Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Surface Science 600 (2006) 4086–4088
SURFACE SCIENCE
www.elsevier.com/locate/susc

Structural analysis of Ge(1 1 1)–3 × 3-Sn surface at low-temperature by reflection high-energy positron diffraction

Y. Fukaya [a,*], A. Kawasuso [a], A. Ichimiya [a,b]

[a] Advanced Science Research Center, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan
[b] Faculty of Science, Japan Women's University, 2-8-1 Mejirodai, Bunkyo-ku, Tokyo 112-8681, Japan

Abstract

We have investigated the structure of Ge(1 1 1)–3 × 3-Sn surface using reflection high-energy positron diffraction. From the intensity analysis based on the dynamical diffraction theory, we determined the equilibrium positions of Sn atoms at 110 K. We found that one Sn atom and the other two atoms in the unit cell are displaced upward and downward, respectively. The height difference between the two inequivalent Sn atoms was evaluated to be 0.26 Å, which is in good agreement with those obtained in the previous theoretical and experimental studies. We also found that the first-layer Ge atoms are considerably relaxed downward (~0.35 Å) as compared with the ideal Ge bulk positions. The large shift is induced by the adsorption of Sn atoms.

Keywords: Surface structure; Reflection high-energy positron diffraction (RHEPD); Total reflection; Germanium; Tin

1. Introduction

Recently, low-dimensional physics attracts much attention because the structural and electronic properties drastically change depending on the dimensionality. As regards two dimensional system, Sn/Ge(1 1 1) surfaces have been extensively studied as a prototype of two dimensional metal/semiconductor system. For this surface, Sn atoms of 1/3 monolayer (ML) occupy the T_4 sites on the bulk truncated Ge(1 1 1) surface (see Fig. 1). In scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) observations at room temperature, a $\sqrt{3} \times \sqrt{3}$ periodicity appears, while below ~220 K, a 3 × 3 periodicity appears [1,2]. Two different components for the Sn 4d core level were also identified by photoemission spectroscopy [3]. That is, Sn atoms are not placed at a single height but have two different heights. In actual, the structural analyses by glancing-incidence X-ray diffraction [4] and the LEED combined with surface X-ray diffraction [5] demonstrated a rippled configuration in the 3 × 3 phase. However, it is still not clear that which of the one-up/two-down or two-up/one-down models corresponds to the 3 × 3 phase [6]. Moreover, the mechanism of the $\sqrt{3} \times \sqrt{3}$–3 × 3 phase transition is also not fully revealed [6]. Thus, to determine the structures of the Sn/Ge(1 1 1) surface, more surface-sensitive structural tools are strongly desired [6].

In reflection high-energy positron diffraction (RHEPD), incident positrons are totally reflected at the surface layer when the kinetic energy is smaller than the energy barrier of the crystal [7,8]. Therefore, the reflected positrons include the information related only to the topmost surface under the total reflection condition. One can determine the coordinates and the thermal vibration amplitudes associated with the first surface layer without any influences from the bulk [9,10]. Above the critical angle of the total reflection, the reflected positrons include the information about the topmost and underlying layers because the incident positron beam can penetrate the topmost layer. In this paper, we measured the RHEPD rocking curve from a Ge(1 1 1)–3 × 3-Sn surface at low-temperature. By means

---

[*] Corresponding author. Tel.: +81 27 346 9330; fax: +81 27 346 9432.
E-mail address: fukaya.yuki99@jaea.go.jp (Y. Fukaya).

