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Re-investigation of the Bi-induced Si(111)-($\sqrt{3} \times \sqrt{3}$) surfaces by low-energy electron diffraction

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ABSTRACT

The atomic structures of the Bi/Si(111)-($\sqrt{3} \times \sqrt{3}$) reconstructed surfaces obtained at different adsorbate coverages were studied by dynamical low-energy electron diffraction (LEED) I–V analysis. The experimentally obtained I–V curves of the β-Bi/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface, which is formed by a Bi coverage of 1 ML, showed good agreement with the curves calculated for the milk stool model, a model proposed in the literature. In contrast to this result, the I–V curves of the α-phase obtained at a coverage of 1/3 ML do not agree with those reported in early LEED studies. We found that the I–V curves reported in the former LEED studies resemble closely to the results obtained for the surface on which the β and α-phases coexist. Based on the obtained I–V curves, we propose a more reliable structural model for the α-phase, and present the way to determine the presence of a high quality α-phase by using LEED.

1. Introduction

Systems in which heavy element atoms are adsorbed on light element substrates show giant spin splitting [1–4] that originates from the so-called Rashba–Bychkov (RB) (or simply Rashba) effect [5]. This RB effect attracted great attention due to the possibility of controlling electron spin without external magnetic field in spintronics devices. Of the systems with spin-split electronic structures, the Si(111)-($\sqrt{3} \times \sqrt{3}$) surface formed by the adsorption of 1 ML of Bi (hereafter the β-phase) was reported to show not only a giant RB splitting [2,4], but also a peculiar RB splitting that cannot be explained by a simple RB effect [4]. Since the peculiar splitting originates from the 2D symmetry of the surface, this report indicates that a complete understanding of the surface atomic structure is required to fully comprehend the RB effect on a semiconductor surface. A 1/3 ML Bi adsorption on a Si(111) surface leads to another ($\sqrt{3} \times \sqrt{3}$) reconstruction (hereafter the α-phase). However, although this α-phase has possibility to show an interesting RB splitting, no split was observed in a previous photoemission study [6]. This can be explained by two reasons. Firstly, the RB splitting on the α-phase is small and was under the detection limit of the experimental setup, and secondly the quality of the sample used in Ref. [6] was low and thus the observation of the splitting was blurred out. These mean that the α-phase is still a candidate to show the RB splitting, and "a proper understanding about the atomic structure" of this surface and "a detailed knowledge about the sample preparation" are indispensable.

In this study, we report the atomic structure of the Bi/Si(111)-($\sqrt{3} \times \sqrt{3}$) surfaces studied by low-energy electron diffraction (LEED) I–V method and the preparation method of a high quality α-phase. The I–V curves of the β-phase show good agreement with the curves reported in the former LEED studies [7,8] and also with those calculated for the milk stool model [9] shown in Fig. 1(a), which is widely believed to be the most appropriate structural model for the β-phase. However, in contrast to this result, the I–V curves of the α-phase do not agree with those reported in the former studies [7,8], which were used as references to prepare the sample in Ref. [6]. Taking the results obtained for the surface on which the β-phase and the α-phase coexist into account, we conclude that the difference arises from the higher sample quality used in the present study. That is, the annealing temperatures used in Refs. [6–8] were too low to form an α-phase with high quality. We also propose a more reliable atomic structural model for the α-phase based on the reinvestigated I–V curves, and present how to determine a high quality α-phase by using LEED.

