



# Bismuth–indium two-dimensional compounds on Si(111) surface



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## ABSTRACT

Using scanning tunneling microscopy (STM) observations, it has been found that codeposition of Bi and In onto Si(111)  $7 \times 7$  surface, followed by 250–550 °C annealing, induces formation of a set of the ordered (Bi, In)/Si(111) stable structures, including  $2\sqrt{3} \times 3$ ,  $5 \times 5$ ,  $\sqrt{7} \times \sqrt{7}$  and  $2 \times 2$ . Under appropriate conditions, the structures can occupy almost the entire surface, except for  $2\sqrt{3} \times 3$  which is formed only locally. Scanning tunneling spectroscopy has demonstrated that the  $5 \times 5$  and  $\sqrt{7} \times \sqrt{7}$  structures are semiconducting, while the  $2 \times 2$  is metallic. The  $5 \times 5$ ,  $\sqrt{7} \times \sqrt{7}$ , and  $2 \times 2$  structural models have been proposed on the basis of DFT calculations and comparison of simulated and experimental STM images.

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## 1. Introduction

Present work has been done in the frame of searching surface alloys on silicon with spin-split bands due to Rashba effect as promising materials for spintronics. The choice of the Bi–In couple was dictated by the following reasons. Bismuth forms one-layer structure on the Si(111) surface,  $\beta\text{-}\sqrt{3} \times \sqrt{3}$  reconstruction [1] with a giant spin splitting of surface-state bands [2,3,4]. However, the split bands are located in the valence band without crossing the Fermi level [2,3,4]. Meanwhile, for spintronic applications, materials with metallic properties having spin-splitting near Fermi level and which can be grown on a semiconductor are actually required. Thus, thin Bi film on Si(111) has to be modified by another metal to get required properties. Two alloys of this kind, Si(111) $\sqrt{3} \times \sqrt{3}$ -(Bi, Na) [5] and Si(111) $4 \times 4$ -(Bi, Ag) [6], have already been discovered, but both have certain drawbacks. The first alloy, Si(111) $\sqrt{3} \times \sqrt{3}$ -(Bi, Na), has a giant spin splitting of metallic surface-state bands, but it is unstable against even low-temperature heating. The second one, Si(111) $4 \times 4$ -(Bi, Ag), is stable up to ~250 °C, but it has a modest spin-splitting and it cannot be formed as well-ordered array in a simple way, because formation of other (Bi, Ag)/Si(111) structures occurs locally at any local lack or excess of Bi [6]. Indium is thought to be a promising candidate to complete the metal pair. Bismuth and indium hypothetically could form the III–V semiconductors, but there has been no report on synthesis of this compound. On the other hand, alloys

of these metals in a wide range of compositions are metallic and are usually used as a solder or, much rare, in ultra-reliable accumulators. Thus, one can expect that possible low-dimensional Bi–In alloys on Si(111) might be thermally stable and metallic. An additional interest to the growth of the atom-layer Bi–In compounds is associated with very recent theoretical predictions that two-dimensional III–V compounds might possess honeycomb structure and exhibit the properties of two-dimensional topological insulator [7,8]. Though such a behavior was predicted to various III–V pairs, it has never been yet realized in experiment [9]. Thus, finding an appropriate III–V compound remains a challenging task.

The results of the present study on the (Bi, In)/Si(111) system have revealed that Bi–In pair forms a set of surface alloys having  $5 \times 5$ ,  $\sqrt{7} \times \sqrt{7}$ , and  $2 \times 2$  periodicities, each of which can occupy almost the entire surface. The plausible atomic models of the structures have been constructed using density-functional-theory calculations. It appears that none of the (Bi, In)/Si(111) structures possesses honeycomb atomic arrangement predicted theoretically. Among others, the Si(111) $2 \times 2$ -(Bi, In) is the only metallic structure and might be thought as a promising spintronics material with spin-split metallic bands, but it suffers from the limited size of domains and high density of defects.

## 2. Experimental and calculation details

Experiments were carried out with Omicron STM and low energy electron diffraction (LEED) operated in an ultrahigh vacuum ( $\sim 7.0 \times 10^{-11}$  Torr). Atomically-clean Si(111) $7 \times 7$  surfaces were prepared in situ by flashing to 1280 °C after the samples were first

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outgassed at  $\sim 600$  °C for several hours. Bismuth was deposited from commercial HTEZ40 cell. Deposition rate of Bi was calibrated using Si(111) $\beta\text{-}\sqrt{3} \times \sqrt{3}$ -Bi surface (1 monolayer Bi [1]) as a reference by room temperature (RT) deposition of Bi onto Si(111) $7 \times 7$  followed by annealing at 500 °C. (1 monolayer (ML) =  $7.83 \times 10^{14}$  atoms/cm<sup>2</sup> for Si(111).) Deposition of indium was carried out from a tantalum tube. Deposition rate of In was calibrated by formation of the Si(111) $4 \times 1$ -In surface containing 1 ML of In [10]. Annealing temperature of the samples in the range of 250–600 °C was measured by thermocouple.

