Atomic structure and electronic properties of the In/Si(111)2×2 surface

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The Si(111)2×2-In reconstruction can be considered as a precursor phase for the formation of the metallic $\sqrt{7} \times \sqrt{3}$ phases of In overlayers on a Si(111) surface. Using the *ab initio* random structure searching method, comparison of simulated and experimental scanning tunneling microscopy images, and resemblance of the calculated band structure to the experimental angle-resolved photoelectron spectra, we examined various 2×2 structure models with 0.5, 0.75, 1.0, and 1.25 monolayer In coverage. The only model which fits well all the requirements is the one-monolayer model, where three In atoms in the T_4 sites form a trimer centered in the H_3 site and the fourth In atom occupies the on-top (T_1) site.

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I. INTRODUCTION

The In/Si(111) system has attracted a great deal of attention of the researches starting from the very early ages of surface science [1,2]. It has been found that depending on the preparation conditions a set of well-defined metal-induced reconstructions can be formed [3,4] displaying a variety of structural and electronic properties. The set includes $\sqrt{3} \times \sqrt{3}$, $\sqrt{31} \times \sqrt{31}$, 4×1, $\sqrt{7} \times \sqrt{3}$ (of two types, so-called hex-$\sqrt{7} \times \sqrt{3}$ and rec-$\sqrt{7} \times \sqrt{3}$), and 2×2 reconstructions. Though a great body of information has been accumulated during the last almost 50 years, interest in the In/Si(111) reconstructions is preserved nowadays stimulated by recent fascinating discoveries. In particular, the Si(111)4×1-In reconstruction has been found to exhibit a metal-insulator transition to the "8×2" structure at 120 K [5,6]. Physical mechanism underlying this transition remains a debated subject till now [7–9]. Atomic structure of the complicated $\sqrt{31} \times \sqrt{31}$ reconstruction has been refined [10]. Several In/Si(111) reconstructions have been found as a result of specific preparation conditions [11,12].

However, the most advanced recent results have been associated with the $\sqrt{7} \times \sqrt{3}$ reconstructions. Unusual structural transitions (e.g., that to the hexagonal $\sqrt{7} \times \sqrt{7}$ structure) have been detected upon cooling the hex-$\sqrt{7} \times \sqrt{3}$ surface [13]. For the rec-$\sqrt{7} \times \sqrt{3}$ surface reconstruction (which resembles a nearly free two-dimensional electron-gas system [14]) metallic-type conductivity down to 10 K [15] and superconducting transition around 3.0 K [16–18] (i.e., close to that in bulk In) have been found. These were thought as inherent properties of one-atomic-layer thick In film, because to that moment it was commonly accepted that the rec-$\sqrt{7} \times \sqrt{3}$ phase is essentially an In(100) atomic layer (having 1.2 ML In coverage) atop a bulklike Si(111) surface. Meanwhile, the hex-$\sqrt{7} \times \sqrt{3}$ phase was considered to be a pseudomorphic In/Si(111) layer having 1.0 ML In coverage. The suggested In contents for both phases were derived from the high-resolution STM images which display five and six round protrusions (thought to correspond to In atoms) per $\sqrt{7} \times \sqrt{3}$ unit cell for the hex phase and rec phase, respectively [19]. However, very recently the composition of the $\sqrt{7} \times \sqrt{3}$ phases has

been reconsidered and their new structural models have been proposed, namely single-layer model with 1.2 ML In for the hex phase and double-layer model with 2.4 ML In for the rec phase. The concept was proposed by Regamonti etal. [20] and has received its development and confirmation in the subsequent works [21–23].

The viewpoint on the composition of $\sqrt{7} \times \sqrt{3}$ phases urges a reconsideration on the In/Si(111) phase diagram, in particular for In deposition onto Si(111)$\sqrt{3} \times \sqrt{3}$-In surface held at room temperature (RT). It is known that in this case the original $\sqrt{3} \times \sqrt{3}$ structure changes with In deposition sequentially to 2×2, hex-$\sqrt{7} \times \sqrt{3}$, and rec-$\sqrt{7} \times \sqrt{3}$ structures [13,24–27]. This is believed to be the most straightforward procedure to fabricate $\sqrt{7} \times \sqrt{3}$ phases in a controlled way. Note that an alternative procedure with flash heating relatively thick In layers RT deposited onto Si(111)7×7 produces typically a mixture of two $\sqrt{7} \times \sqrt{3}$ phases in the uncontrolled proportion [19] which hampers identifying the actual structure (hex or rec) of the characterized surface [15–17].

