# Double-Layer In Structural Model for the In/Si(111)-$\sqrt{7} \times \sqrt{3}$ Surface

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We demonstrate by using density functional calculations that the In/Si(111)-$\sqrt{7} \times \sqrt{3}$ surface consists of an In double layer, contrary to the prevailing idea that the In overlayer on this surface is just one atom thick and thus can be used to represent the ultimate 2D limit of metal overlayer properties. The double-layer In structure is sound energetically and microscopically and, above all, well reproduces the measured photoemission band structure that could not be fairly compared with any single-layer In model. The present double-layer model urges a reconsideration on the recent experimental claims that the In overlayer properties were pushed to a single-layer limit in this surface.

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Metal overlayers grown on semiconductor surfaces form an important class of condensed matter systems. Especially, the one-atom-thick metal layers have attracted great attention as an initial stage of the layer growth and also as a model system ideal for exploring intriguing low-dimensional metallic properties [1–4]. The electronic structure in the single-layer regime, in general, is so subtle and sensitive to the underlying atomic structure that a proper structural information is essential in correctly understanding the nature of the observed electronic phenomena, but the structural determination is usually a matter of long debates due to the complex interface configurations and/or inaccurate coverage information [5–7].

One interesting system in this regard is the In/Si(111)-$\sqrt{7} \times \sqrt{3}$ surface. In this surface, the In overlayer is generally assumed to be one atom thick [8–11] and has been used to explore the ultimate 2D limits of In overlayer properties, such as the observation of 2D nearly free-electron parabolic bands in photoelectron spectroscopy studies [12,13], the persistence of In superconductivity with a surprisingly high $T_C$ close the bulk value [14,15], and the report as a rare example of single-layer systems still exhibiting metallic transport properties [16]. It is known that there exist two different In-derived $\sqrt{7} \times \sqrt{3}$ phases that are topographically distinguished in scanning tunneling microscopy (STM) experiments: one with quasi-rectangular images (hereafter, $\sqrt{7}$-rect) and the other with quasihexagonal images ($\sqrt{7}$-hex) [8–10]. Both phases typically coexist [8], but, due to a metastable nature of the $\sqrt{7}$-hex phase [11], it is possible to obtain a single $\sqrt{7}$-rect phase by handling the temperature or the In coverage [13,16].

Despite many studies, however, the accurate In coverages and structural details of the $\sqrt{7}$-rect and $\sqrt{7}$-hex phases have not been quantified yet. Even the In layer thickness is still an issue to be resolved. Although the single-layer In picture has been prevailing from early works [8–11,13–16], there are also experimental suggestions for more-than-one-atom layer thickness: for instance, an implication of In multiple layers from the observation of superreflection points in a reflection high-energy electron diffraction study [17], an apparent STM height difference that the $\sqrt{7} \times \sqrt{3}$ phase appears higher by about 2 Å than the coexisting, single-layer 4 × 1 phase [8,18], and a double-layer estimation inferred from the quantitative calibration of In coverages in a low-energy electron microscopy study [19]. It thus remains a question whether the recent experiments [13–16] correctly demonstrated the true single-layer limit of the In overlayer properties.

In this Letter, we explore the atomic structure of the In/Si(111)-$\sqrt{7} \times \sqrt{3}$ surface by using density functional theory (DFT) calculations. We focus on the $\sqrt{7}$-rect phase since this phase is known to form a stable phase and, moreover, is equipped with the band structure measured by an angle-resolved photoelectron spectroscopy (ARPES) study [13], allowing a stringent spectroscopic test for any structural model we consider. Our finding is very interesting: the best structural model features an In double layer, in contrast with the prevailing idea of "an one-atom-thick In layer" on Si(111)-$\sqrt{7} \times \sqrt{3}$ that was the underlying theme of recent experimental reports [13–16]. In what follows, it is demonstrated that the double-layer In model is energetically, microscopically, and spectroscopically sound.

DFT calculations were performed using the Vienna *ab initio* simulation package within the generalized gradient approximation [20] and the ultrasoft pseudopotential scheme [21]. The Si(111) surface is modeled by a periodic slab geometry with six atomic layers and a vacuum spacing of about 12 Å. The calculated value 2.364 Å is used as the bulk Si-Si bond length. In atoms are adsorbed on the top of the slab, and the bottom of the slab is passivated by H atoms. The electronic wave functions are expanded in a plane-wave basis with a kinetic energy cutoff of 151 eV. A $4 \times 6 \times 1$ $k$-point mesh is used for the $\sqrt{7} \times \sqrt{3}$ Brillouin-zone integrations. All atoms but the bottom two Si layers held fixed at the bulk positions are relaxed until the residual force components are within 0.001 eV/Å. Similar calculation schemes were used in previous studies of the Pb/Si(111)-$\sqrt{7} \times \sqrt{3}$ surfaces [4,22].