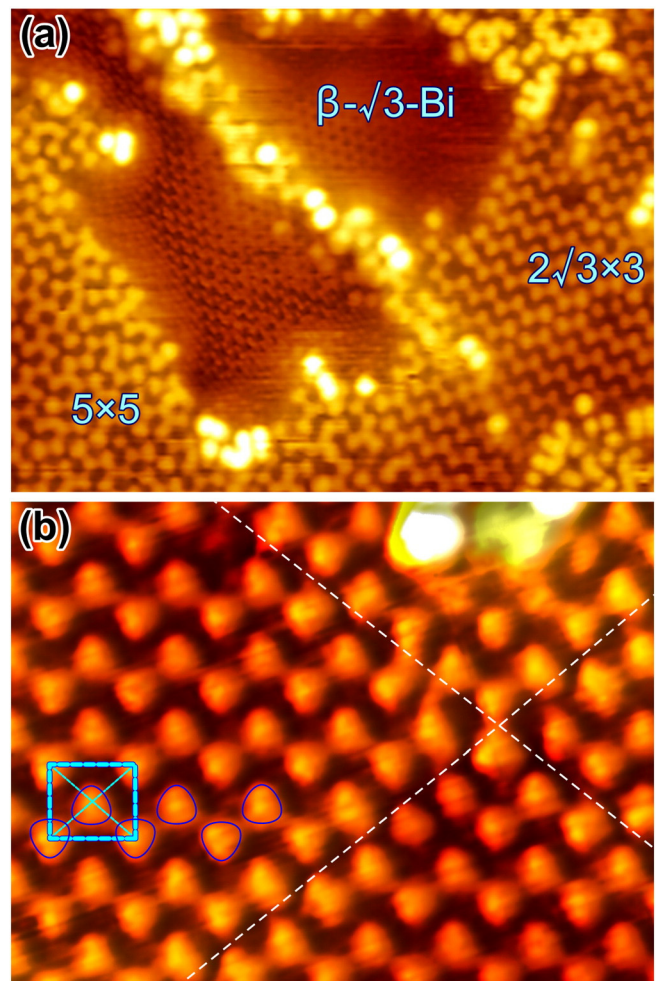
For evaluation of composition of each (Bi, In)/Si(111) structure, a set of experiments was conducted where doses of In and Bi were varied and area fractions occupied by new and known structures were measured in the STM images. The initial surface was usually the Si(111) $\alpha\text{-}\sqrt{3} \times \sqrt{3}$ -Bi which contains nominally 1/3 ML Bi and 2 (or 0) ML Si [1]. In these experiments growth temperatures were chosen as low as possible to avoid significant desorption of metals, namely 250 °C for the  $2 \times 2$  structure and 350 °C for the  $5 \times 5$  and  $\sqrt{7} \times \sqrt{7}$  structures. The data set on structure area fractions versus In and Bi doses was analyzed to extract the Bi-In composition of a given structure. As for the Si coverage incorporated in the structure, it is typically deduced from the quantitative evaluation of Si mass transport (e.g., from step shifts or “hole-island” pair areas). In the present experiments, no essential Si mass transport was detected when the Si(111) $\alpha\text{-}\sqrt{3} \times \sqrt{3}$ -Bi was taken as initial surface. Taking into account that the latter surface is nominally silicon free, all the (Bi, In)/Si(111) structures were concluded to incorporate two (or zero) monolayers of Si.

To verify the (Bi, In)/Si(111) structural models, their stability was evaluated using the plane-waves total-energy calculations based on density functional theory (DFT) [11] with projector-augmented wave pseudopotentials [12] using Vienna Ab Initio Simulation Package (VASP) [13,14]. For the exchange and correlation functional, the generalized gradient approximation (GGA) [15] has been employed. The electronic wave functions were expanded in a plane-wave basis set with an energy cutoff of 20 Ry. The surface was simulated by periodic slab geometry with a calculated structure unit supercell containing eight Si atomic layers and Bi–In layers according to the proposed model. The dangling bonds of the bottom slab layer were saturated by hydrogen atoms, which as well as bottom bilayer silicon atoms were fixed, while the rest atoms were free to move. A vacuum region of approximately 15 Å was incorporated within each periodic unit cell to prevent interaction between adjacent surfaces. The geometry was optimized until the total energy is converged to  $10^{-4}$  eV and the total force is converged to  $10^{-3}$  eV/Å. The sensitivity of formation energies on kinetic energy cutoff, k-points setup, and the total energy/force numerical accuracy has been tested and found to have a negligible effect on the total energy differences. Simulated STM images of the relaxed models were generated from local density of states (DOS) according to Tersoff–Hamann approach [16].

### 3. Results and discussion

It has been found that codeposition of Bi and In onto Si(111) surface followed by annealing at 250–550 °C can lead to the formation of several ordered structures, including those having  $2\sqrt{3} \times 3$ ,  $5 \times 5$ ,  $\sqrt{7} \times \sqrt{7}$ , and  $2 \times 2$  periodicities. Among them, the  $5 \times 5$ ,  $\sqrt{7} \times \sqrt{7}$ , and  $2 \times 2$  under appropriate conditions can occupy almost the whole surface and display distinct LEED patterns.