The 2×2 reconstruction can be thought as a precursor phase for the formation of the hex-$\sqrt{7} \times \sqrt{3}$ since the transition from one phase to another occurs just upon RT In deposition. Moreover, the same transition, as well as the reversed transition, hex-$\sqrt{7} \times \sqrt{3}$ to 2×2, can be induced locally using scanning tunneling microscope (STM) tip-driven attraction/repulsion of surface In atoms to/from a given area [28,29]. Atomic structure of the 2×2 remains unknown. This is believed to stem from the previously accepted phase diagram where the 2×2 phase occurring in between $\sqrt{3} \times \sqrt{3}$ with 0.33 ML In and hex-$\sqrt{7} \times \sqrt{3}$ with 1.0 ML In could adopt only 0.5 or 0.75 ML In. Attempts to build a satisfactory structural model for these coverage values have failed. A "new" phase diagram allows the 2×2 phase to adopt also 1.0 ML In.

In the present paper we report on the results of the thorough examination of the various 2×2 structure models with 0.5, 0.75, 1.0, and 1.25 ML In coverage (i.e., with two, three, four, and five In atoms per 2×2 unit cell) using the *ab initio* random structure searching (AIRSS) method, comparison of

simulated and experimental STM images, and comparison of the calculated band structure with the experimental angle-resolved photoelectron spectroscopy (ARPES) data. The only model which fits well all the requirements is the one with four In atoms per 2×2 unit cell (hence, with 1.0 ML In), where three In atoms in the T_4 sites form a trimer centered in the H_3 and the fourth In atom occupies the on-top (T_1) site.

II. EXPERIMENTAL AND CALCULATION DETAILS

Our experiments were performed with the Omicron MUL-TIPROBE ARPES system operated in an ultrahigh vacuum ($\sim 2.5 \times 10^{-10}$ mbar). An atomically clean Si(111)7×7 surface was prepared *in situ* by flashing to 1280 °C after the sample was first outgassed at 600 °C for several hours. Indium was deposited from the Ta crucible at a rate of 0.06 ML/min. The In/Si(111)2×2 reconstruction was prepared by In deposition onto the In/Si(111)$\sqrt{3} \times \sqrt{3}$ held at RT. Structural quality of the formed In/Si(111)2×2 surface was evaluated using STM observations. ARPES measurements were conducted using a VG Scienta R3000 electron analyzer and high-flux He discharge lamp ($h\nu = 21.2$ eV) with a toroidal-grating monochromator as a light source. For ARUPS measurements samples were cryogenically cooled down to 78 K.

First-principles calculations based on density functional theory [30,31] were performed using projector-augmented-wave potentials [32], as implemented in the Vienna *ab initio* simulation package (VASP) [33,34]. The exchange-correlation functional was treated in the local density approximation (LDA) [35]. The kinetic cutoff energy was 400 eV, and a Monkhorst-Pack $6 \times 6 \times 1$ k-point mesh was used to sample the Brillouin zone. The Si(111)2×2 supercell geometry was simulated by a repeating slab of four Si bilayers and a vacuum region of ~ 15 Å. Si atoms in the bottom bilayer were fixed at their respective bulk positions, the top three bilayers were allowed to fully relax, and dangling bonds on the bottom surface were saturated by hydrogen atoms. The sensitivity of total energies on slab thickness, vacuum region, kinetic energy cutoff, etc. have been tested, and the geometry optimization is performed until the residual force was smaller than 20 meV/Å. The band structures with spin-orbit coupling effect were calculated and presented. We also verified the surface states and projected bulk bands by using symmetrical Si double surface models and the results were consistent with the single one-side surface model. In order to find the most stable structures of each In/Si(111)2×2 structure with different In coverage, we used the *ab initio* random structure searching (AIRSS) [36] method which has already proven to be an efficient and effective method for exploring unanticipated structures of solids [37], point defects [38], surfaces [39], and clusters [40]. The basic algorithm is simple: We take a population of random sensible structures and relax them through energy minimization. Details of the used AIRSS procedure are given in the Supplemental Material [41–43]. In this study, only the most stable structures of each In/Si(111)2×2 with different In coverage were presented.

