



Surface structure of Si(111)-(8 × 2)-In determined by reflection high-energy positron diffraction

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ABSTRACT

By using reflection high-energy positron diffraction (RHEPD) and first-principles calculations, we investigated an In/Si(111) surface on which the quasi-one-dimensional In atomic chains that exhibit the metal–insulator transition were formed. From the analyses of rocking curves, we found the transformation of the zigzag chain structure of In atomic chains to hexagon structures below 130 K along with the phase transition from the 4×1 to the 8×2 periodicities. The band structure calculated with the optimum hexagon structure displays the gap opening of 60 meV, which indicates the semiconducting character. This confirms the recent theoretical prediction that the hexagon structure is energetically favored at low temperatures [C. González, F. Flores, J. Ortega, Phys. Rev. Lett. 96 (2006) 136101].

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1. Introduction

One-dimensional structures frequently exhibit a metal–insulator transition originating from the distortion due to the Peierls instability that results in lower symmetries [1]. The In-adsorbed Si(111) (In/Si(111)) surface is one of such one-dimensional structures [2,3]. On this surface, In atomic chains with a zigzag chain structure having a periodicity of 4×1 are formed at room temperature, as shown in Fig. 1a [4–6]. One-dimensional metallic conduction occurs along the In atomic chains [7]. In 1999, Yeom et al. found that the periodicity changed from 4×1 to 8×2 below 130 K [8]. Based on the angle-resolved photoemission spectroscopy (ARPES) observations, they reported that below 130 K, the metallic conduction along the In atomic chains vanishes [8]. From the electrical conductivity measurements using the microscopic four-point probe method, Tanikawa et al. confirmed the occurrence of metal–insulator transition below 130 K [9].

To determine the structure of In atomic chains at low temperatures, many extensive studies have been carried out using scanning tunneling microscopy (STM) [10–14], photoemission spectroscopy (PES) [15,16], high-resolution electron-energy-loss spectroscopy (HREELS) [17], low-energy electron diffraction (LEED) [18], surface X-ray diffraction (SXRD) [19], and first-principles calculation [20–22]. Most of the results support the fact that at low temperatures, In atomic chains consist of trimers, as shown in Fig. 1b [19,22].

However, it is proposed that more drastic structural changes, such as the hexagon formation as shown in Fig. 1c, should be considered to explain the appearance of the band gap [23,24]. Thus, more detailed structural analyses are required to reveal the structural changes in the In atomic chains at low temperatures.

Reflection high-energy positron diffraction (RHEPD) is a powerful surface method owing to total reflection [25,26]. When the glancing angle of a positron beam is sufficiently small, the positrons are totally reflected at the first surface layer due to the presence of positive potential barriers. The critical angle is given by $\theta_c = \arcsin(V/E)^{1/2}$, where V and E denote the mean inner potential of crystals and the accelerating voltage of the incident positron beam, respectively [26]. For example, at $E = 10$ kV, θ_c is estimated to be 2.0° when $V = 12$ V for an Si crystal. Under the total reflection condition, the diffraction intensities are found to be very sensitive to the structures and thermal vibration of the first surface layers. In this study, by using RHEPD, we examined the structure of In atomic chains on the In/Si(111) surface at low temperatures. We also performed the first-principles calculations using the optimized structure. Finally, we show the electronic surface band structures calculated using the optimized structure.

2. Experimental procedure

A specimen was cut from an mirror-polished n-type Si(111) wafer with a resistivity of 1–10 Ω cm. To obtain a clean 7×7 -reconstructed surface, the specimen was flashed several times at 1473 K in an ultra-high vacuum chamber evacuated with a base