We begin with a typical single-layer In model that was experimentally suggested to account for the quasi-rectangular STM images of the $\sqrt{7}$-rect phase [8–10]. We introduced a uniform rectangular array of In atoms that was set to lattice-match the bulk-terminated Si(111)-$\sqrt{7} \times \sqrt{3}$ surface with a coverage of 1.2 ML (here, 1 ML refers to one In atom per Si). At this coverage, the atomic density of the In layer is almost the same as that of the bulk In(001) layer (equivalent to 1.19 ML). Figure 1(a) shows the optimized structure, which still retains a quasi-rectangular In arrangement with an In-Si interlayer spacing of 2.54 Å in average. This single-layer In structure is energetically stable with an adsorption energy of 2.79 eV per In atom, which is larger than the bulk cohesive energy 2.33 eV. As seen in Fig. 1(b), however, its simulated STM images are not satisfactory when compared with the experimental quasi-rectangular STM images [9,10]. Figure 1(c) shows the calculated band structure, but, disappointingly again, the In-derived surface states cannot be fairly compared with the ARPES band structure of Rotenberg *et al.* [13]. Lateral shifts of the In layer relative to the underlying Si(111) substrate were found to produce energetically comparable (within less than 0.02 eV per atom) quasi-rectangular In configurations with varying band structures, but none was successful in reproducing the ARPES band structure.

We next try a double-layer In model for the $\sqrt{7}$-rect phase in consideration of experimental suggestions for multiple layer thickness. Figure 2 shows the employed double-layer structural model, where we simply put a new rectangular In layer of 1.2 ML on the hollow sites of the above-mentioned quasi-rectangular In layer so that it may resemble the top two surface layers of the In(001) surface. In the optimized structure, while the In sublayer still remains quasi-rectangular, the top layer forms an almost regular lattice ($a_1 = 3.22$ Å and $a_2 = 3.34$ Å in average) close to the bulk In(001) square lattice ($a_0 = 3.29$ Å). The In-In interlayer spacing is 2.40 Å in average, a little shorter than the bulk value 2.55 Å, and the In-Si interlayer spacing is 2.58 Å in average, similar to that of the single-layer case. Indeed, its simulated quasi-rectangular topographic images are found to compare well with the STM measurements [9,10]. Such a double-layer formation is energetically favored: the adsorption energy for the second In layer is 2.49 eV per In atom, which is still larger than the bulk cohesive energy 2.33 eV. In view that the bulk cohesive energy could be regarded as the chemical potential for In atoms, the double-layer formation starting from the preexisting single-layer configuration is thermodynamically preferred to the bulk island formation. In contrast, the $\sqrt{7}$-rect phase is not likely to support a triple In layer: we found in our calculations that the adsorption energy for the third In layer is 2.29 eV per In atom, a little less than the bulk cohesive energy. That is, the formation of an In triple layer is unstable against the bulk island formation. Therefore, the double-layer In thickness is given a unique status in the adsorption thermodynamics.

A really fascinating feature of the double-layer model is the calculated band structure. As shown in Fig. 2(c), the double-layer In structure displays In-derived surface states, the binding energies and dispersions of which compare very well with the ARPES band structure. This excellent agreement between theory and experiment is in contrast with the overall failure seen in the single-layer model. Surviving such a stringent spectroscopic test, the double-layer In structure is very promising as the structural model for the $\sqrt{7}$-rect phase.

The present double-layer model also provides a clear quantification of the previous experimental suggestions for the In thickness given in a rather qualitative manner. The presence of two different In layers in our model naturally explains not only the observation of superreflection or