III. RESULTS AND DISCUSSION

As the first step of consideration, we have applied the AIRSS method to elucidate the most stable configurations formed upon placing two, three, four, and five In atoms onto the 2×2 unit cell of the bulklike-terminated Si(111) surface. The obtained configurations are shown in Fig. 1. In particular, the most stable configuration with two In atoms (0.5 ML In) appears to be the one with In atoms occupying the T_4 sites [Fig. 1(a)]. The nearest candidate structure with In atoms in the H_3 sites is by 200 meV per unit cell less stable. One can notice in Fig. 1(a) that the configuration has actually a C_{1h} symmetry due to the chainlike structure with 2×1 periodicity. In the most stable configuration with 0.75 ML In [Fig. 1(b)], In atoms occupy three T_4 sites leaving the fourth T_4 site vacant. The structure has C_{3v} symmetry. The rival structure with In atoms forming chains is 141 meV less stable. The most stable configuration with 1.0 ML In contains three In atoms in the T_4 sites forming a trimer centered in the H_3 site and one more In atom occupying the T_1 site [Fig. 1(c)]. It has C_{3v} symmetry and is 133 meV more stable than the configuration when In atoms form a trimer centered in the T_4 site (three In atoms in the H_3 sites and one more In atom occupying the T_1 site). For 1.25 ML In coverage, the most stable configuration has C_{1h} symmetry and complicated structure which can be denoted as pentagon-hexagon chains [Fig. 1(d)]. Consideration based on thorough evaluation of the formation energies taking into account
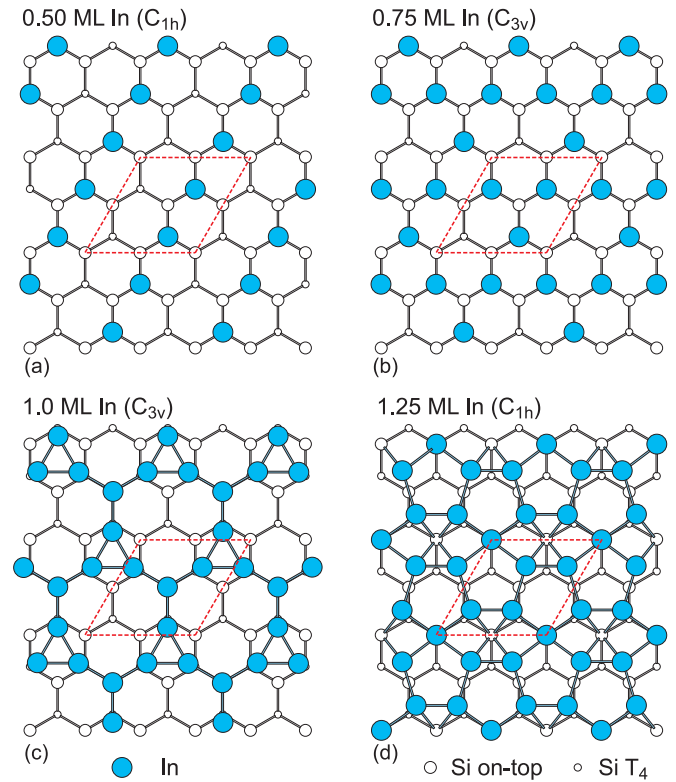

FIG. 1. (Color online) The most stable model configurations of the In/Si(111)2×2 surface determined using AIRSS method for In coverage of (a) 0.5 ML, (b) 0.75 ML, (c) 1.0 ML, and (d) 1.25 ML. In atoms are shown by blue circles, Si atoms are shown by open circles, the larger for on-top Si atoms in T_1 sites, the smaller for the Si atoms in the T_4 site. The 2×2 unit cell is outlined by the red dotted line.
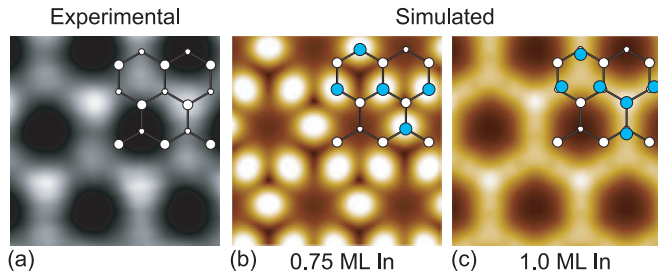
FIG. 2. (Color online) (a) Filled-state (+1.3 V) experimental STM image of the In/Si(111)2×2 surface compared with the simulated STM images (+1.0 V) for (b) 0.75-ML model and (c) 1.0-ML model. To tie the STM images to the surface structure, the schematic of the Si(111) surface structure is superposed on the experimental STM image and model structures on the corresponding simulated STM images. In atoms are shown by blue circles, Si atoms are shown by open circles, the larger for on-top Si atoms in T_1 sites, the smaller for the Si atoms in the T_4 site.

chemical potentials of bulk In and Si, as well as of stable Si(111) surface, demonstrates that the 1.0-ML structure possesses the highest stability among structures with other In coverage [41].

