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First-principles Study of Geometric and Electronic Structures of Si(111)-$\sqrt{7}\times\sqrt{3}$-In Surface Reconstruction

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In order to determine the structures of Si(111)-$\sqrt{7}\times\sqrt{3}$-In surfaces and to understand their electronic properties, we construct six models of both hexagonal and rectangular types and perform first-principles calculations. Their scanning tunneling microscopic images and work functions are simulated and compared with experimental results. In this way, the hex-H3' and rect-T1 models are identified as the experimental configurations for the hexagonal and rectangular types, respectively. The structural evolution mechanism of the In/Si(111) surface with indium coverage around 1.0 monolayer is discussed. The $4\times1$ and $\sqrt{7}\times\sqrt{3}$ phases are suggested to have two different types of evolution mechanisms, consistent with experimental results.

Key words: Surface reconstruction, Si(111)-$\sqrt{7}\times\sqrt{3}$-In, Density functional theory, Scanning tunnelling microscopic image

I. INTRODUCTION

In recent years, semiconductor surfaces with a few layers of metal covered have attracted lots of attentions. These low-dimensional structures can show diverse electronic phenomena, such as charge density waves [1, 2], metal-insulator transitions (MIT) [3], Wigner lattices [4], high-temperature superconductivity [1], supercurrents, and metallic transport [5, 6].

These surface reconstructions are sensitive to temperature and metal atom coverage, and this is especially true for silicon surfaces covered with indium atom [7–10]. With increase of indium coverage, a series of phases have been found [11], including $7\times7$, ($\sqrt{3}\times\sqrt{3}$)R30°, ($\sqrt{3}\times\sqrt{3}$)R90°, $4\times1$, $\sqrt{7}\times\sqrt{3}$, $2\times2$, and (1×1)R30°. These surfaces gradually evolve from semiconductor ($7\times7$) to 1D metal (4×1), and finally to 2D metal ($\sqrt{7}\times\sqrt{3}$). These phases with similar indium coverage can coexist and are easy to transform to each other [12]. In these Si(111)-In surfaces, two different kinds of motifs can be seen. One kind is the triangle motif, in e.g. Si(111)-($\sqrt{3}\times\sqrt{3}$)In (abbreviated to ($\sqrt{3}\times\sqrt{3}$)I) surface [13, 14], which is similar to the cases of clean Si(111)-(7×7) and Si(111)-(5×5) surfaces. The other kind is the belt motif, including Si(111)-4×1-In (abbreviated to 4×1), Si(111)-$\sqrt{7}\times\sqrt{3}$-In (abbreviated to $\sqrt{7}\times\sqrt{3}$) and 2×2 surfaces.

On the experimental hand, the $\sqrt{7}\times\sqrt{3}$ structures have been extensively investigated by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Two different structures of hexagonal-$\sqrt{7}\times\sqrt{3}$ (abbreviated to hex-) and rectangular-$\sqrt{7}\times\sqrt{3}$ (abbreviated to rect-) types have been reported by Kraft et al. [11, 15, 16]. The indium coverage was 1.0 ML (monolayer) for hex-$\sqrt{7}\times\sqrt{3}$ and 1.2 ML for rect-$\sqrt{7}\times\sqrt{3}$, respectively. Recently, Vlachos et al. found that the $\sqrt{7}\times\sqrt{3}$ phase existed at coverage of 1.2–2.2 ML from LEED when investigating growth of indium protrusion on the Si(111) surface [17]. Xue group verified that the 1.0 ML indium coverage $\sqrt{7}\times\sqrt{3}$ surface was a 2D superconductor [18], which was proposed by Rotenberg et al. [19]. Furthermore, metallic transport has been found on this monoatomic layer surface by Shiro et al. for the first time [6]. A reversible phase transition was found by Saranin et al. in the pseudomorphic hex-$\sqrt{7}\times\sqrt{3}$-In layer on Si(111) [12], which indicated that the hex-$\sqrt{7}\times\sqrt{3}$ surface was a basic fragment. Similar result has been found by Tringides group when they studied the diffusion of indium atoms on silicon surface [20].

Up to now, most theoretical works in this field are concentrated on the 4×1 surface [21–23], while the structures and electronic properties of other surfaces have not received enough attention. However, the structure and the MIT mechanism of the Si(111)-4×1-In surface are still under debate [23]. The $4\times1$ and $\sqrt{7}\times\sqrt{3}$ surfaces share the same belt motif and close indium coverage. Therefore, the $\sqrt{7}\times\sqrt{3}$ surfaces may give some clues to the puzzles on Si(111)-4×1-In surface. Besides, the reversible structural transformation based on the $\sqrt{7}\times\sqrt{3}$-In surface is suggested to be used to modulate

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self-assembly and electronic properties.