Let us consider growth conditions and STM appearance of each structure starting with the Si(111) $2\sqrt{3} \times 3$ -(Bi, In). The  $2\sqrt{3} \times 3$  structure develops only locally at the boundaries between Bi–In  $5 \times 5$  compound and bare  $\beta\text{-}\sqrt{3} \times \sqrt{3}$  regions (Fig. 1a). In the high-resolution filled-state STM images (Fig. 1b) the  $2\sqrt{3} \times 3$  structure shows up as zigzag chains of protrusions running along the  $\langle 1\text{-}2\text{ }1 \rangle$  (i.e.,  $\sqrt{3}$ ) direction. The unit cell (outlined by frame in Fig. 1b) has a rectangular shape with sides of  $2\sqrt{3}a$  and  $3a$ , where  $a = 3.84$  Å, lattice center of Si(111) $1 \times 1$  lattice. Spacing between nearest protrusions within the zigzag chain



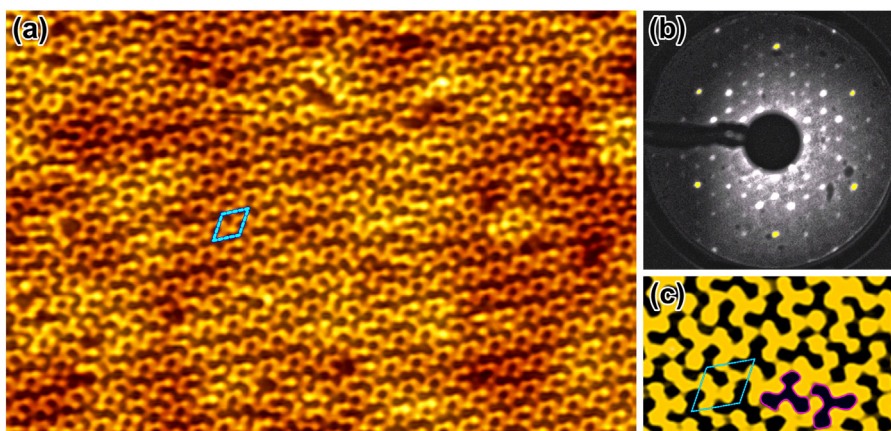
**Fig. 1.** (a)  $280 \times 210$  Å<sup>2</sup> filled-state ( $V_s = -0.9$  V) STM image of the (Bi, In)/Si(111) surface containing domains of various structures,  $5 \times 5$ -(Bi, In),  $2\sqrt{3} \times 3$ -(Bi, In) and bare  $\beta\text{-}\sqrt{3} \times \sqrt{3}$ -Bi. Typically, the  $2\sqrt{3} \times 3$ -(Bi, In) structure develops locally at regions adjacent to the  $\beta\text{-}\sqrt{3} \times \sqrt{3}$ -Bi phase. Disordered areas are occupied by the transient  $2 \times 2$ -(Bi, In) structure (for details see the text about the  $2 \times 2$ -(Bi, In) and Fig. 4c). (b) Enlarged ( $100 \times 75$  Å<sup>2</sup>) filled-state ( $V_s = -0.9$  V) STM image of the  $2\sqrt{3} \times 3$ . The  $2\sqrt{3} \times 3$  unit cell is outlined with light blue rectangle. The protrusions making a zigzag chain is outlined by dark blue lines to guide the eye. In the unit cell the diagonals are drawn to demonstrate that the “central” protrusion is not located in the geometric center of the unit cell. It means that distance between protrusions in the zigzag chain is  $2a$ , but not  $\sqrt{2}1/2a$ . Boundaries between different domains of the structure are marked with white dashed lines.

equals  $2a$ . Protrusions have a shape of smoothed triangles with their corners being oriented outward the chain (Fig. 1b).

Composition of the  $5 \times 5$  structure was estimated as  $0.51 \pm 0.05$  ML of Bi, and  $0.57 \pm 0.07$  ML of In. However, the most well-ordered array of the  $5 \times 5$ -(Bi, In) is formed over almost the entire surface, when Bi and In are overdeposited onto the Si(111) $7 \times 7$  and annealed at 550 °C for a relatively long period (up to 5–7 min). Excess Bi and In atoms just desorb from the surface. The  $5 \times 5$  structure is able to be formed with about twice more adsorbed Bi and In than necessary. Fig. 2b demonstrates that a properly prepared surface displays a bright and sharp  $5 \times 5$  LEED pattern.

Filled-state STM images of the  $5 \times 5$  structure show up as rather complicated patterns built of intersecting bright protrusions and dark depressions (Fig. 2a). In general, it is used to describe STM images in terms of the shape and arrangement of bright protrusions. However, in the present particular case of  $5 \times 5$  structure, we believe that it is more convenient to concentrate attention on the shape and arrangement of the dark depressions. Fig. 2c illustrates such a visualization showing the fragment of the  $5 \times 5$  structure with greatly enhanced