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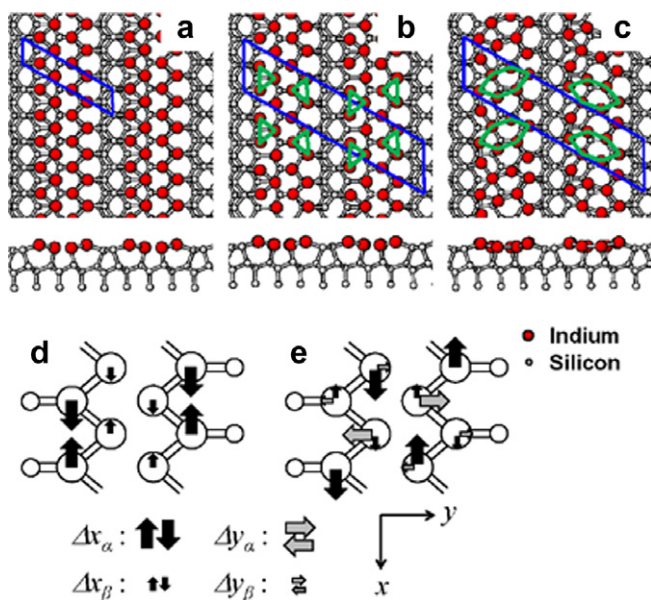


Fig. 1. Schematic representations of various structures of the In/Si(111) surface: (a) the zigzag chain structure, which was determined by surface X-ray diffraction techniques at room temperature; (b) the trimer structure proposed after performing various experiments at low temperatures and the first-principles calculations; and (c) the hexagon structure proposed by the first-principles calculations. Blue parallelograms indicate the unit cells of the 4×1 and 8×2 structures. The displacement modes for the trimer and hexagon structures are displayed in (d) and (e), respectively. The large and small arrows indicate two different amounts of atomic displacements of the In atoms when the surface structure is changed from the zigzag chain structure to the trimer or hexagon structures, respectively.

pressure of 5×10^{-8} Pa. One monolayer ($7.8 \times 10^{14} \text{ cm}^{-2}$) of indium atoms was deposited on the 7×7 -reconstructed surface at 673 K using an electron beam evaporator. The formations of the Si(111)-(4 \times 1)-In surface at room temperature and Si(111)-(8 \times 2)-In surface at 60 K were confirmed using reflection high-energy electron diffraction.

A highly parallel and focused positron beam was generated using an ^{22}Na source and electromagnetic lenses. The energy of

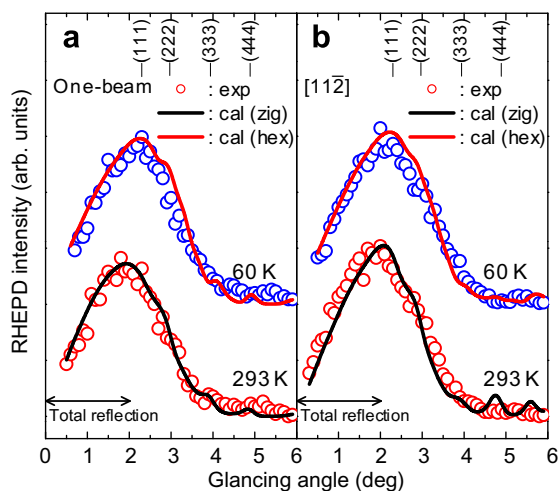


Fig. 2. RHEPD rocking curves from the Si(111)-(4 \times 1)-In at 293 K and Si(111)-(8 \times 2)-In at 60 K (a) at the one-beam condition and (b) at the $[11\bar{2}]$ incidence. The acceleration voltage of positrons is 10 kV. The circles indicate the measured curves. The black and red lines represent the curves calculated on the basis of the dynamical diffraction theory using the zigzag chain (Fig. 1a) and hexagon (Fig. 1c) structures, respectively. The total reflection region corresponds to $\theta < 2^\circ$.

