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Triple-domain effects on the electronic structure of Pb/Si(111)-($\sqrt{7}\times\sqrt{3}$): Density-functional calculations

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ABSTRACT

Electronic structure of the Pb/Si(111)-($\sqrt{7}\times\sqrt{3}$) surface has been studied by using density-functional theory calculations for a representative structural model with a coverage of 1.2 ML. Our calculations do not reproduce all the bands reported in an angle-resolved photoemission spectroscopy (ARPES) study, but we find that this discrepancy could be resolved by taking into account the effect of the triple-domain structure of the ($\sqrt{7}\times\sqrt{3}$) surface samples. We also find that, while the calculated Fermi surface for a single-domain ($\sqrt{7}\times\sqrt{3}$) surface bears a ($\sqrt{7}\times\sqrt{3}$) periodicity, the overlap of the Fermi surfaces for three different ($\sqrt{7}\times\sqrt{3}$) domains reveals an effective (1×1) periodic pattern similar to the (1×1) Fermi surface measured for the ($\sqrt{7}\times\sqrt{3}$) surface. Thus, the unusual (1×1) pattern appearing in the measured Fermi surface is not likely due to any strong (1×1) potential in the ($\sqrt{7}\times\sqrt{3}$) surface as was speculated in the ARPES study.

1. Introduction

Metal overlayers on semiconductor surfaces have attracted much attention because of their low dimensional electronic properties [1–3]. A prototypical example is the Pb/Si(111) surface. This surface is known to have an abrupt interface due to the low solubility between Pb and Si and thus has long served as a test ground for traditional issues such as Schottky barrier problems on metal–semiconductor junctions [4–6]. The Pb/Si(111) surface is also a subject of recent interest in relation with quantum size effects found in the growth pattern of Pb islands [7,8]. and two-dimensional superconductivity observed in a few Pb layers [9,10].

One atomic layer of Pb grows up to about 1.33 ML (here, 1 ML refers to one Pb atom per Si), and various monolayer phases are observed depending on coverage, temperature, and annealing history [11–16]. The structures of sub-monolayer phases, the mosaic phase at 0.16 ML and the β-($\sqrt{3}\times\sqrt{3}$) and (3×3) phases at 0.33 ML, are well understood [13,14,17–19]. At high coverages of 1–1.33 ML, the ($\sqrt{7}\times\sqrt{3}$), α-($\sqrt{3}\times\sqrt{3}$), (1×1), devil's staircase (DS), hexagonal incommensurate (HIC), and striped incommensurate (SIC) phases are found [12,13,15,17,20–23]. The ($\sqrt{7}\times\sqrt{3}$) and α-($\sqrt{3}\times\sqrt{3}$) phases have been considered as basic building blocks because the DS phase is constructed by a linear combination of the two phases [22] and the HIC and SIC phases are composed of the α-($\sqrt{3}\times\sqrt{3}$) domains separated by domain walls of the "almost" ($\sqrt{7}\times\sqrt{3}$) phase [11]. Of the two basic structural units, the ($\sqrt{7}\times\sqrt{3}$) phase is well realized as a pure phase, but the α-($\sqrt{3}\times\sqrt{3}$) phase is always found as a mixture with the ($\sqrt{7}\times\sqrt{3}$) phase [24]. For this reason the ($\sqrt{7}\times\sqrt{3}$) phase has been studied extensively, but there are still debates on the coverage of Pb, the atomic structure, and the electronic properties [13,16,18,20,24–27].

In their surface X-ray diffraction study, Kumpf et al. [26] proposed a structural model for the ($\sqrt{7}\times\sqrt{3}$) phase based on a Pb coverage of 1.2 ML. As seen in Fig. 1(a), this model is featured by one additional Pb atom per unit cell adsorbed on a hollow site of the ideal (1×1) phase with every surface Si atom covered by one Pb atom. On the other hand, in their scanning tunneling microscopy (STM) study, Hwang et al. [27] suggested another structural model with a Pb coverage of 1.0 ML. This model is slightly modified from the ideal (1×1) phase: three of the five Pb atoms in the ($\sqrt{7}\times\sqrt{3}$) unit cell form a trimer by displacing to a hollow site (H_3 or T_4) as shown in Fig. 1(b). In addition, Švec et al. [28] reported in a recent STM study that two different-coverage ($\sqrt{7}\times\sqrt{3}$) phases are likely. They pointed out that the experiments suggesting the 1.0 ML coverage [20,27] and the experiments suggesting the 1.2 ML coverage [22,23,26] had different sample preparation methods, and also demonstrated that the initial ($\sqrt{7}\times\sqrt{3}$) phase prepared by the method of Refs. [20] and [27] evolves into a different ($\sqrt{7}\times\sqrt{3}$) phase by depositing small amounts of Pb, which corresponds to the ($\sqrt{7}\times\sqrt{3}$) phase assigned to be 1.2 ML [23]. Density functional theory (DFT) studies [25,29,30] reported that the 1.0 ML trimer model of Hwang et al. [27] is energetically unstable: this model relaxes into an almost perfect (1×1) phase [25]. A recent DFT study of Hsu et al. [30] proposed an alternative 1.0 ML model, but they showed that this model fails to reproduce the band structure measured in an angle-resolved photoemission spectroscopy (ARPES) study by Choi et al. [24]. The