0039-6028/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2005.11.069

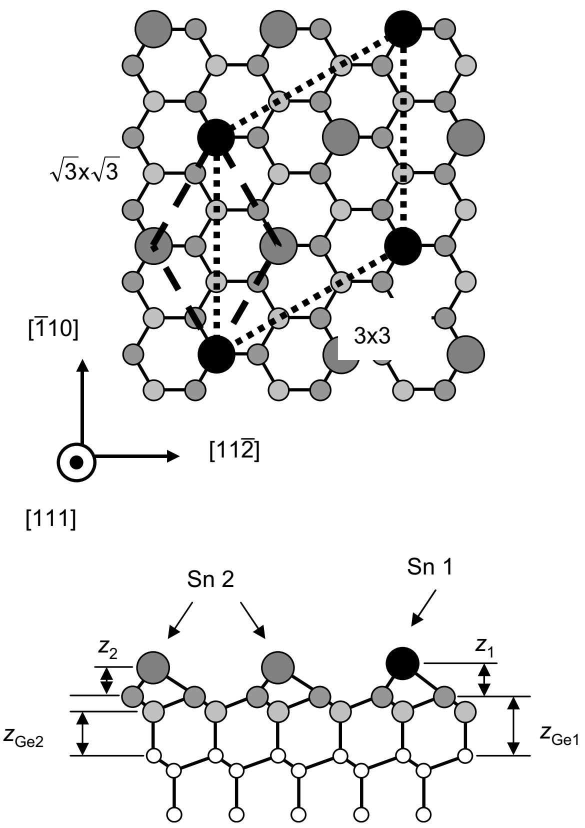

Fig. 1. Schematic drawings of the structure model for the Sn/Ge(1 1 1) surface. The upper panel is top view and the lower one is side view. Dotted and dashed lines show an unit cell of the 3×3 and $\sqrt{3}\times\sqrt{3}$ phases, respectively. In the Ge(1 1 1)–3×3-Sn surface, the Sn atoms denoted as large circles have two different heights. Small circles denote the Ge atoms.

of the structural analysis based on the dynamical diffraction theory, we determined the vertical positions of Sn adatoms.

2. Experimental procedure

Sample ($15\times5\times0.5$ mm^3) was cut from a n-type mirror-polished Ge(1 1 1) wafer with a resistivity of ~35 Ω cm. This was cleaned by repeated cycles of Ar$^+$ sputtering below a pressure of 10^{-3} Pa and annealing at approximately 1000 K until sharp $c2\times8$ spots appeared in a reflection high-energy electron diffraction (RHEED) pattern. Subsequently, 1/3 ML Sn atoms were deposited keeping the sample temperature at 500 K. The formation of the 3×3 periodicity upon cooling was confirmed in the RHEED pattern. Positron beam was generated using a ^{22}Na source and magnetic lenses, which was described elsewhere [11]. The beam energy was 10 keV. The glancing angles (θ) were changed up to 6° at a step of 0.1° by rotating the sample holder and the rocking curve was measured at 110 K. The sample temperature was measured using a thermocouple attached at the sample holder. The incident azimuth was set at 7.5° away from the [1 1 $\bar{2}$] direction, which corresponds to the so-called one-beam condition [12]. Under the one-beam condition the diffraction intensities depend on the atomic positions normal to the surface because the simultaneous reflections are sufficiently suppressed.

3. Results and discussion

Fig. 2 shows the RHEPD rocking curve for the specular spot from the Ge(1 1 1)–3×3-Sn surface at 110 K. The critical angle of the total reflection region is evaluated to be $\theta < 2.17°$ using the mean inner potential (14.3 V) of the Ge bulk [13] and Snell's law [8]. The intense (1 1 1) Bragg peak overlapped by the total reflection and the weak (4 4 4) Bragg peak can be seen in the curve. Also, it can be clearly seen that there is a distinct dip in the total reflection region. This dip structure reflects the height of the adatoms [8]. Assuming that the absorption becomes sufficient when the positron beam interferes between the adatom and underneath layers, we can estimate the height of the adatoms from the substrate using the Bragg equation ($2d\sin\theta = \lambda$, where d is the height of the adatoms and λ is the wave length of the incident positron beam). Since the glancing angle of the dip is 1.9°, the height, d, from the first Ge layer corresponds to 1.84 Å. This value is compatible to the averaged value of the height of Sn atoms obtained in the theoretical and experimental studies [4,5,14]. This is a rough estimation to expect the averaged vertical spacing of the adsorbed atoms.

