reflection never occurs in the case of electrons because of the negative crystal potential for electrons.

Using electro-magnetic lenses we developed a positron beam, which is more coherent as compared to the previous beam [3]. This leads to the successful observation of the fractional order diffraction spots. In this article, we demonstrate the structural analyses of Ge(111)/Pb, Sn and Si(111)/In surfaces. We report the mechanism of their phase transitions.

### Experiment

For the study of Ge(111)/Pb and Ge(111)/Sn surfaces, the substrates ( $15\times 5\times 0.5$  mm<sup>3</sup>) were cut from a mirror-polished n-type Ge(111) wafer with a resistivity of 35  $\Omega$ cm. These were cleaned by repeated cycles of Ar<sup>+</sup> sputtering below a pressure of  $10^{-3}$  Pa and by annealing at approximately 1000 K until the sharp  $c2\times 8$  spots appeared in the reflection high-energy electron diffraction (RHEED) pattern. Subsequently, 1/3 ML of Sn or Pb atoms were deposited keeping the sample temperature at 500 K. The formations of Ge(111)- $3\times 3$ -Sn and Ge(111)- $3\times 3$ -Pb surfaces upon cooling were confirmed from the RHEED patterns. For the study of Si(111)/In surface, the substrate ( $15\times 5\times 0.5$  mm<sup>3</sup>) was cut from a mirror-polished n-type Si(111) wafer with a resistivity of 10  $\Omega$ cm. To form the Si(111)- $7\times 7$  surface, the flashing was carried out at 1473 K by direct resistive heating. The Si(111)- $4\times 1$ -In surface was obtained by depositing 1 ML of In atoms onto the Si(111)- $7\times 7$  surface at 670 K.

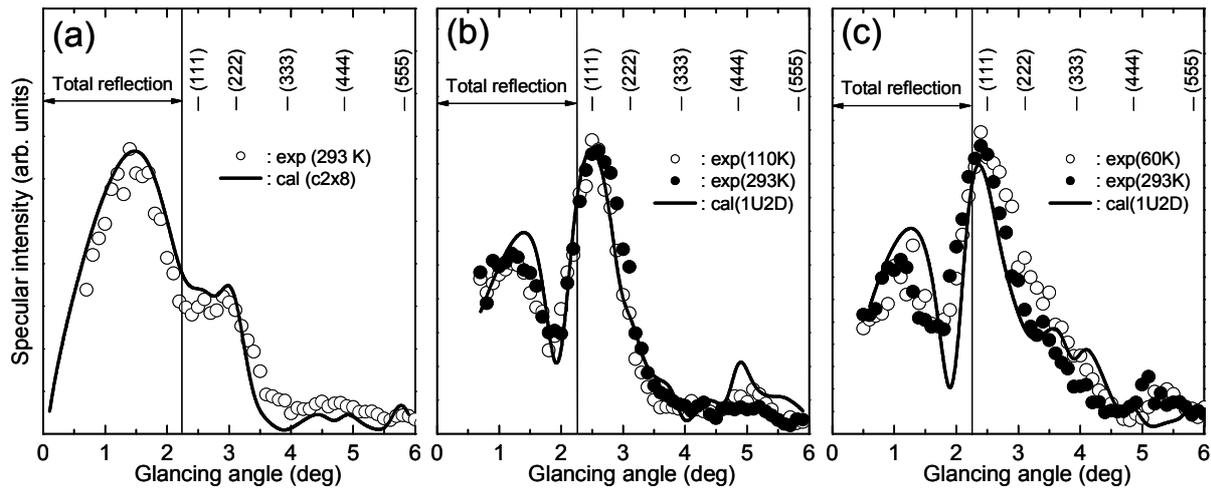


Figure 1 RHEPD rocking curves at  $7.5^\circ$ -off oriented from the  $[11\bar{2}]$  for (a) clean Ge(111)- $c2\times 8$  surface at 293 K, (b) Ge(111)/Sn surface at 110 K and 293 K and (c) Ge(111)/Pb surface at 60 K and 293 K. Solid lines in (b) and (c) are the calculated rocking curves assuming the one-up-two-down structures.

A well-focused (1mm diameter) positron beam with an energy of 10 keV, a flux of  $10^4$   $e^+$ /sec and a brightness of  $10^7$   $e^+$ /sec/cm<sup>2</sup>/rad<sup>2</sup>/V was generated using a  $^{22}\text{Na}$  source (3.7GBq), a tungsten-mesh moderator, an improved positron gun and electro-magnetic lenses. The details were described elsewhere [3]. The beam was irradiated onto the sample surfaces at glancing angles ( $\theta$ ) of  $0.3$ - $6.5^\circ$  and back-reflected beam was detected using a multi-channel plate with a phosphor plane (Hamamatsu F2226-24P). The phosphor plane images were observed using a charge-coupled device camera connected to a personal computer.