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1.2 ML model of Kumpf et al. [26] has also been examined by DFT studies [14,25,29,30]. This model is energetically stable and is capable of explaining experimental STM images,[18,25] but the calculated band structure by Hsu et al. [30] is still in partial disagreement with the ARPES result of Choi et al. [24]. Moreover, the ARPES study [24] reported that the measured Fermi surface of the $(\sqrt{7}\times\sqrt{3})$ surface shows an apparent (1×1) pattern, which lead to a suggestion that the electrons near the Fermi level (E_F) in the $(\sqrt{7}\times\sqrt{3})$ surface are possibly subject to a strong (1×1) potential, but the nature and origin of such (1×1) potential in the $(\sqrt{7}\times\sqrt{3})$ surface remain unclear.

In the present DFT study, we correctly explain the electronic structure of the Pb/Si(111)-$(\sqrt{7}\times\sqrt{3})$ surface based on the 1.2 ML structural model of Kumpf et al. [26]. Playing a key role in the present study is the coexistence of three different $(\sqrt{7}\times\sqrt{3})$ domains in the surface samples studied by ARPES study [24]. By incorporating the triple-domain effects into analysis, our calculations reproduce well the ARPES band structure and the (1×1) periodicity on the Fermi surface, which was not achieved by previous calculations for a single-domain $(\sqrt{7}\times\sqrt{3})$ surface. The Fermi surface and a part of surface band structure calculated in the present study were successfully used in a recent paper to support the ARPES finding of an interesting Si hole band which has an extremely light effective mass due to the interaction with a Pb-derived empty band [31].

2. Method

We carry out DFT calculations by employing the Vienna *ab-initio* simulation package [32] with the use of generalized gradient approximation [33] and ultrasoft pseudopotentials [34]. The Si(111) surface is simulated by a periodic slab geometry. A slab consists of six atomic layers, and the vacuum spacing between two slabs is equivalent to six atomic layers (~12 Å). Pb atoms are adsorbed on the top of the slab, and the bottom of the slab is passivated by H atoms. The contact potential difference arising from the use of such asymmetric slabs is handled by using the correction scheme of Neugebauer and Scheffler [35]. We expand the electronic wave functions in a plane-wave basis set of 188 eV. Brillouin-zone integrations in the $(\sqrt{7}\times\sqrt{3})$ surface are done with a $4\times6\times1$ k-point mesh. The calculated bond length of the bulk Si is 2.364 Å. All atoms but the bottom two Si layers held at bulk positions are relaxed until the residual force components are within 0.05 eV/Å. The used parameters for the slab thickness, vacuum spacing, k-point mesh, and plane-wave energy were found to produce good convergence: the calculated adsorption energies converge within 0.02 eV per Pb atom.

3. Results

Fig. 1(b) shows the optimized 1.2 ML model for the Pb/Si(111)-$(\sqrt{7}\times\sqrt{3})$ surface. This model was proposed in the X-ray study of Kumpf et al. [26] and its main feature is an additional Pb atom adsorbed on the H_3 (or T_4) site of the ideal 1.0 ML model. We first examined the energetics for the Pb atom adsorbed on the H_3 site. Fig. 2 shows the total energy as a function of the height of the Pb atom. Upon adsorption, the Pb atom arrives at a metastable state at ~4.6 Å from the top Si layer (corresponding to ~1.8 Å from the layer of the original Pb atoms). The Pb atom can easily overcome a low energy barrier of 0.07 eV and reach the lowest energy state at ~2.8 Å from the top Si layer. The final structure forms an almost flat Pb layer with a small rumpling of 0.12 Å. We also found a similar energy curve for the Pb adsorption on the T_4 site (not shown). The calculated equilibrium structure compares well with the results of previous DFT studies, [14,25] but the theoretical results do not agree in the height of the added Pb atom with the X-ray study of Kumpf et al. [26] While the X-ray study reported that the hollow-site Pb atoms can best be described by two split atomic positions (corresponding to 2.6 Å and 3.2 Å in Fig. 2), the calculated energy curve shows only one local energy minimum at ~2.8 Å. The possibility of two equilibrium Pb heights was carefully examined in the previous DFT study of Chan et al., [14] but they also identified only one equilibrium Pb height. Thus, the origin of the disagreement between experiment and theory is yet to be clarified.