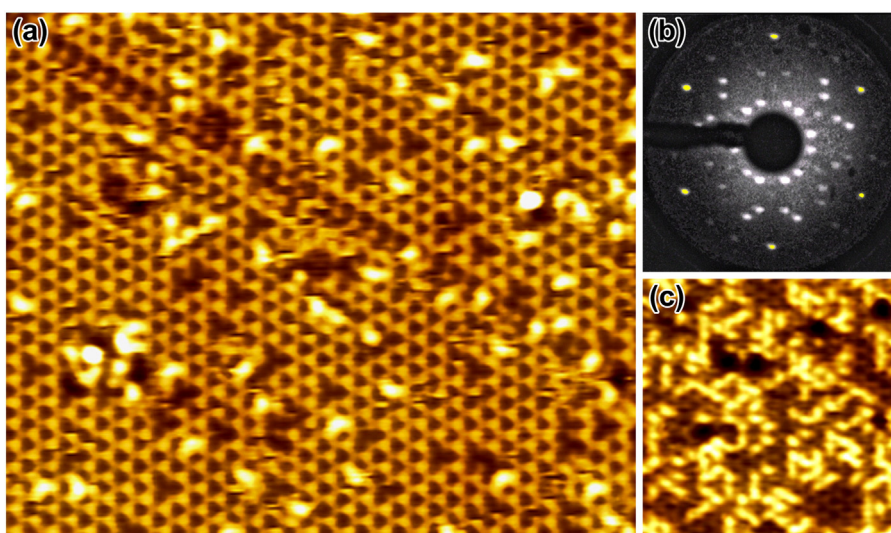
**Fig. 2.** (a)  $450 \times 300 \text{ \AA}^2$  filled-state ( $V_s = -1.1 \text{ V}$ ) STM image of the  $5 \times 5$ -(Bi, In) structure. The  $5 \times 5$  unit cell is outlined by a dashed blue frame. (b) LEED pattern of the structure ( $E_p = 46 \text{ eV}$ ) with  $1 \times 1$  reflections being marked by yellow color to guide the eye. (c)  $100 \times 60 \text{ \AA}^2$  fragment of the surface area with enhanced contrast and changed color palette to visualize its arrangement as an ordered array of the dark propeller-like features with two possible orientations (corresponding "propellers" are outlined with magenta line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

contrast and appropriately adjusted color pattern. One can see that the structure can be described as a regular array of dark depressions having a shape of propellers. Note that in different domains propellers might occur in the two different orientations as indicated in Fig. 2c. We would like to note, that the protrusions in the ideally ordered array have a shape of the interlinked bright propellers of two kinds, with more and less bright centers, but if the array is poorly ordered, the shape of the bright protrusions is not regular (Fig. 2a,c).

Compared to the  $5 \times 5$ , the  $\sqrt{7} \times \sqrt{7}$  structure is formed upon annealing at lower temperature and/or at shorter annealing period. The  $\sqrt{7} \times \sqrt{7}$  composition was estimated as  $0.43 \pm 0.03 \text{ ML}$  of Bi and  $0.85 \pm 0.06 \text{ ML}$  of In. To form well-ordered arrays of the structure one has to deposit  $0.5 \text{ ML}$  of Bi and  $0.9 \text{ ML}$  of In onto  $\text{Si}(111)7 \times 7$  and anneal the surface at  $\sim 500 \text{ }^\circ\text{C}$ . In the filled-state STM images the  $\sqrt{7} \times \sqrt{7}$  structure shows up basically as a honeycomb-like array. However, every second protrusion forming honeycomb looks brighter than its neighbors and at certain tip conditions the brightness contrast is so great that an array has an appearance like that in the STM image shown in Fig. 3a. Another characteristic feature of the  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) array is a presence of the defects seen as bright elongated protrusions in filled-state STM images. Density of these defects can dramatically differ for different

samples and it was noted that defect density is maximal when formation of the  $\sqrt{7} \times \sqrt{7}$  structure is accompanied by developing domains of the  $\text{Si}(111)4 \times 1$ -In phase which are formed due to predominant desorption of Bi. Additional deposition of small amounts of In or Bi at room temperature as well as subsequent annealing does not affect the defect density. Thus, the defects might be associated with excess Si atoms liberated during structural transformations. Remind that  $\text{Si}(111)7 \times 7$  contains  $2.08 \text{ ML Si}$ ,  $\text{Si}(111)4 \times 1$ -In  $0.5 \text{ ML Si}$  and  $\text{Si}(111)\sqrt{7} \times \sqrt{7}$ -(Bi, In) (as well as  $\text{Si}(111)5 \times 5$ -(Bi, In) and  $\text{Si}(111)2 \times 2$ -(Bi, In))  $2.0 \text{ ML Si}$ .

Composition of the  $2 \times 2$ -(Bi, In) structure was estimated as  $0.68 \pm 0.05 \text{ ML}$  of Bi and  $1.0 \pm 0.1 \text{ ML}$  of In. The structure can be formed by RT codeposition of Bi and In onto  $\text{Si}(111)7 \times 7$  surface followed by annealing in the temperature range from  $250 \text{ }^\circ\text{C}$  to  $500 \text{ }^\circ\text{C}$ . In STM images, the  $2 \times 2$ -(Bi, In) surface shows as small domains with honeycomb structure separated by wide dark boundaries oriented along the main  $\text{Si}(111)$  crystallographic directions,  $\langle 10\bar{1} \rangle$ . The  $2 \times 2$ -(Bi, In) domains containing three or more rows of the honeycomb cells always incorporate inner defects. The defect is a lack of two nearest-neighbor protrusions. This kind of defects is typical for structures, where protrusions are representation of the conjugated trimers; if the mutual atom is absent, then both trimers become incomplete. One can notice that a



**Fig. 3.** (a)  $300 \times 250 \text{ \AA}^2$  filled-state ( $-1.0 \text{ V}$ ) STM image and (b) LEED pattern ( $E_p = 35.5 \text{ eV}$ ) of the  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) structure. (c)  $180 \times 180 \text{ \AA}^2$  filled-state ( $V_s = -1.0 \text{ V}$ ) STM image of the  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) structure containing a high density of bright-feature defects which are plausibly associated with Si adatoms.