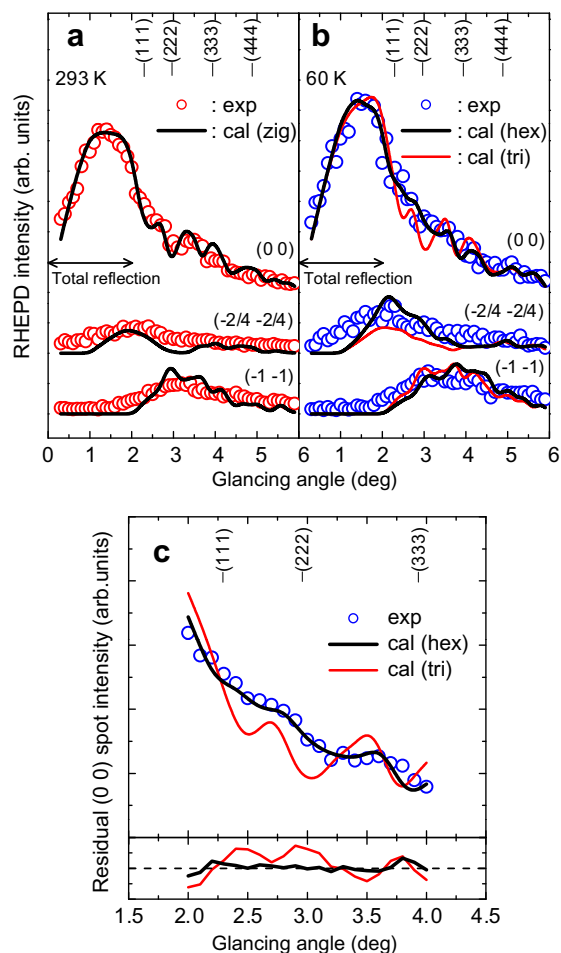


Fig. 3. RHEPD rocking curves from the In/Si(111) surface at (a) 293 K and (b) 60 K. The azimuth of the incident positron beam corresponds to the $[1\bar{1}0]$ direction. The acceleration voltage of positrons is 10 kV. The circles indicate the measured curves. In (c), the data acquisition time of the rocking curves is three times as long as that of the curves in (b) while the glancing angle range is between 2.0° and 4.0° . The black lines at 293 K and 60 K represent the curves calculated on the basis of the dynamical diffraction theory using the zigzag chain structure (Fig. 1a) and the optimized hexagon structure, respectively. The red line at 60 K indicates the calculated curve using the trimer structure (Fig. 1b). The total reflection region corresponds to $\theta < 2^\circ$. In the lower part of (c), the residuals between the measured and the calculated curves of the (00) spot along the $[1\bar{1}0]$ direction are also plotted.

the positron beam was set at 10 keV. The details of the beam apparatus have been described elsewhere [27]. The diffracted positrons were detected using a microchannel plate with a phosphor plane. The diffraction patterns were observed by a charge-coupled device camera. By changing the glancing angle (θ) of the incident positron beam, rocking curves were obtained at 60 K and 293 K.

3. Computational

Based on the density functional theory (DFT) with a local-density approximation (LDA)¹ the band structures were calculated. A slab type super-cell ($26.6 \text{ \AA} \times 7.68 \text{ \AA} \times 31.4 \text{ \AA}$) include 16 surface In atoms, 104 substrate Si atoms (three bilayers) and 16 bottom H atoms that terminate the Si dangling bonds. The vacuum region was assumed to be 21.2 \AA . The norm-conserving pseudopotentials

¹ Advance/PHASE is an improved version of the *ab initio* simulation code PHASE for commercial use at AdvanceSoft Corporation. The original code PHASE has been developed at the Japanese national project Revolutionary Simulation Software 21th Century (RSS21).

and the ultrasoft potentials were used for the Si and the In atoms, respectively. For the calculation of the wave functions the energy cutoffs of the plane-wave basis set for the calculation of the wave functions and the charge densities were 25 Ry and 225 Ry, respectively. The four k -points were used to sample the Brillouin zone.

4. Results and discussion

Figs. 2 and 3 show the RHEPD rocking curves measured from the 4×1 phase at 293 K and the 8×2 phase at 60 K under the one-beam condition (the azimuthal angle is 7.5° away from the $[1\bar{1}\bar{2}]$ direction), at the $[1\bar{1}\bar{2}]$ and $[1\bar{1}\bar{0}]$ incidences, respectively. For the one-beam condition and $[1\bar{1}\bar{2}]$ incidence, only the (00) spot intensities are plotted because the other spots have extremely weak intensities. In all the rocking curves, intense total reflection peaks are observed, while the shape of the rocking curve changes depending on the azimuthal angle, thereby reflecting the anisotropic surface structure.