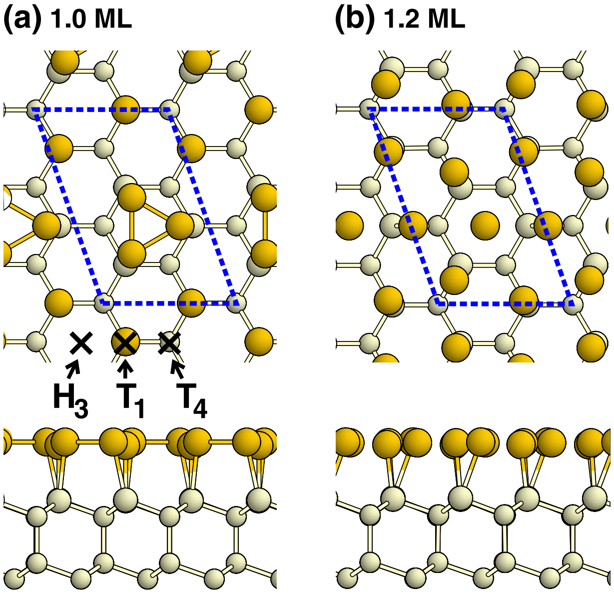

Fig. 1. Schematic of the Pb/Si(111)-$(\sqrt{7}\times\sqrt{3})$ surfaces: (a) 1.0 ML and (b) 1.2 ML models. Large and medium balls represent the Pb and first-layer Si atoms, respectively. Small balls represent the rest of Si atoms. Dashed lines represent the $(\sqrt{7}\times\sqrt{3})$ unit cell. Crosses represent three high-symmetry surface sites.

We next investigate the electronic structure of the optimized 1.2 ML model shown in Fig. 1(b). The calculated band structure is shown in Fig. 3(a). There are strong surface bands within the bulk band gap, some of which cross E_F, and weak surface bands with small dispersions located at about 0.5–1.0 eV below E_F. We found that the surface bands near E_F have entirely the Pb $p_{x,y}$ character, indicating the inplane Pb–Pb metallic bonding, and the deeply-bound dispersionless bands have mainly the Pb p_z and Si p_z characters, indicating the interfacial Pb–Si covalent bonding, as seen in the charge characters of representative surface states (S_1 and S_2) displayed in Fig. 3 and also in the projected density of state (PDOS) obtained for the Pb and Si p orbitals shown in Fig. 4(a). The present calculations give insight into the electronic nature underlying the superconductivity in the Pb/Si(111)-$(\sqrt{7}\times\sqrt{3})$ surface, which was observed in a recent ARPES study of Zhang et al. [10] and attributed to the interplay between the Pb–Pb metallic and the Pb–Si covalent bonds. The charge characters of the S_1 and S_2 states shown in Fig. 3 confirm the experimental interpretation that the Pb–Pb and Pb–Si bondings have *metallic* and *covalent* bonding nature, respectively. While the bands for the Pb–Si covalent bonds are fully occupied, the bands for the Pb–Pb metallic bonds cross E_F and thus are solely responsible for the observed superconductivity. It is also notable that the metallic states with the Pb $p_{x,y}$ character is effectively decoupled from the substrate, as is evident from a comparison of the PDOS between the Pb/Si(111) surface and the frozen Pb layer isolated from the Si(111) substrate: the Pb $p_{x,y}$ peak of the isolated Pb layer [in Fig. 4(b)] undergoes only small changes near E_F upon adsorption [in Fig. 4(a)], while its PDOS for the Pb p_z component changes noticeably with a new strong peak at about 0.7 eV below E_F.

The calculated band structure is in good agreement with the band structure reported in the DFT study of Hsu et al., [30] but both theoretical band structures are in partial disagreement with the ARPES bands reported by Choi et al. [24]: In Fig. 3(a), while the bands dispersing upward (downward) from $\overline{K}_1$ ($\overline{M}_1$) to $\overline{M}_1$ ($\overline{\Gamma}$) near E_F compare well with the ARPES bands, there is no trace of two ARPES