group of defects might self-assemble into an ordered linear structure with doubled  $2a$  (i.e., with  $4a$ ) periodicity. These features are responsible for the faint 1/4-order reflections seen in the LEED pattern from the  $2 \times 2$ -(Bi, In) surface (Fig. 4b). When formation of the  $2 \times 2$ -(Bi, In) structure is conducted with a Bi deficit the transient pre- $2 \times 2$  structure develops which STM image is shown in Fig. 4c. Its characteristic features are incomplete honeycomb rings and single round protrusions having a lower STM contrast. The pre- $2 \times 2$  structure can form on the surface even at  $\sim 1/3$  ML of Bi.

In order to characterize electronic properties of the found (Bi, In)/Si(111) structures, we conducted scanning tunneling spectroscopy (STS) measurements on  $2 \times 2$ ,  $\sqrt{7} \times \sqrt{7}$ ,  $5 \times 5$  (Bi, In)/Si(111) structures and also on the intact Bi/Si(111)- $\beta\sqrt{3} \times \sqrt{3}$  surface taken as a reference. The obtained STS results are summarized in Fig. 5. One can clearly see that the  $\sqrt{7} \times \sqrt{7}$ ,  $5 \times 5$  as well as the  $\beta\sqrt{3} \times \sqrt{3}$ -Bi are semiconductors with wide band-gap. The latter is in agreement with the reported STS data on  $\beta\sqrt{3} \times \sqrt{3}$ -Bi [17]. The (Bi, In)/Si(111) $2 \times 2$  is the only structure that exhibits metallic properties. One can see that the band gaps of the  $\sqrt{7} \times \sqrt{7}$  or  $5 \times 5$  structures and that of the  $\beta\sqrt{3} \times \sqrt{3}$ -Bi phase intersect in a narrow bias region but are shifted in the opposite directions. This might cause electronic effects, like those which show up as cloudy features near the  $5 \times 5/\beta\sqrt{3} \times \sqrt{3}$ -Bi boundary in Fig. 1a.

With the knowledge on the estimated compositions and bearing in mind STM appearance of the ordered (Bi, In)/Si(111) structures, one can propose tentative models of their atomic arrangement. We considered all structures except for the  $2\sqrt{3} \times 3$ -(Bi, In) one. Disregard of the  $2\sqrt{3} \times 3$ -(Bi, In) structure was dictated by two reasons. First, being a local structure, it is not of principal interest for any further investigation. Second, the fact that it forms only locally hampers accurate experimental determination of its composition, hence experiment does not provide solid ground to start reliable modeling. Thus, let us start with the structure that has the smallest unit cell, namely  $2 \times 2$ -(Bi, In). Taking into account that the structure contains  $\sim 0.7$  ML of Bi, 1.0 ML of In and 2.0 ML of Si, it seems reasonable to suggest that this is a two-atom-layer system with three Bi atoms per  $2 \times 2$  unit cell in the top layer and four In atoms in the bottom layer residing on the bulk-like truncated Si(111) $1 \times 1$  surface. A honeycomb-like appearance of the  $2 \times 2$ -(Bi, In) surface provides a hint that the top atomic layer might be built of conjugated trimers. Several models of this type with various positions of atoms were considered using DFT calculations. The relaxed atomic model having the lowest surface energy is presented in Fig. 6. According to the model, In atoms are located near and exactly in the on-top ( $T_1$ )

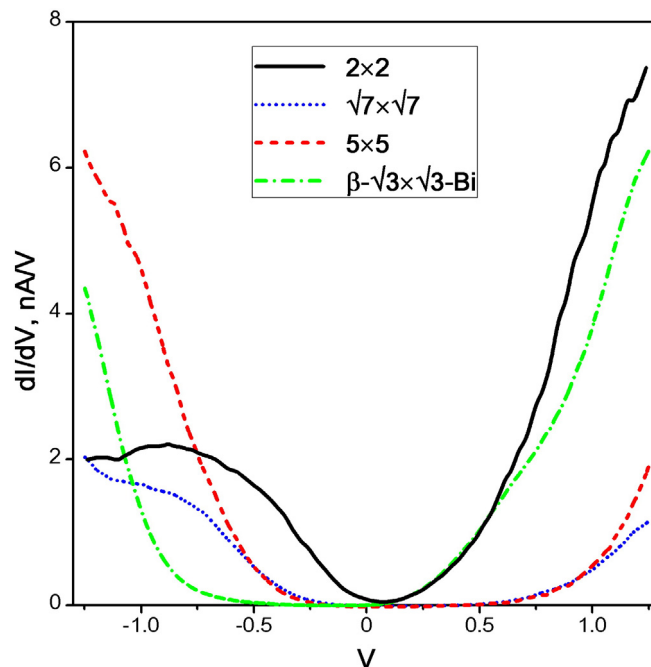


Fig. 5. STS spectra of the (Bi, In)/Si(111) structures,  $2 \times 2$  (black solid line),  $\sqrt{7} \times \sqrt{7}$  (blue dotted line),  $5 \times 5$  (red dashed line), and that of the  $\beta\sqrt{3} \times \sqrt{3}$ -Bi (green dashed-dotted line) given for comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

positions,  $2.6 \text{ \AA}$  above the upper Si atom layer, while Bi atoms are in  $T_4$  positions,  $1.9 \text{ \AA}$  above the In layer. Each Bi atom can be visualized as sitting on a pedestal of three In atoms. Comparison of the simulated and experimental STM images reveals a fairly good agreement (see Fig. 6b).