At the one-beam condition, the simultaneous reflections parallel to the surface are sufficiently suppressed, and hence, the rocking curve is mostly sensitive to the vertical positions of surface atoms [28]. As shown in Fig. 2a, the one-beam rocking curves from the 4×1 phase at 293 K and the 8×2 phase at 60 K are nearly the same. This suggests that the heights of the In atoms from the substrate are maintained during the phase transition [29]. Fig. 2b shows that the rocking curves at the $[1\bar{1}\bar{2}]$ incidence for the 4×1 phase at 293 K and the 8×2 phase at 60 K are also nearly the same. This indicates that the structural change upon the phase transition is hardly detected in this diffraction condition. On the contrary, Fig. 3 shows that at the $[1\bar{1}\bar{0}]$ incidence, the rocking curves from the 4×1 phase at 293 K and the 8×2 phase at 60 K differ significantly. At 293 K, small peaks are observed in the shoulder of the (00) rocking curve at glancing angles ranging from 2.5° to 4.5° . At 60 K, the intensity increases and the profile becomes sharp in the total reflection region. Moreover, the small peaks observed in the shoulder of the rocking curve ($2.5^\circ < \theta < 4.5^\circ$) disappear. This is more clearly seen in Fig. 3c. The above-mentioned result indicates that the structural transformation of the In atomic chains occurs upon phase transition, and it can be detected at the $[1\bar{1}\bar{0}]$ incidence.

To examine the atomic configurations of the 4×1 phase at 293 K and the 8×2 phase at 60 K, we calculated the rocking curves based on the dynamical diffraction theory [30] taking into account the triple domains of the In/Si(111) surface. The Debye temperatures for the In atoms and the underlying Si atoms were assumed to be 108 K [18] and 610 K [31], respectively. The absorption potentials for the In and Si atoms were assumed to be 0 and 1.7 V, respectively [32,33]. From the rocking curve analyses under the one-beam condition, the vertical positions of the upper and lower In atoms from the zigzag Si chain were determined to be 0.99 Å and 0.55 Å, respectively [29]. As indicated by the black lines in Figs. 2 and 3, all the rocking curves obtained from the 4×1 phase at 293 K are in good agreement with those calculated by assuming the zigzag chain structure determined by SXRD [4]. Thus, it is confirmed that the zigzag chain structure is formed at 293 K. Since the rocking curves at the one-beam condition and the $[1\bar{1}\bar{2}]$ incidence do not change upon the phase transition, it is rather difficult to determine whether structures other than the zigzag chain structure are formed at low temperatures. Two models, namely, the trimer and hexagon structures, are proposed as the ground state structures from the first-principles calculations [22,23]. The rocking curves calculated by assuming the three structural models mentioned above were certainly very similar to each other under the one-beam condition and the $[1\bar{1}\bar{2}]$ incidence. Therefore, to determine the structure of the 8×2 phase at 60 K,

Table 1

Structure parameters for the Si(111)-(8 × 2)-In surface at 60 K

		$\Delta\alpha$	$\Delta\beta$	R (%)
Trimer		$\Delta\alpha = \Delta x_\alpha, \Delta y_\alpha = 0$	$\Delta\beta = \Delta x_\beta, \Delta y_\beta = 0$	
	This study	0.56 Å	0.00 Å	2.2
	Theory (Ref. [22])	0.14 Å	0.09 Å	2.7
Hexagon		$\Delta\alpha = \Delta x_\alpha = \Delta y_\alpha$	$\Delta\beta = \Delta x_\beta = \Delta y_\beta$	
	This study	0.59 Å	0.09 Å	2.1
	Theory (Ref. [23])	0.62 Å	0.21 Å	2.3

For comparison, the values obtained using the first-principles calculations are also listed. The averaged values with respect to $\Delta\alpha$ and $\Delta\beta$ from theory are displayed (see text).

we should analyze the rocking curve at the $[1\bar{1}\bar{0}]$ incidence as described below.