Although lots of experimental progress has been made on the $\sqrt{7}\times\sqrt{3}$-In surfaces, there is no theoretical work on the structures and electronic properties of these surfaces so far. In this work, via ab initio calculations, we identify the structures of the $\sqrt{7}\times\sqrt{3}$-In surfaces by simulating their STM images, and obtain their electronic properties including surface energies and work functions. The structural stability is also discussed.

II. CALCULATION DETAILS

The calculations have been performed by the Vienna 
ab initio simulation package (VASP) [24, 25]. The 
PAW-PW91 methods have been employed to describe 
the interaction between the electrons and the ions [26]. A kinetic cutoff energy of 400 eV is chosen. For higher accuracy, the indium 4d electrons are included in the valence electrons. Up to 12 layers of silicon have been included, among which the bottom 4 layers are constrained to the calculated lattice constant of bulk silicon (5.46 Å) and the other 8 layers are fully relaxed. For all the models, the dangling bonds of the bottommost silicon atoms are saturated with hydrogen. The Si–H bond length is constrained to 1.49 Å. A vacuum of 15.0 Å is used to minimize unphysical interaction between cells. The $\sqrt{9}\times\sqrt{13}$ Monkhorst-Pack k-point grid has been employed to ensure computation accuracy [27]. In the present study, six models of $\sqrt{7}\times\sqrt{3}$-In including three kinds of high-symmetry sites are considered, as illuminated in Fig.1. The simulated STM images are obtained as the iso-density contours of the local density of states based on the Tersoff-Hamann approximation [28]. The tips are 1.5 Å above the top indium atoms.

The surface energies are defined as,

$$E_{\text{surf}} = \frac{E_{\text{total}} - N_{\text{In}} \times \mu_{\text{In}} - N_{\text{Si}} \times \mu_{\text{Si}} - N_{\text{H}} \times \mu_{\text{H}}}{N_{\text{Si}(1\times1)}}$$

In this equation, $N_X$ (X=In, Si, or H) is the number of the X atoms in the $\sqrt{7}\times\sqrt{3}$ cell, and $\mu_X$ stands for the chemical potential of the element X. The silicon and indium chemical potentials are calculated as the energy per atom of bulk silicon and indium, and the hydrogen chemical potential are calculated from hydrogen molecule.

Because all the models have the same numbers of layers and the same size, we will thereafter use the relative surface energy $\Delta E$ for simplicity. The relative surface energies are all compared with that of the rect-T4 model (because it is the lowest) and defined as

$$\Delta E = \frac{E_{\text{model}} - E_{\text{rect-T4}} - (N_{\text{In}} - 6) \times \mu_{\text{In}}}{N_{\text{Si}(1\times1)}}$$

For the rect-$\sqrt{7}\times\sqrt{3}$ models $N_{\text{In}}$ is 6, and for the hex-$\sqrt{7}\times\sqrt{3}$ models $N_{\text{In}}$ is 5. For all the models, the surface size $N_{\text{Si}(1\times1)}$ is 5, i.e., there are 5 primitive Si(111)-1×1 cells.
III. RESULTS AND DISCUSSION

A. Relaxed structure and STM images

As shown in Fig.1 (a), (b), and (c), the indium coverage of the hexagonal structures is 1.0 ML. For the fully relaxed hexagonal structures, almost all the indium atoms in the models of T4 and H3 are located on the T4 and H3 sites. Actually, the hex-T4 and hex-H3 models can be regarded as pseudomorphic of silicon-1×1-In surface. In the hex-H3′ model, three indium atoms are around the H3 sites, and the other two indium atoms are around the T4 sites. In the hex-H3 and hex-T4 model, all the indium atoms are at nearly same height. But in the hex-H3′ model, the biggest height difference between the indium atoms is 0.26 Å, which is very close to the experimental value of 0.25 Å [11].

The rectangular structures are shown in Fig.1 (d), (e), and (f). With the coverage of 1.2 ML, six indium atoms can be found in each cell. For each model, two indium atoms are shared by two cells on the short side, and the other four indium atoms are in the center of the cell. In rect-T4 and rect-H3, the motif of the central four indium atoms is a parallelogram. While in the rect-T1 model, this motif is nearly rectangular. The height differences of indium atoms on the surfaces are 0.62, 0.57, and 0.56 Å for rect-T4, rect-H3, and rect-T1, respectively. All of these values are very close to each other and comparable with the experimental result 0.75 Å [11]. Compared with the hexagonal structures, the surface indium layers in the rectangular structures are much more rugged.