For the  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) structure, it was proposed that this is one-atom-layer compound containing three Bi and about six In atoms per  $\sqrt{7} \times \sqrt{7}$  unit cell. The three Bi atoms were suggested to make a trimer like that in the Si(111) $\beta\sqrt{3} \times \sqrt{3}$ -Bi phase [1]. It seems reasonable to assume that the trimer is centered in  $T_4$  site by analogy with the  $\beta\sqrt{3} \times \sqrt{3}$ -Bi structure. Taking the Bi trimer in  $T_4$  site as a basis we tested various models of the structure varying number of In atoms and their positions. The lowest-energy relaxed model is shown in Fig. 7a. It

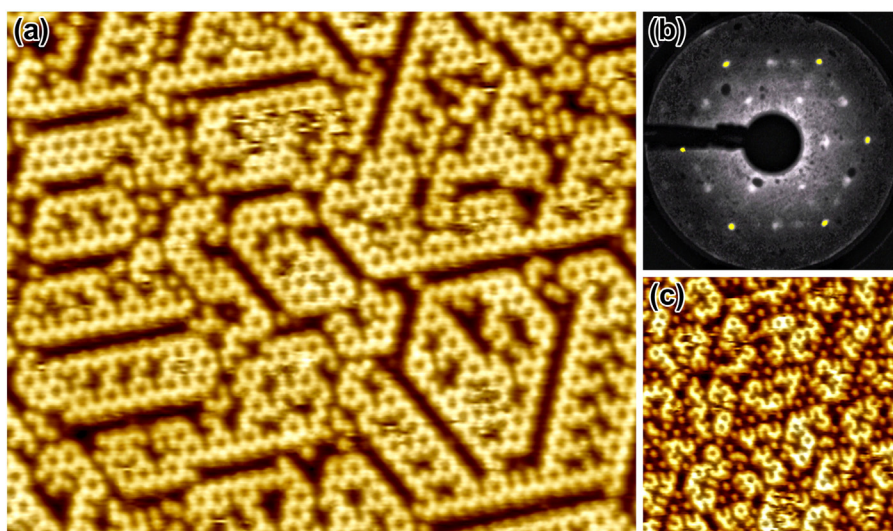
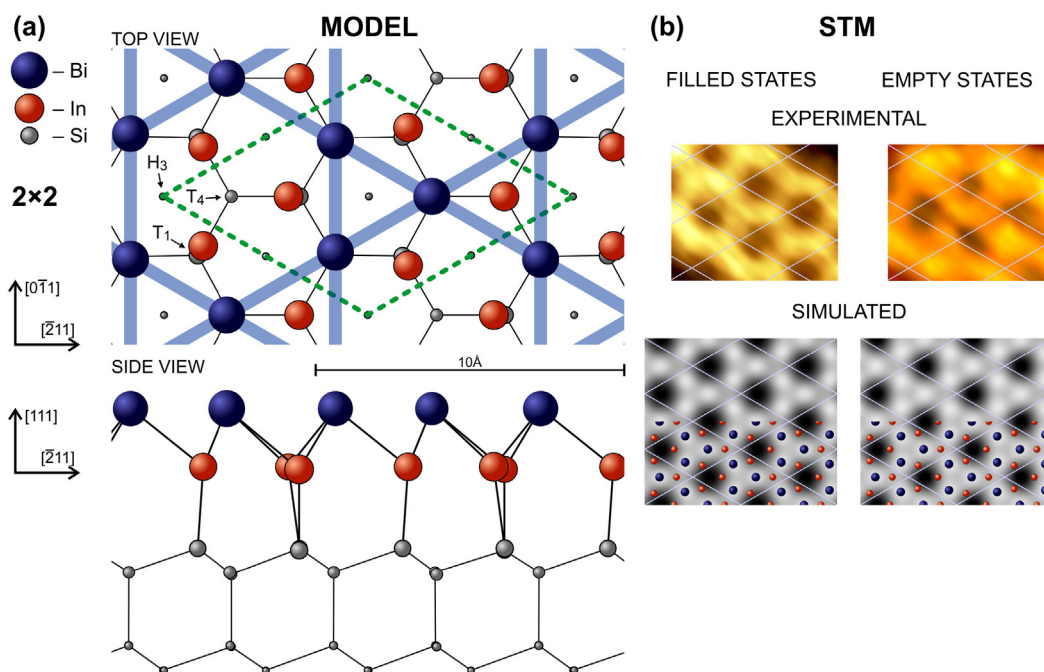


Fig. 4. (a)  $300 \times 250 \text{ \AA}^2$  filled-state ( $-1.0 \text{ V}$ ) STM image and (b) LEED pattern ( $E_p = 40 \text{ eV}$ ) of the  $2 \times 2$ -(Bi, In) structure containing 1.0 ML In and 0.7 ML Bi. (c)  $200 \times 200 \text{ \AA}^2$  filled-state ( $V_s = -1.6 \text{ V}$ ) STM image of the transient pre- $2 \times 2$ -(Bi, In) structure with Bi deficit ( $-0.5 \text{ ML Bi}$ ). Annealing temperature was  $350 \text{ }^\circ\text{C}$  in both cases.