According to previous studies [19,22,23], the trimer or hexagon structures may be formed at low temperatures. In the trimer structure, the possible displacement mode is the pairing between two In atoms in both the outer and inner In arrays along the x -direction, as shown in Fig. 1d. The pairing displacements of the two outer In atoms are mutually correlated and also that of the two inner In atoms is mutually correlated because of the symmetry. No displacements exist along the y -direction. In the hexagon structures, the displacement modes are more complex. Six In atoms cooperatively move along both the x - and y -directions with different displacements so as to attain the hexagon configuration, as shown in Fig. 1e. The remaining two outer In atoms move away from the hexagon along the x -direction with the same amount of displacement as one of the two above-mentioned displacements. Therefore, there may be a rule regarding the displacement direction and the amount of individual In atoms. If we define the two different displacements as $\Delta\alpha$ and $\Delta\beta$, in the trimer structure, $\Delta x_\alpha = \Delta\alpha, \Delta y_\alpha = 0, \Delta x_\beta = \Delta\beta,$ and $\Delta y_\beta = 0$, where the subscripts α and β indicate the two different displacements. Similarly, in the hexagon structure, $\Delta x_\alpha = \Delta y_\alpha = \Delta\alpha,$ and $\Delta x_\beta = \Delta y_\beta = \Delta\beta$. By assuming the two structures mentioned above, we calculate the rocking curve so as to minimize the reliability factor (R) between the measured and calculated curves of the (00), $(-2/4 -2/4)$, and $(-1 -1)$ spots [31]. Obviously, the fitting parameters are $\Delta\alpha$ and $\Delta\beta$ in both the cases. The displacement directions are given in Fig. 1d and e.

The optimum values of $\Delta\alpha$ and $\Delta\beta$ obtained from the curve fittings are summarized in Table 1. In the trimer structure, we obtained $\Delta\alpha = 0.56$ Å and $\Delta\beta = 0.00$ Å with $R = 2.2\%$. Although the calculated rocking curve reproduced the experimental results, $\Delta\alpha$ (=0.56 Å) considerably deviates from that ($\Delta\alpha = 0.14$ Å) predicted from the theoretical study [22]. Considering the covalent bond length (2.9 Å) of the In atoms, $\Delta\alpha = 0.56$ Å is physically unacceptable. Even though the rocking curve is reproduced, it should be an artificial coincidence. We also calculated the rocking curve by assuming the trimer structure developed by the theoretical study [22], as shown by the red² line in Fig. 3b and c. However, in this case, the curve shape at $\theta > 2^\circ$ was hardly reproduced and R (=2.7%) is a little bit worse. In the hexagon structure, we obtained $\Delta\alpha = 0.59$ Å and $\Delta\beta = 0.09$ Å. These values are in good agreement with those predicted by the theoretical study [23]. Moreover, $R = 2.1\%$ is better than that obtained by assuming using the trimer structure and the experimental error ($R = 2.5\%$). The bond lengths between the In atoms are close to the covalent bond length of the In atoms. The surface energy for the optimized hexagon structure could be considerably smaller than that for the compressed trimer structure obtained in this study. The rocking curve calculated using the optimum hexagon structure is in good agreement with the measured curves at 60 K, as indicated by the black line

² For interpretation of color in Figs. 1–3, the reader is referred to the web version of this article.

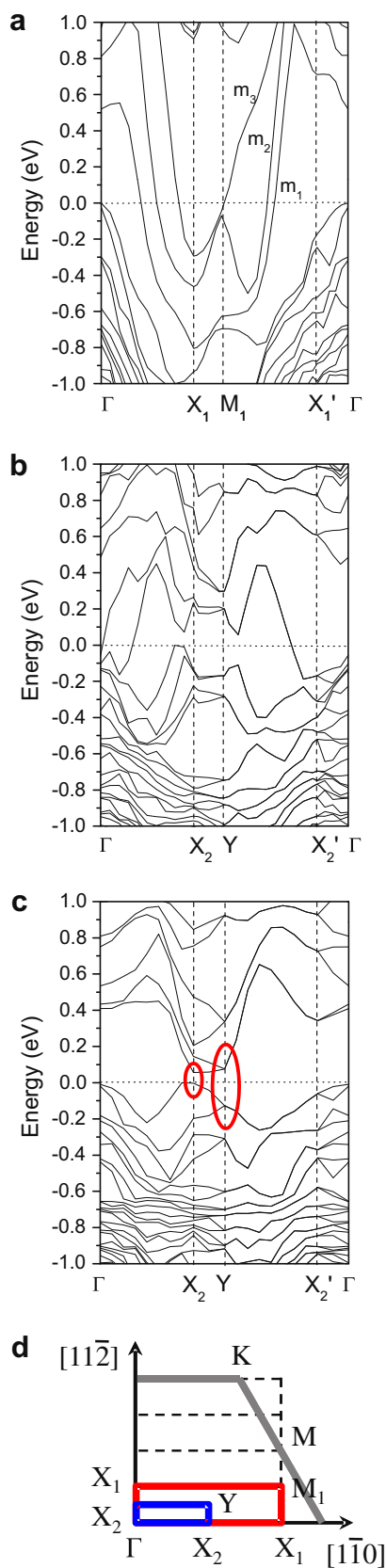


Fig. 4. Surface electronic band structures calculated using (a) the zigzag chain, (b) the trimer, and (c) the optimum hexagon structures. The surface Brillouin zone was sketched in (d).