2. Experimental details

The measurements were carried out in an ultra-high vacuum (UHV) chamber equipped with a LEED optics. An *n*-type (Sb-doped) Si (111) sample was cleaned by direct resistive heating up to 1520 K,

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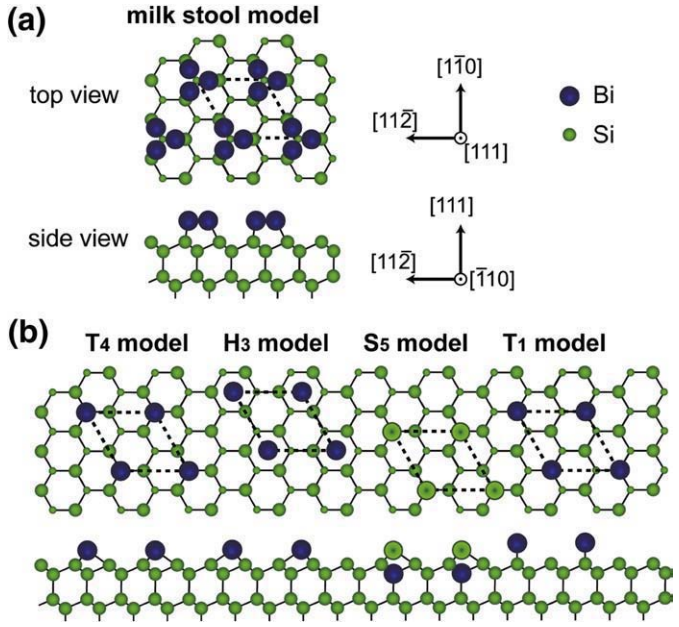

Fig. 1. Schematic illustration of models examined for the Bi/Si(111)-($\sqrt{3}\times\sqrt{3}$) surface structures. (a) A model for the β-phase with a Bi coverage of 1.0 ML, and (b) models for the α-phase with a Bi coverage of 1/3 ML.

and a sharp (7×7) LEED pattern was observed after the annealing. Three different Bi/Si(111)-($\sqrt{3}\times\sqrt{3}$) surfaces were prepared by depositing 1.2 ML of Bi onto a clean Si(111) surface at a substrate temperature of ~300 K, followed by annealing at 570 K, 720 K and 870 K for 1 min each. These annealing processes lead to Bi coverages of approximately 1.0 ML, 0.65 ML, and 1/3 ML, i.e. the β-phase, a surface on which both the β-phase and the α-phase exist (the mixed surface) and the α-phase [10]. Note that the β-phase was obtained after annealing the sample at a temperature between 470 and 590 K, and the α-phase was reported to be obtained after annealing at ca. 620 K in Refs. [6–8]. In contrast to these former studies, we could obtain the α-phase only after annealing the Bi/Si(111) surface at 870 K.

The LEED spot intensity was recorded at 80 K with a computer controlled data acquisition system equipped with a digital CCD camera [11]. For structural analysis, we have measured the LEED I–V curves for 16 inequivalent diffraction spots within an incident energy range of 50–350 eV at 1 eV energy step. In order to determine the atomic positions, full dynamical calculations were performed using a Barbieri–Van Hove symmetrized automated tensor LEED package [12]. Ten phase shifts were used to represent the atomic scattering ($l_{max}=9$), and further structural refinement utilized 13 phase shifts ($l_{max}=12$). The real part of the inner potential was determined during the theoretical- and experimental-curve fitting. The damping was represented by an imaginary part of the potential of −5.0 eV. Debye temperatures of 120 K and 650 K were used for Bi and Si atoms, respectively. The Pendry *R*-factor (R_P) [13] was used to direct the automated search algorithm, and the best agreement of experimental and theoretical I–V curves involved minimizing R_P.

3. Results and discussion

The top view and the side view of the examined structural models of (a) the β-phase and (b) the α-phase are displayed in Fig. 1. The Bi trimer units are located at the T_4 site in the milk stool model, the structural model that is believed to be the most appropriate one for the β-phase. Regarding the structural model of the α-phase, Bi atoms are situated on the outermost threefold symmetry sites in the T_4, H_3 and T_1-site models, and the Bi adatoms and Si atoms situated just below the T_4-site are replaced in the S_5-site model. Of these models, the T_4-site model was considered as the most appropriate surface structure of the α-phase in the former studies, such as LEED I–V [7,8], surface X-ray diffraction (SXRD) [14] scanning tunneling microscopy (STM) [15,16] and theoretical calculation [17]. However, as shown in Table 1, the atomic position of Bi reported in these studies does not show good agreement.