To make a proper choice between the above stable configurations, we have simulated their filled-state STM images and compared them with the experimental one (Fig. 2). It is worth noting that acquiring the high-resolution empty-state STM images of In/Si(111)2×2 is often problematic and results sometimes in STM images with different appearance [25,44]. Having no clear arguments to conclude what the "true" empty-state STM image of 2×2-In looks like, we have limited our consideration by only the filled-state images. In the experimental filled-state STM images, the In/Si(111)2×2 surface has a characteristic honeycomb appearance [Fig. 2(a)] which has been detected in many STM studies [13,25,28,44]. The image unambiguously demonstrates that the surface has a C_{3v} symmetry, which means that the models with 0.5 and 1.25 ML In (having C_{1h} symmetry) can be safely ruled out. Hence, only the models with 0.75 and 1.0 ML In (having C_{3v} symmetry) are left as plausible candidates and their simulated STM images are shown in Figs. 2(b) and 2(c), respectively. One can see that among the two models the 1.0-ML model demonstrates much clearer resemblance with the experimental image, while for the 0.75-ML model the congruence is not apparent. Moreover, the simulated STM image of the 1.0-ML model reproduces nicely all the fine features of the experimental image. Namely, each characteristic hexagon in the STM image is built of six protrusions, three bright and three dim. It has been experimentally determined in Ref. [25] that the bright protrusions are located in the T_1 sites and dim protrusions are in the H_3 sites. The same is given by the model, where the bright protrusions correspond to single In adatoms in the T_1 sites, while the dim protrusions correspond to In trimers centered in the H_3 site. In conclusion, consideration based on comparison of the simulated and experimental STM images favors greatly the 2×2-In model with 1.0 ML In coverage.

The next step is to compare the calculated electronic structures with the experimental ARPES spectrum of the In/Si(111)2×2 surface. The results of calculations are summarized in Fig. 3. The main conclusion which can be derived
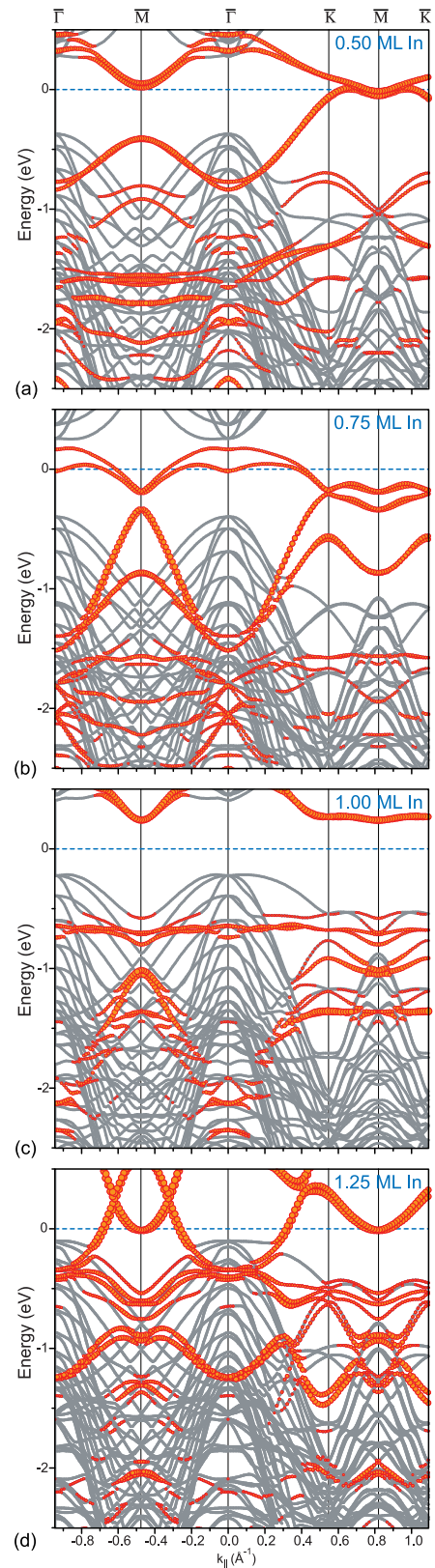