shown in Fig. 3b and c and the red lines shown in Fig. 2. To highlight the difference between the curves using the trimer and the optimized hexagon structures, we plotted the residuals between the measured and the calculated curves at the $[1\bar{1}0]$ incidence (lower part of Fig. 3c). As mentioned before, significant differences of the curves between the surface structures are observed at glancing angles ranging from 2.5° to 4.5° . As shown in the lower part of Fig. 3c, in the case of the trimer structure, the differences in this range are large. On the other hand, using the optimized hexagon structure, these differences become small and the agreement with the measured curve is improved. Thus, it is confirmed that the In atomic chains comprise hexagons at low temperatures. A large displacement of In atoms may explain the appearance of the band gap, as predicted theoretically.

To confirm the gap opening at low temperature, we also calculated the surface band structures. Fig. 4 shows the electronic surface band structures calculated on the basis of the first-principles calculations¹. The Γ - X (Γ - X_1) direction corresponds to the $[1\bar{1}0]$ direction, which is parallel to the In chain, as shown in Fig. 4d. In the band structure using the zigzag chain structure, three surface bands denoted as m_1 , m_2 , m_3 cross the Fermi level, as shown in Fig. 4a. Thus, the 4×1 surface composed of the zigzag chain is metallic. The band structure calculated in this study is consistent with the ARPES measurement [2] and the theoretical calculation [20]. In particular, the dispersions of the m_1 , m_2 , m_3 bands are in good agreement with the ARPES measurements [2].

Fig. 4b represents the surface band structure calculated using the atomic positions of the trimer model [22]. Due to the formation of the trimer structure, the surface band structure is complexly changed from that of the zigzag chain structure. The band structure calculated in this study is also in agreement with the previous theoretical study [22]. In the vicinity of X_2 and Y points, the surface bands open the gaps of 72 meV and 167 meV, respectively. The surface density of state in the trimer structure is reduced as compared with the zigzag chain structure. However, the surface bands near Γ and X'_2 points still cross the Fermi level. Therefore, the 8×2 surface composed of the trimer structure has a metallic character. This result contradicts the surface electronic conductivity [9] and the ARPES measurements [15]. These measurements suggest the gap opening, the values of the band gap are estimated as about 300 meV [9] and 80–150 meV [15], respectively. These measurements clearly indicate that the low-temperature phase is semiconducting.

Fig. 4c shows the surface band structure calculated using the optimum hexagon structure in this study. The surface band structure is close to the previous theoretical calculations [23], although there is a difference between the 4×2 and 8×2 structure. The band gaps at X_2 and Y points are estimated as 60 meV and 202 meV, respectively. These values are in good agreement with the ARPES measurement (80 meV at X_2 and 150 meV at Y) [15] and the scanning tunneling spectroscopy (STS) measurement (160 meV) [14]. It should be noted that all of the surface bands do not cross the Fermi level, as shown in the previous calculations [23]. Hence, the low-temperature phase composed of the optimized hexagons of the In atoms is semiconducting. This result is consistent with the previous theoretical study [23]. However, the band gap obtained is smaller than that of the previous one. In our model, the inner In atoms in the hexagons are slightly shifted toward the In chain direction as compared to the original hexagon model [23]. Therefore, the slight shifts of the In atoms leads to the narrowing of the band gap.

5. Summary

In conclusion, the zigzag chain structure of the In atomic chains on the In/Si(111) surface changes to a hexagon structure at low

temperatures. This explains the appearance of the band gap after the metal–insulator (semiconductor) transition. In addition to the structural determination, the surface Debye temperature will be reported elsewhere, this temperature is important to describe the electronic and thermal transportation phenomena, based on the surface sensitivity of RHEPD.

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