For more accurate determination of the height of Sn atoms, we analyzed the rocking curve based on the dynamical diffraction theory [15,10]. The thermal vibration amplitude of Sn atoms was assumed to be 0.048 Å from the intensity slope between 110 K and 293 K. For the

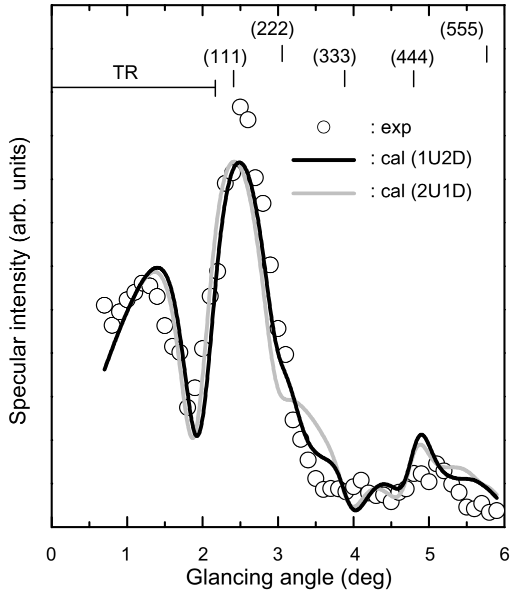

Fig. 2. RHEPD rocking curve from the Ge(1 1 1)–3×3-Sn surface under the one-beam condition at 110 K. Open circles indicate the measured points. Black solid line shows the calculated curve using the optimized heights of Sn atoms for the one-up/two-down model. Gray line shows the calculated curve using the one-down/two-up model. The total reflection region is denoted as TR.

Table 1
Vertical positions of the Ge(1 1 1)–3 × 3-Sn surface

z_1 (Å)	z_2 (Å)	Δz (Å)	z_{Ge1} (Å)	z_{Ge2} (Å)	R (%)
2.02 ± 0.24 [+0.84]	1.76 ± 0.10 [+0.58]	0.26	2.91 ± 0.05 [−0.35]	2.24 ± 0.06 [−0.21]	3.07

The notations of these parameters are defined in Fig. 1. z_1 and z_2 indicate the heights of the one Sn atom and the other two Sn atoms from the first Ge layer, respectively. z_{Ge1} and z_{Ge2} denote the heights of the first and second Ge layers from the third Ge layer, respectively. The values in brackets show the relative shifts from the ideal positions for the Ge bulk. The shift toward the surface-normal direction is defined as +.

underlying Ge layers, the amplitudes of 0.045 Å was used [16]. The absorption potential resulting from the electronic excitation in the Ge layer was assumed to be 1.1 V [17]. That of Sn atoms was assumed to be 0 V because the effect of the electronic excitations at the topmost surface layer is weak [9,10]. Four independent heights (denoted as z_1 (1/9 ML) and z_2 (2/9 ML)) of two inequivalent Sn atoms, the first-, and the second-layer Ge atoms (denoted as z_{Ge1} and z_{Ge2}) shown in Fig. 1 were varied so as to minimize the difference between the experimental and calculated curves. The goodness of fit was judged by the reliability factor defined in [10].

The black line in Fig. 2 shows the best-fit calculated curve. The calculated curve is in good agreement with the measured one ($R = 3.07\%$). As listed in Table 1, we obtained $z_1 = 2.02$ Å and $z_2 = 1.76$ Å at 110 K. This structure is consistent with the one-up/two-down model. The spacing between the up and down atoms ($\Delta z = 0.26$ Å) obtained here is also in good agreement with that (0.26 Å) obtained in the density functional theory (DFT) calculations [14]. We also calculated the rocking curve for the one-down/two-up model, as shown by the gray line in Fig. 2. The difference between the measured and calculated curves arises at the positions of the dip and the peak in the total reflection region. Also, there is a large difference in the shape of the shoulder at around 3.5°. The measured curve can not be reproduced by the one-down/two-up model. Thus, the present RHEPD rocking curve analysis suggests that the one-up/two-down model is responsible for the structure of Ge(1 1 1)–3 × 3-Sn surface at low-temperature. It should be noted that the first-layer Ge atoms are averagely shifted to the inner bulk (downward) by ~0.35 Å as compared with the ideal Ge bulk positions. This value is much greater than those obtained in the previous experimental studies [4,5]. However, the displacements of the Ge layers have a tendency to shift to the inner bulk when the number of the Ge layers used in the DFT calculations increases, as pointed out in [14]. Therefore, it is probable that the relaxation of the Ge layer is large. The large relaxation of Ge atoms is considered to be related to the adsorption of Sn atoms and lead to the small shift of the second-layer Ge atoms.