**Fig. 6.** (a) Atomic model of the (Bi, In)/Si(111)  $2 \times 2$  structure (top and side views). Bi atoms are shown by blue circles, In atoms by orange circles and Si atoms by small gray circles. The Bi–Bi bonds within trimers are shown by blue lines. The  $2 \times 2$  unit cell is outlined by the green dashed line. Location of the  $T_1$ ,  $T_4$  and  $H_3$  sites are indicated. (b) Experimental and simulated STM images of the (Bi, In)/Si(111)  $2 \times 2$  surface. In the lower half of simulated STM images, the model structure is superposed on the image. The  $2 \times 2$  unit cell grid is highlighted by faint gray lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

contains six In atoms forming a large triangle. One can see that the Bi trimer and In triangle occupy their own half unit cells. Indium atoms of the structure take bridge positions of  $T_1$ – $T_4$  and  $T_4$ – $H_3$  directions. Variation of the atom height within the Bi–In layer is only  $\sim 0.4$  Å, namely, In atoms at the triangle sides are located  $\sim 0.4$  Å higher than In atoms in the triangle corners. This height difference of In atoms seems to be responsible for the difference in brightness of the protrusions, their counterparts, in the experimental and simulated filled-state STM images (Figs. 3a and 7b). As for the Bi trimers, one can see that they are seen as depressions in the filled-state images and as bright protrusions in the empty-state images (Fig. 7b).

Because the  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) and  $5 \times 5$ -(Bi, In) structures seem to be kindred, we have suggested that the  $5 \times 5$ -(Bi, In) is also one-atom-layer compound with Bi atoms being arranged in trimers. As the structure contains  $\sim 0.5$  ML of Bi, four Bi trimers per  $5 \times 5$  unit cell seems to be a reasonable guess. Another important hint was gained from the simulated STM images of the  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) structure, namely one can notice that Bi trimers appear as dark depressions in the filled-state STM images (Fig. 7b). Thus, four Bi atoms were placed in the  $5 \times 5$  unit cell in a way that they would produce characteristic dark propeller-like features in the filled-state STM images. The left adsorption sites were filled with In atoms which number was varied from 13 to 15. The positions of In atoms were varied also. The minimal-energy structure incorporates 14 In atoms occupying various sites (Fig. 7c). Among them, two atoms sit in regular sites,  $T_1$  and  $H_3$ , the other reside in non-regular sites close to the bridge sites between  $T_1$  and  $T_4$ . The atom height variation within the Bi–In layer is  $\sim 0.9$  Å where the highest atom is In atom in the  $T_1$  site and the lowest one is that in the  $H_3$  site. Therefore, the protrusion in the  $H_3$  site is much dimmer than that in the  $T_1$  position in the simulated images. Qualitatively similar difference can be noticed in the experimental filled-state STM image for the centers of the two bright propellers in the unit cell (Fig. 7d). In the experimental STM observations, we were unable to acquire high-quality empty-state STM images due to unstable tunneling conditions. Therefore, the comparison of simulated and experimental images was get only for the filled states. One can see a