FIG. 3. (Color online) Calculated band structure for the models (containing eight Si bilayers) of the In/Si(111)2×2 surface with In coverage of (a) 0.5 ML, (b) 0.75 ML, (c) 1.0 ML, and (d) 1.25 ML. The surface state bands are indicated by red, the projected quantum well states are shown in gray. The size of the red symbols reflects the weight of the states in the surface In atoms.
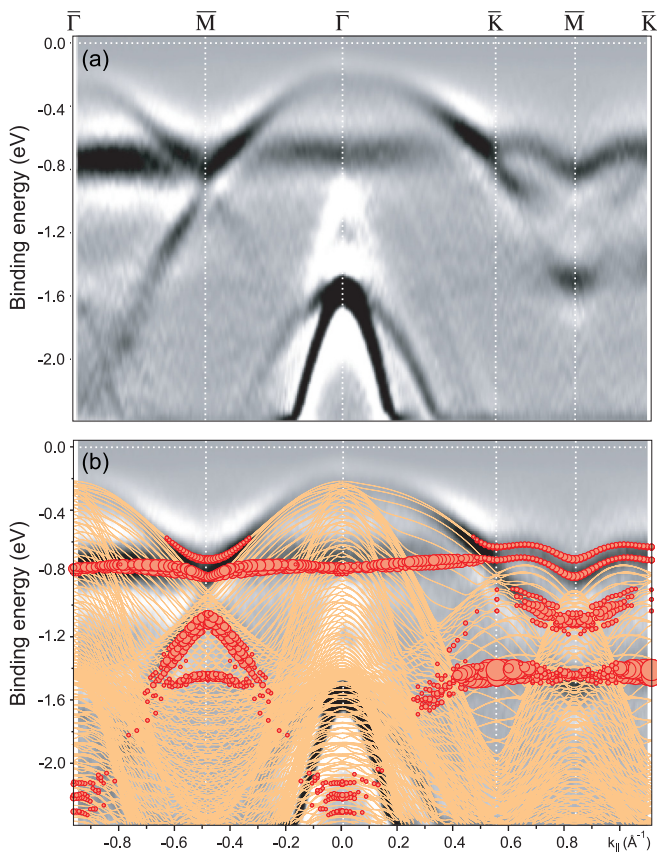
FIG. 4. (Color online) (a) Experimental ARPES spectrum from the In/Si(111)2×2 surface. (b) Calculated surface-state band structure (38 Si bilayers model) superposed with experimental ARPES spectrum. The size of the red symbols reflects the weight of the states in the surface In atoms.

model structures are metallic. Experimental ARPES spectrum shown in Fig. 4(a) demonstrates that the In/Si(111)2×2 surface is, indeed, a semiconductor having no bands crossing the Fermi level. Moreover, one can see that the calculated electronic structure of the 1.0-ML model reproduces nicely all the main features of the experimental ARPES spectrum [see Fig. 4(b)]. Thus, the 2 × 2-In model with 1.0 ML In coverage is also the best model from the viewpoint of its electronic properties.

In addition, the proposed 1.0-ML model is supported by the reported core-level photoemission spectroscopy data [45] which demonstrate that the In 4d spectrum for 2 × 2-In contains two components, of which the main component (C_1) constitutes 73.9% intensity, while the the extra component (C_3) yields 26.1% intensity. The C_1 is similar to that for $\sqrt{3} \times \sqrt{3}$-In and assumed to be related to the In adatoms on the T_4 site. The C_3 component is due to the In adatoms occupying a qualitatively different site. Assuming this site to be T_1, one can see a clear resemblance between the proposed 1.0-ML model and these data.

IV. CONCLUSION

In conclusion, the one-monolayer model of the In/Si(111)2×2 surface, where three In atoms in the T_4 sites form a trimer centered in the H_3 site and the fourth In atom occupies the T_1 site, has been found to be the only one to fit all the available requirements. It has the lowest formation energy, its simulated STM image reproduces all the features of the experimental STM image, and its calculated band structure coincides with that obtained in the ARPES experiments.

is that the promising 1.0-ML model is the only one which displays clear semiconductor properties, while all the other

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