As stated in introduction, the $\sqrt{3} \times \sqrt{3}$–3 × 3 phase transition is known to occur on the Sn/Ge(1 1 1) surface at around 200 K. Several models, e.g., surface charge density wave (SCDW) [1,2] and dynamical fluctuation of the rippled structure (order–disorder) [18], are proposed for the phase transition but it is still in debates. To clarify the phase transition mechanism, reliable structure analysis is also needed above 200 K.

4. Summary

In summary, we analyzed the RHEPD rocking curve for the specular spot from the Ge(1 1 1)–3 × 3-Sn surface at 110 K under the one-beam condition. We found the rippled (one-up/two-down) model can reproduce the experimental result. We also found that at the interface of the metal/semiconductor for Sn/Ge(1 1 1) the large relaxation of Ge atoms occurs, suggesting the reexamination of the surface structure experimentally and theoretically.

References

[1] J.M. Carpinelli, H.H. Weitering, E.W. Plummer, R. Stumpf, Nature (London) 381 (1996) 398.
[2] J.M. Carpinelli, H.H. Weitering, M. Bartkowiak, R. Stumpf, E.W. Plummer, Phys. Rev. Lett. 79 (1997) 2859.
[3] R.I.G. Uhrberg, T. Balasubramanian, Phys. Rev. Lett. 81 (1998) 2108.
[4] O. Bunk, J.H. Zeysing, G. Falkenberg, R.L. Johnson, M. Nielsen, M.M. Nielsen, R. Feidenhans'l, Phys. Rev. Lett. 83 (1999) 2226.
[5] J. Zhang, Ismail, P.J. Rous, A.P. Baddorf, E.W. Plummer, Phys. Rev. B 60 (1999) 2860.
[6] M.E. Dávila, J. Avila, H. Ascolani, G. Le Lay, M. Göthelid, U.O. Karlsson, M.C. Asensio, Appl. Surf. Sci. 234 (2004) 274.
[7] A. Kawasuso, S. Okada, Phys. Rev. Lett. 81 (1998) 2695.
[8] A. Ichimiya, Solid State Phenom. 28&29 (1992/1993) 143.
[9] A. Kawasuso, Y. Fukaya, K. Hayashi, M. Maekawa, S. Okada, A. Ichimiya, Phys. Rev. B 68 (2003) 241313(R).
[10] Y. Fukaya, A. Kawasuso, K. Hayashi, A. Ichimiya, Phys. Rev. B 70 (2004) 245422.
[11] A. Kawasuso, T. Ishimoto, M. Maekawa, Y. Fukaya, K. Hayashi, A. Ichimiya, Rev. Sci. Instrum. 75 (2004) 4585.
[12] A. Ichimiya, Surf. Sci. 192 (1987) L893.
[13] J. Li, M.R. McCartney, R.E. Dunin-Borkowski, D.J. Smith, Acta Crystallogr. A 55 (1999) 652.
[14] J. Ortega, R. Pérez, F. Flores, J. Phys. Condens. Matter 12 (2000) L21.
[15] A. Ichimiya, Jpn. J. Appl. Phys., Part 1 22 (1983) 176.
[16] C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, 1997.
[17] G. Radi, Acta Crystallogr. 26 (1970) 41.
[18] J. Avila, A. Mascaraque, E.G. Michel, M.C. Asensio, G. Le Lay, J. Ortega, R. Pérez, F. Flores, Phys. Rev. Lett. 82 (1999) 442.