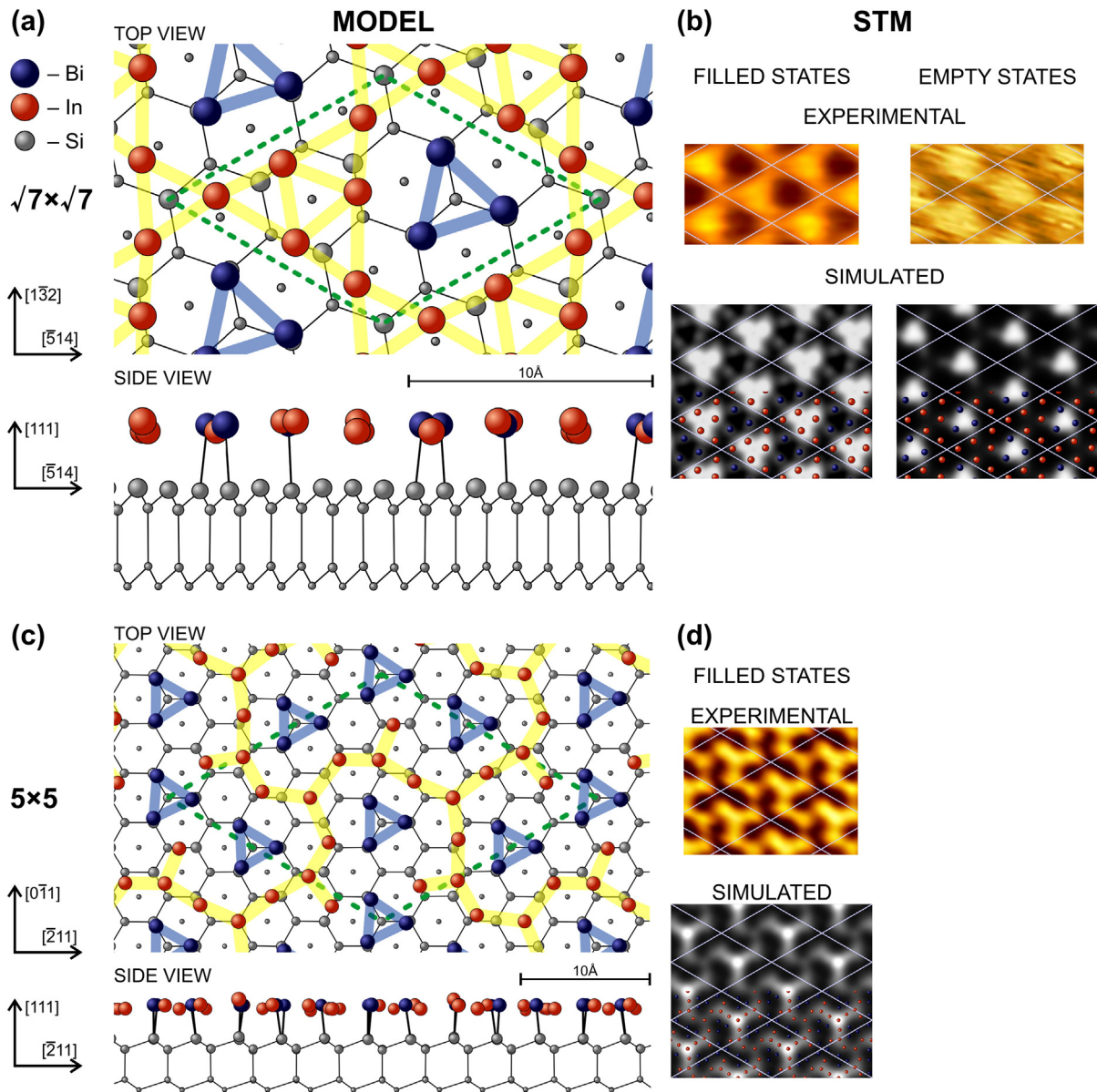
reasonable resemblance bearing in mind that the most peculiar feature of the images is the dark propeller-like depression (Figs. 2c and 7d).

#### 4. Conclusions

Using STM observations, it has been found that several ordered (Bi, In) structures are formed on Si(111) surface depending on the preparation conditions. The structures that can occupy almost the whole surface include  $2 \times 2$ -(Bi, In) containing  $\sim 0.7$  ML of Bi and 1.0 ML of In,  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) containing  $\sim 0.4$  ML of Bi and  $\sim 0.9$  ML of In, and  $5 \times 5$ -(Bi, In) containing  $\sim 0.5$  ML of Bi and  $\sim 0.6$  ML of In. Using DFT calculations, plausible atomic models of the (Bi, In)/Si(111) structures have been proposed. The  $2 \times 2$ -(Bi, In) structure is proposed to be a two-atom-layer system with three Bi atoms per  $2 \times 2$  unit cell forming trimer in the top layer and four In atoms in the bottom layer residing on the bulk-like truncated Si(111)  $1 \times 1$  surface. The  $5 \times 5$ -(Bi, In) and  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) structures are proposed to be one-atom-layer systems in which Bi trimers are surrounded by In atoms. Experimental and model compositions of the structures as well as optimal conditions for their formation are presented in Table 1. None of these structures possess honeycomb-like atomic arrangement of the hypothetical two-dimensional III–V compounds for which the properties of the two-dimensional topological insulators has been predicted. According to the STS data, the  $5 \times 5$ -(Bi, In) and  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) structures are wide band-gap semiconductors, while the  $2 \times 2$ -(Bi, In) structure is metallic. The  $2 \times 2$ -(Bi, In) can be considered as a possible candidate for a spintronics material with spin-split metallic bands, provided that a way to form large defect-free arrays of the structure can be found.

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**Fig. 7.** Atomic models of the (a)  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) and (c)  $5 \times 5$ -(Bi, In) structures (top and side views). Bi atoms are shown by blue circles, In atoms by orange circles and Si atoms by small gray circles. The Bi–Bi and In–In bonds are shown by blue and yellow lines, respectively. The  $\sqrt{7} \times \sqrt{7}$  and  $5 \times 5$  unit cells are outlined by the green dashed line. Experimental and simulated STM images of the (b)  $\sqrt{7} \times \sqrt{7}$ -(Bi, In) and (c)  $5 \times 5$ -(Bi, In) surfaces. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Experimental and model compositions of the (Bi, In)/Si(111) structures and the main conditions to form the surface of the best quality. Compositions are given in monolayers and number of atoms per unit cell (u.c.).

(Bi, In)/Si(111)	Experimental		Model		Main conditions
	Bi, ML	In, ML	Bi, ML (atoms per u.c.)	In, ML (atoms per u.c.)	
$2 \times 2$	$0.68 \pm 0.05$	$1.0 \pm 0.1$	0.75 (3)	1.0 (4)	$T = 350^\circ\text{C}$
$\sqrt{7} \times \sqrt{7}$	$0.43 \pm 0.03$	$0.85 \pm 0.06$	$-0.43$ (3)	$-0.86$ (6)	$T = 500^\circ\text{C}$
$5 \times 5$	$0.51 \pm 0.05$	$0.57 \pm 0.07$	0.48 (12)	0.56 (14)	$T = 550^\circ\text{C}$ , slight initial excess of metals

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