## Results and Discussion

### (a) Ge(111)/Pb and Ge(111)/Sn surfaces

Depositing  $1/3$  ML of Pb or Sn atoms on a clean Ge(111) surface, a  $\sqrt{3}\times\sqrt{3}$  periodicity appears at room temperature. The periodicity changes to  $3\times 3$  below 200-220 K [4-7]. Furthermore, below 40 K, again a  $\sqrt{3}\times\sqrt{3}$  periodicity appears. The metallic conduction vanishes below 40K. It is attributed to the Mott transition [8]. The structures of these surfaces have not yet been revealed. Hence, the above phase transition mechanisms are also not clarified. We determine the surface structures of the  $3\times 3$  phase and high temperature  $\sqrt{3}\times\sqrt{3}$  phase.

Figure 1 shows the RHEPD rocking curves obtained from the clean Ge(111)- $c2\times 8$  surface and after the deposition of Sn and Pb atoms. For the clean Ge(111)- $c2\times 8$  surface, a strong total reflection region appears below  $2.2^\circ$  and the further Bragg peaks from the (111) through the (555) reflections are seen at high glancing angles. No structures appear in the

Table 1 Vertical positions of Sn and Pb adatoms from the first layer of Ge(111) substrate.

|                          | $z_1(\text{\AA})$ | $z_2(\text{\AA})$ |
|--------------------------|-------------------|-------------------|
| Ge(111)- $3\times 3$ -Sn | $2.06\pm 0.24$    | $1.76\pm 0.10$    |
| Ge(111)- $3\times 3$ -Pb | $2.32\pm 0.26$    | $1.81\pm 0.09$    |

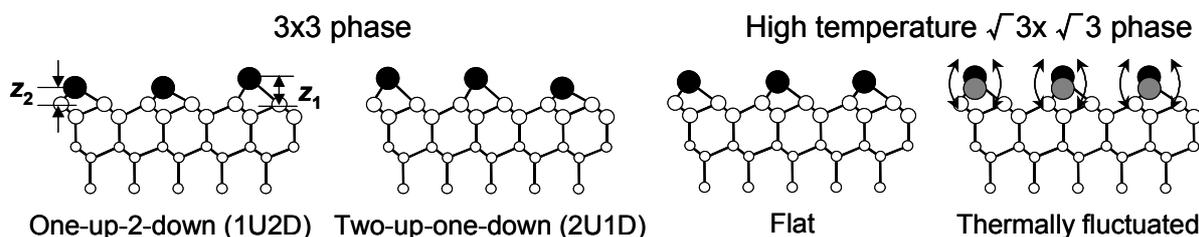


Figure 2 Atomic models of Ge(111)/Sn and Ge(111)/Pb surfaces. Open circles represent Ge atoms and filled circles represent Sn or Pb atoms.