Fig. 2(a)–(c) shows the LEED patterns of the β-phase, the mixed surface and the α-phase. Sharp $\sqrt{3}$ spots are observed in all the three LEED patterns. Regarding the background intensity, the one in Fig. 2 (b) is higher than those in Fig. 2(a) and (c). This high background supports that both the β-phase and the α-phase exist on this surface since a higher background indicates that the quality of this surface is poorer than those of the two other surfaces. Although clear ($\sqrt{3}\times\sqrt{3}$) spots are observed in Fig. 2(a)–(c), there is a difference in spot intensity in the three LEED patterns. For example, the intensities of the (1/3,1/3) spots become stronger as the coverage decreases, while the intensity of the (2/3,2/3) shows opposite behavior. These differences indicate that the atomic surface structure changes depending on the Bi coverage.

In Fig. 3, we show the I–V curves of sixteen inequivalent LEED spots. The blue solid curves are the results of the β-phase, the black dashed ones are those of the mixed surface, and the red solid curves are the results obtained for the α-phase. Note that the peak positions observed in the LEED I–V curves of the mixed surface can be reproduced by those of the β- and α-phases. Of the three curves, the blue ones are similar to the LEED I–V curves of the β-phase reported in a former studies [7,8], but the red curves do not show agreement with the α-phase reported in the same former studies. Indeed, the LEED I–V curves of the α-phase reported previously show agreement with the black dashed curves as shown for the (1/3,1/3) spot in Fig. 3. (The green curve in the figure is the I–V curve of the (1/3,1/3) spot of the surface that was supposed to be the α-phase taken from Ref. [7].) These results indicate that the Bi coverage reported in Refs. [7,8] was underestimated. The underestimated coverage is well explained by the low annealing temperature used in the former studies [6–8], and indicates that a higher annealing temperature of ca. 870 K is necessary to form the α-phase. Since the former LEED I–V measurement was performed with a sample on which both the β- and α-phase coexist, one has to reconsider the LEED I–V curves of the α-phase and thus reinvestigate the atomic structures of the Bi/Si(111)-($\sqrt{3}\times\sqrt{3}$) surfaces.

The Bi/Si(111)-($\sqrt{3}\times\sqrt{3}$) surfaces belong to the plane group *p31m*, and the displacements of atoms were restricted to this symmetry in the calculations, which was performed by allowing Bi and the five topmost Si layer atoms to optimize their positions. (The deeper Si atoms were fixed to the bulk coordinates.) Regarding the β-phase, the best-fit with an R_P value of 0.181 was obtained for the milk stool model shown in Fig. 1. The calculated LEED I–V curves of the β-phase obtained by the milk stool model are shown together with the experimental results in Fig. 4(a). In Fig. 4(b), we show the position of Bi atoms and the atomic displacements of surface Si atoms from the (1×1) bulk coordinates (heavy-line arrows) obtained from the calculation. As summarized in Table 1, the obtained height distance between the Bi layer and the first Si layer (h_{BiSi}), 2.65 Å, shows good

Table 1
The Bi–Bi distance and the height distance between the Bi layer and the first Si layer (h_{BiSi}) for the β-phase, and h_{BiSi} for the α-phase.

	Bi–Bi	h_{BiSi} (β)	h_{BiSi} (α)
Present study	3.04 Å	2.65 Å	1.94 Å
Calc. [17]	3.05 Å	2.64 Å	1.98 Å
LEED I–V [7]	2.928 Å	2.210 Å	1.107 Å
LEED I–V [8]	1.951 Å	2.210 Å	1.107 Å
SXRD [14]		2.70 Å	1.60 Å