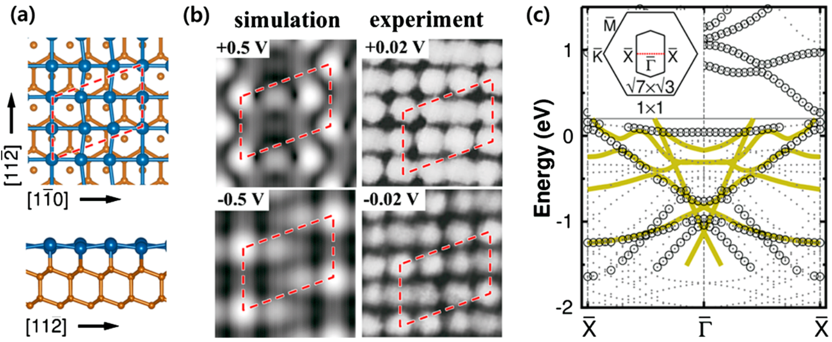

FIG. 1 (color online). Single-layer model for In/Si(111)-$\sqrt{7} \times \sqrt{3}$-rect. (a) Optimized structure. Large (small) balls represent the In (Si) atoms. Dashed lines denotes a $\sqrt{7} \times \sqrt{3}$ unit cell. (b) STM images. Simulations represent the surface of constant density with $\rho = 1 \times 10^{-3}$ $e$/Å$^3$ taken at the bias voltages +0.5 eV (empty states) and −0.5 eV (filled states). Experimental images were taken from Refs. [9,10]. (c) Band structure. Open circles represent the In-derived states which contain more than 50% of charge in the In layer. Solid lines represent the ARPES bands reported in Ref. [13]. The calculated Fermi level was set to zero. For a better comparison, the ARPES bands were shifted by +0.2 eV.

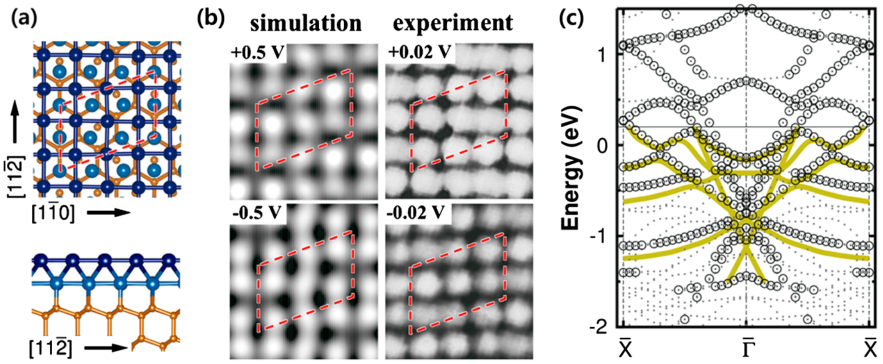

FIG. 2 (color online). Double-layer model for In/Si(111)-$\sqrt{7} \times \sqrt{3}$-rect. (a) Optimized structure. Dark balls represent the top-layer In atoms. (b) STM images taken in the same way as in Fig. 1. (c) Band structure. Open circles represent the In-derived states which contain more than 65% of charge in the In double layer.

double-scattering points in previous electron diffraction studies [17,19], but also clarifies the structural origin underlying the apparent height difference in STM topographs between the In/Si(111)-$\sqrt{7} \times \sqrt{3}$ surface and the In/Si(111)-(4 × 1) surface [8,18]. We calculated the heights of the top In layer from the Si substrate for our double-layer $\sqrt{7}$-rect phase and the well-established single-layer In/Si(111)-(4 × 1) surface [23,24]: the resulting height difference 2.05 Å compares well with the STM measurements of about 2.0 Å [8] and 2.5 Å [18]. Although, despite this apparent height difference, Kraft *et al.* [8] suggested a single In layer on the basis that electronic effects could result in such a height difference even for the same layer thickness because the tip-surface distance is expected to be much smaller on the semiconducting 4 × 1 surface at the same tunneling current. However, the present double-layer $\sqrt{7}$-rect model ensures that such a drastic electronic effect is unlikely in these systems.

Figure 3 shows the detailed electronic structure of the double-layer In model. First, the layer origin of the In-derived surface states is clarified in Fig. 3(a). It is noticeable that the first In layer is responsible for the two linear bands crossing at $\bar{\Gamma}$, which were referred to as quasi-2D free-electron bands forming a nearly circular Fermi contour in the previous ARPES measurement [13]. In our calculations, these bands form almost perfect parabolic bands with an effective mass of 0.94 $m_e$ and the band bottom at −4.61 eV at the $\bar{X}$ point, which could be compared with the values 1.1 $m_e$ and −6.9 eV, respectively, estimated by a model calculation from the ARPES result. Three In bands are crossing the Fermi level ($E_F$), and Fig. 3(b) shows the charge characters of three representative states (denoted as $S_1$, $S_2$, and $S_3$), well displaying their layer distribution and bonding nature. We note that these states near $E_F$ are purely In derived, not interacting with Si. Figure 3(c) shows the Fermi contours constructed by extending the band-structure calculations over the whole $\sqrt{7} \times \sqrt{3}$ Brillouin zone. Our calculations well reproduce the ARPES measurement, most features of which were attributed to the $\sqrt{7} \times \sqrt{3}$ foldings of a nearly circular Fermi contour representing quasi-2D