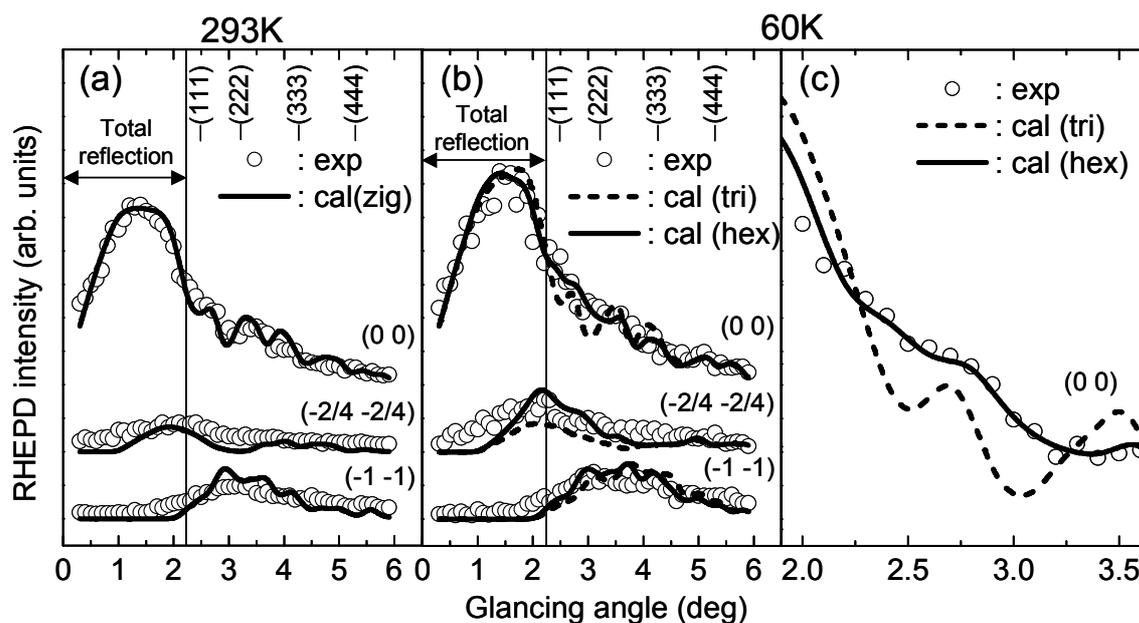


Figure 3 RHEPD rocking curves at the  $[1\bar{1}0]$  incidence from (a) Si(111)- $4\times 1$ -In at 293 K, (b) and (c) Si(111)- $8\times 2$ -In at 60 K. Solid and broken lines are the calculated rocking curves assuming the zigzag chain, the trimer and the hexagon structures.

total reflection region. The experimental curve is well reproduced by the calculation based on the dynamical diffraction theory with the  $c2\times 8$  structure [9].

After the deposition of Sn and Pb atoms, apparent dip structures are seen at  $\theta=1.7$ - $1.9^\circ$  in the total reflection region. Such dip structures are due to the interference of positron waves because of the adsorbed layers. The dip position and depth are related to the vertical position of the adsorbed layer from the substrate and the coverage. Three adatoms are accommodated in the unit cell of the above surfaces. For the  $3\times 3$  phase, so far, two structural models are proposed. That is, (i) two adatoms have the same longer distance from the substrate (two-up-one-down (2U1D) model) and (ii) two adatoms have the same shorter distance from the substrate (one-up-two-down (1U2D) model) as shown in Fig. 2. We analysed the rocking curves of the  $3\times 3$  phases to determine the distance of adatoms from the substrate. Consequently, we confirmed that in the  $3\times 3$  phases the 1U2D structures are formed. Solid lines are the calculated curves with the optimised 1U2D structures. We obtained two distances of the 1U2D adatoms ( $z_1$  and  $z_2$ ) as listed in table 1. These are in good agreement with those obtained in x-ray diffraction and theoretical studies [7,10,11].

The surface periodicity of Ge(111)/Sn and Ge(111)/Pb change from  $3\times 3$  to  $\sqrt{3}\times\sqrt{3}$  above 200-220 K. It is proposed that at high temperatures the height of all adatoms become the same as shown in Fig. 2 (flat model) [10]. Whereas it is also claimed that the 1U2D configuration is conserved at high temperatures but it is thermally fluctuated (thermally fluctuated model) [12]. In Fig. 1, the rocking curves show no significant changes upon heating. This means that no structural phase transition occurs upon heating. Therefore, it is concluded that the high temperature phases are explained as the thermally fluctuated 1U2D structures [13,14].

### (b) Si(111)/In surface

On this surface, quasi-one-dimensional In atomic chains along  $\langle 110 \rangle$  directions are formed [15]. The metallic conduction observed at room temperature vanishes below 120 K [16,17]. This phenomenon is explained as the Peierls transition. The surface periodicities are  $8\times 2$  and  $4\times 1$  below and above 120 K, respectively. However, the configuration of In atoms at low temperatures is still unknown and hence the metal-insulator transition is not fully elucidated. We reveal the metal-insulator transition of Si(111)/In surface from the structural point of view.

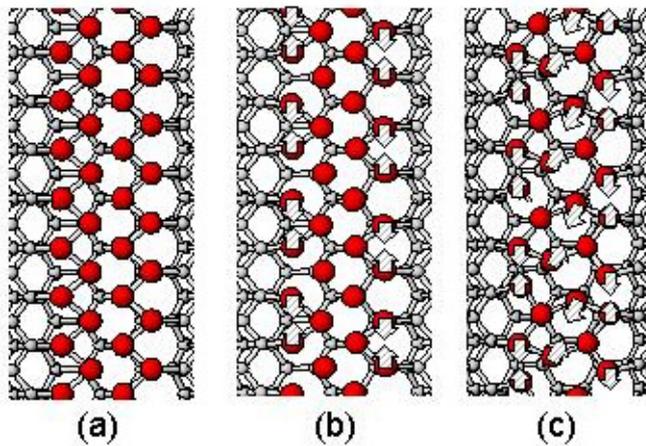


Figure 4 Structures of Si(111)/In surfaces: (a) zigzag chain structure, (b) trimer structure and (c) hexagon structure. Large circles represent In atoms. Small circles represent Si atoms. Arrows show the displacement directions of In atoms from the positions on the zigzag chain structure.