The simulated STM images of the six structures are shown in Fig.2, from which we can easily see their relations with corresponding structural features. In the images of the hexagonal models, there are five bright points in one cell, and the bright points are right on top of the indium atoms. In the hex-T4 and hex-H3 images, the bright points show a honeycomb character, as the indium atoms do. In the hex-H3′ image, in each cell there is a zigzag bright chain composed of two bright points, which is parallel with the short side of the cell ([112] direction). Between two neighboring zigzag chains, we can find a chain of rhombi in the same direction. Compared with other two points, the nodal points on the rhombus chains are a little darker. In the hex-H3′ model, the zigzag chain atoms and the rhombus chain atoms are around the T4 and H3 sites, respectively. In the experimental STM images of the hexagonal structures [16], dimers of bright spots can be found in the [110] direction, and among them there are three weak spots. The dimers of bright spots and one weak spot between them make the rhombus chains, and the other weak dimers make the zigzag chains. Therefore, the simulated STM image of hex-H3′ agrees with the experimental image very well.

The simulated rectangular images have six bright positions in each cell, as shown in Fig.2 (d), (e), and (f).

FIG. 2 The simulated STM images of Si(111)-\(\sqrt{7}\times\sqrt{3}\)-In models, with bias voltage of +2 V. The models are: (a) hex-T4, (b) hex-H3, (c) hex-H3′, (d) rect-T4, (e) rect-H3, (f) rect-T1. The pictures are drawn with the software Xcrysden [30].

The zigzag chains as in the hex-H3′ image can be found in all the three rectangular images. But different from the hex-H3′ image, in the rectangular images the rhombus chains are replaced by rectangular chains composed of two big bright points and two small bright points. The differences between the images of the rectangular models lie in the relative position and size of the points in the zigzag chain. In the rect-T4 and rect-H3 models, the bright points can be divided into three kinds based on their sizes. The four rectangular spots can be divided into a big dimer and a small dimer, and the sizes of the zigzag chain spots are in the middle. However, in the rect-T1 image, the sizes of the zigzag chain points are different. One of them is close to that of the big dimer, and the other one is close to that of the small dimer. Therefore, only two different sizes can be found in the rect-T1 image. Another differences between the rect-T1, rect-T4, and rect-H3 images lies in the positions of the zigzag chain atoms. In the rect-T1 image, the zigzag chains slide a little in the [112] direction, compared with the rect-T4 and rect-H3 chains. As shown in Fig.2 (d)–(f), the zigzag chains in the rect-T4 and rect-H3 images are around the T4 sites, and in the rect-T1 image the zigzag chain atoms are much closer to the T1 sites. This movement renders the chain positions directly on the extension line of the big dimers and the small dimers, which changes the surface motif to a rectangle. In the short side direction ([112]), the points alternate bright and less bright, and in the vertical direction ([110]), the points alternate three bright and three less bright. These alternations in both directions exactly reproduce the experimental features.

By comparing the simulated STM images and the height differences of In atoms, we find that the hex-H3′ and rect-T1 models can best reproduce the experimen-
of chains in the vertical direction of indium atom. Besides, in the rect-T1 image, a new kind of chains is generated.

The surface motif is determined by both the indium-indium interaction and the silicon-indium interaction. With the increase of indium coverage, the indium-indium distance becomes shorter, and thus their interaction gets stronger. The slide of the zigzag chains further shortens the indium-indium distance, and enhances the interaction between the indium chains. With low coverage, the indium-indium interaction is weak, and the surface structure is determined mainly by the silicon-indium interaction. With high coverage, the interaction of indium-indium becomes strong, the indium layers will tend to keep their bulk order and make the surface metallic. With middle coverage, the strengths of the two interactions are comparable, thus the mismatch between Si(111) and In(111) will be a key factor to the structure and electron properties.

Same with the rect-T1 model, the 4×1 phase possesses the similar belt motif in the direction of [110]. In such Si(111)-In surface, two kinds of indium monatomic layers have been found, i.e., the substitutional-layer and the adatom layer. Different from the 4×1 phase, the indium atoms in the $\sqrt{7} \times \sqrt{3}$ phases are located on the silicon layer uniformly. The 4×1 structure might be regarded as a substitutional-layer structure with additional recombination of the Si surface. The height difference between the $\sqrt{7} \times \sqrt{3}$ and 4×1 structures is about 2.7 Å in experiment [12], and the transformation between the $\sqrt{7} \times \sqrt{3}$ and 4×1 structures is difficult. On the other hand, the $\sqrt{31} \times \sqrt{31}$ and 4×1 phases are easy to coexist and transform. The $\sqrt{31} \times \sqrt{31}$ surface is a substitutional-layer structure, which makes it easy to coexist with and transformed to the 4×1 structures [14]. Therefore, although with similar indium coverage, the evolution mechanisms of the 4×1 and $\sqrt{7} \times \sqrt{3}$ phases are quite different. The same conclusion has also been drawn by Saranin et al. based on the experimental results on (In, Au)/Si(111) surface [31].