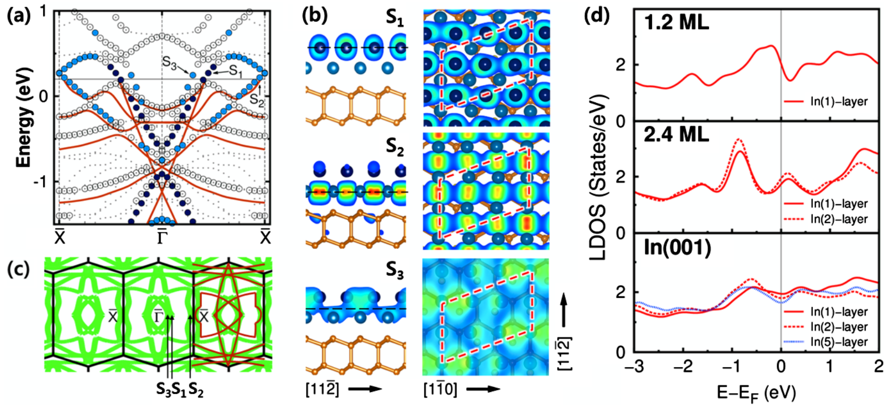

FIG. 3 (color online). Electronic structures of the In double layer. (a) Layer-resolved band structure. Dark and gray circles represent the In states which contain more than 50% of charge in the top and second In layer, respectively. (b) Charge characters of the three surface states marked in (a). The right panels show the in-plane charge distribution on the cross section marked by long dashed lines in the left panels. (c) Fermi contours (thick lines) in comparison with the ARPES data (thin lines) of Ref. [13]. The contour map was obtained at $E_F$ + 0.2 eV for a better comparison with the experiment. (d) LDOS for three different In systems: 1.2 ML, 2.4 ML, and In(001).

free-electron bands [13]. It is interesting to see the structural origin of the contour passing through the $S_2$ point near the zone boundary: in the ARPES study [13], this contour was attributed to an In-Si bonding by assuming a single In layer, but its origin is an inplane In-In bonding localized in the In sublayer in our model, as clearly seen from the calculated charge character in Fig. 3(b).

Finally, our analysis of local density of states (LDOS) demonstrates that the In double layer already reveals its bulk electronic structure. Figure 3(d) shows the layer-resolved LDOS spectra for the double-layer In structure in comparison with those for the single-layer In model and the In(001) surface. While the single-layer In/Si(111) model features a single broad peak near $E_F$, at $-0.20$ eV, the double-layer In/Si(111) surface produces a different spectrum, with two distinct peaks at $-0.84$ and 0.15 eV. Noticeable is that the two In layers produce almost the same LDOS spectra, which indicates that the LDOS for the top In layer is greatly affected by the presence of the In sublayer, thereby forming as a whole a different overlayer system that is distinguished in electronic nature from the single-layer In structure. More interestingly, the LDOS spectra for the In double layer compare well with those for the top-two surface layers of In(001), apart from a little energy shift reflecting different substrate effects, which already recovered the LDOS feature of a bulk In layer (here, represented by the 5th In layer). In view of this bulk-like LDOS feature, it is not surprising that the In overlayer of the In/Si(111)-$\sqrt{7}\times\sqrt{3}$ surface was reported to interestingly show bulk-like electronic properties in superconductivity [14] and metallic transport [16] measurements.

It is worth mentioning that the present double-layer model for the $\sqrt{7}$-rect phase sheds light on the structure of the $\sqrt{7}$-hex phase. The $\sqrt{7}$-hex phase has been assumed to have a single In layer with a coverage of about 1 ML [8], but it is also known that the $\sqrt{7}$-rect phase evolves from the $\sqrt{7}$-hex phase by deposition of a relatively small amount of In (0.15 ML) [11] and both phases typically coexist with almost the same height in STM topographs [8]. It is thus inferred that the $\sqrt{7}$-hex phase also consists of an In double layer with a little less In coverage than the $\sqrt{7}$-rect phase (2.4 ML in our model).

In conclusion, our DFT calculations provide a double-layer In structural model for the In/Si(111)-$\sqrt{7}\times\sqrt{3}$-rect surface. The double-layer In picture is energetically sound and correctly reproduces the microscopic and spectroscopic features reported for this overlayer system. Therefore, the recent experimental claims that the In overlayer properties were pushed to the ultimate limit of one-atom thickness in the In/Si(111)-$\sqrt{7}\times\sqrt{3}$ surface should be reconsidered.

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