is formed as shown in Fig. 4(b) [18-20]. The agreement between experiments and calculation assuming the trimer structure seems to be well. However, carefully to see, the calculated curves for the (0, 0) and  $(\frac{2}{4}, \frac{2}{4})$  spots deviate from the experiment at  $\theta > 2^\circ$ . This is clearly seen in Fig. 3(c). The calculated rocking curve with the trimer structure shows a waving feature and hence it is not compatible with the experiment. Through detailed analysis, we eventually found that In atoms undergo more complicated displacements as shown in Fig 4(c) that is comparable to the hexagon structure [21]. The calculated rocking curve with the hexagon structure is smoother and in good agreement with experiment. This allows us to conclude that the structure of the Si(111)/In surface changes from the zigzag chain to the hexagon configurations below 120 K.

An important question is if the appearance of insulator phase is explained considering the hexagon structure. We carried out the first principles calculation considering the zigzag chain, the trimer and the hexagon structures using the PHASE code [22]. Figure 5 shows the calculated band structures. It is found that in the cases of the zigzag chain and trimer structures no band gaps appear.

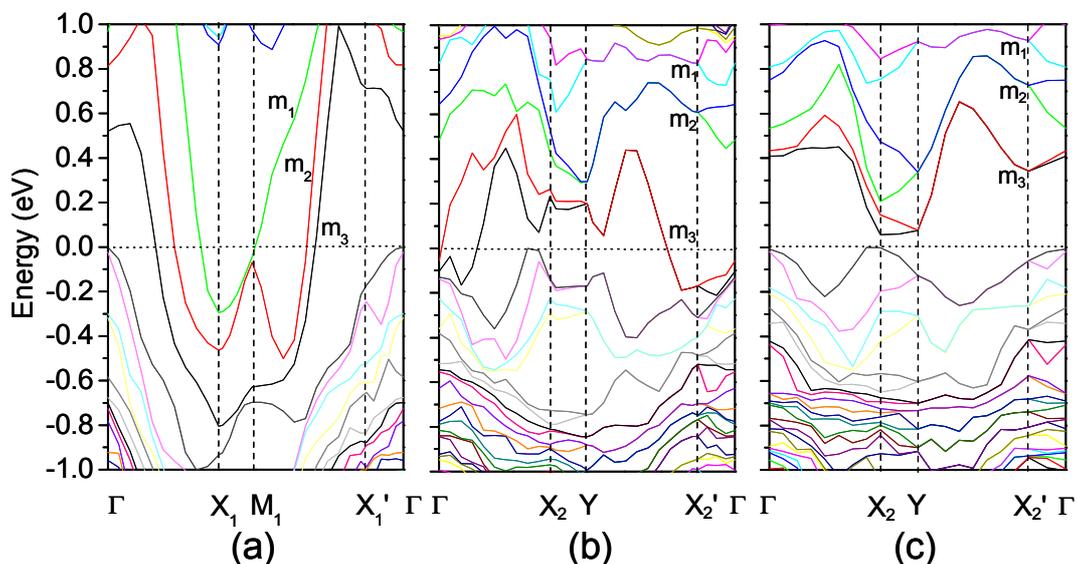


Figure 5 Band structures calculated with (a) the zigzag structure, (b) the trimer structure and (c) the hexagon structure.

Figure 3 shows the rocking curves of observed diffraction spots at 293 K and 60 K for the  $[1\bar{1}0]$  incidence. As shown in Fig. 3(a), the rocking curves at 293K are well reproduced by the calculation based on the dynamical diffraction theory assuming the zigzag chain structure shown in Fig. 4(a). This is consistent with the results of previous studies [18,19]. From Fig. 3(b), the (00) spot intensity increases in the total reflection region at 60 K. The intensities of  $(\frac{2}{4}, \frac{2}{4})$  and  $(\bar{1}, \bar{1})$  spots also increase at 60 K. Figure 3(c) shows the detailed profile of the (0,0) spot intensity at high glancing angles. It is seen that the profile becomes smooth at high glancing angles.

It is proposed that at low temperatures the trimer structure is

This is consistent with the fact that at room temperature the zigzag structure is formed and the metallic conduction occurs. The trimer structure hardly explains the appearance of insulator phase at low temperature. In the case of the hexagon structure, a band gap of 30 meV appears at the  $X_2$  point. This just explains that the insulating feature of Si(111)- $8\times 2$ -In. The band structure is also consistent with that obtained in the angle resolved photoemission spectroscopy study [16].

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**Atomic Scale Study of Surface Structures and Phase Transitions with Reflection**

**High-Energy Positron Diffraction**

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