### B. Structural evolution mechanism

It is interesting that with the addition of one indium atom into a unit cell, the motif of the surface transforms from hexagonal to rectangular. In this transformation, there are significant changes of indium-indium distances. The indium-indium distances in the hex-T4 and hex-H3 models are between 3.83 and 3.88 Å, close to the silicon-silicon distance in the Si(111) surface, 3.83 Å. In the hex-H3' model, the indium-indium distances are 3.34 and 3.40 Å in the zigzag chains, and between 3.45 and 4.17 Å in the rhombus chains. The distances between the chains are about 4.7 Å. In the model of rect-T4 (H3, T1), the In-In distances in the zigzag chains are between 3.38 (3.34, 3.38) and 3.40 (3.40, 3.39) Å, and the distances between the zigzag chains and the rectangle chains are between 3.45 (3.21, 3.10) and 4.00 (4.08, 3.44) Å. Again, the indium-indium distances in the hex-H3' and rect-T1 models are consistent with the experimental STM results. Therefore, we identify the hexagonal and rectangular structures as these two models, respectively.

From the images of hex-H3' and rect-T1, we can see that the characteristic of indium zigzag chains is kept under the transformation with the addition of one indium atom. Besides, in the rect-T1 image, a new kind of chains in the vertical direction [110] are generated.

### C. Energetic sequences and work function

To compare the relative stability of the proposed models, we calculate their surface energies and list them in Table I. For both the hexagonal and rectangular structures, the T4 models are the most stable. If we take into consideration of the negative lattice mismatch...
(\sim 15\%) between the In(111) and Si(111) lattice constant (3.24 Å vs. 3.83 Å), it is reasonable that the rectangular structure with coverage of 1.2 ML is more stable than the hexagonal structure with coverage of 1.0 ML. The hex-T4 and hex-H3 models are more stable than the hex-H3’ model, which seems to be contradicted to our above conclusion. However, we would like to insist the identification of hex-H3’ as the experimental hexagonal structure, and attribute this to the kinetic effect in the making process of the $\sqrt{7} \times \sqrt{3}$ surface. In experiments, the $\sqrt{7} \times \sqrt{3}$ surfaces are usually generated via high temperature annealing methods, therefore it is likely that a non-global minimum structure is obtained. Recent experiments reveal that with increase of indium coverage, most Si(111)-In surfaces except 4×1 gradually change to 1×1 phase [30]. This implies that experimental $\sqrt{7} \times \sqrt{3}$ phase might be a meta-stable phase [20], consistent with our above discussions.

For the hexagonal structures, the work functions of the hex-H3 and hex-T4 models are similar. The work function of the hex-H3’ model is about 0.12 eV higher than those of the hex-H3 and the hex-T4 model. For the rectangular structures, the work function of the rect-T4 model is similar to that of the hex-H3’ model, while the work function of the rect-H3 model is about 0.1 eV higher than that of the rect-T4 model. The rect-T1 model has the highest work function. For the hex-H3’ and rect-T1 models, the work function of the rectangular one is about 0.2 eV higher than that of the hexagonal one. On the experimental side, it is found that the work function of Si(111)-7×7 surface is about 4.6 eV and the work function of In/Si(111) surface around 1.0 ML at room temperature is 0.3 eV smaller [33, 34]. Here we predict the work function of the hex-H3’ model to be 4.34 eV, which is close to the experimental 1.0 ML result. Nevertheless, in experiments most of the 1.0 ML results should correspond to the 4×1 structure rather than the hex-$\sqrt{7} \times \sqrt{3}$ structure. The temperature effect is also found to be important to the work function of In/Si(111) surface. Therefore, we suggest more experimental investigations on the $\sqrt{7} \times \sqrt{3}$ surfaces, especially the surface electronic properties.

IV. CONCLUSION

In summary, we investigated the atomic structures of Si(111)-$\sqrt{7} \times \sqrt{3}$-In surfaces by theoretical simulations. Six models of the hexagonal and rectangular types have been constructed and calculated. By comparing their simulated STM images, height differences of In atoms and work functions with experiments, we identify the hex-H3’ and rect-T1 models as the experimental structures. These structures have higher energies than the others in zero temperature calculations. We propose that kinetic processes are crucial in making these surfaces. The rising mismatch between Si and In with indium coverage is expected to change the balance between the interactions of In-In, Si-Si, and Si-In, therefore determines the motifs of the Si(111)-$\sqrt{7} \times \sqrt{3}$-In surfaces. The growth mechanisms of the $\sqrt{7} \times \sqrt{3}$ phases are different from that of the 4×1 phase. The temperature and coverage induced phase transformations on these surfaces give these systems good potential on modulation of electronic structure.

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