

Bismuth–Indium–Sodium two-dimensional compounds on Si(111) surface



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ABSTRACT

Using scanning tunneling microscopy (STM) observations, it has been found that room temperature (RT) deposition of Na onto the (Bi,In)/Si(111) surfaces, namely the 2×2 and $\sqrt{7} \times \sqrt{7}$, induces formation of a joint bismuth–indium–sodium structure without changing of the initial periodicity. For the 2×2 -(Bi,In), Na atoms “conceal” defects and domain boundaries, while the $\sqrt{7} \times \sqrt{7}$ -(Bi,In) is reconstructed into the new Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure. The first structure is temperature unstable, but the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) is thermostable and can be formed by ordinary codeposition of the metals onto the Si(111) 7×7 surface followed by annealing at 350–360 °C. Scanning tunneling spectroscopy (STS) has demonstrated that the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) is semiconductor with a ~ 0.5 eV energy gap. The structural model of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) has been proposed on the basis of DFT calculations and comparison of simulated and experimental STM images as well as density of states (DOS) and STS spectra.

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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. In the previous work [1] it was discovered that Bi–In pair forms on Si(111) surface a set of surface alloys having 5×5 , $\sqrt{7} \times \sqrt{7}$, and 2×2 periodicities, each of which can occupy almost the entire surface. Only one of them, the Si(111) 2×2 -(Bi,In), is metallic structure, but it suffers from the limited size of domains and high density of defects. The others have more perfect surface than the 2×2 -(Bi,In), but they are semiconductors [1]. Meanwhile, for spintronic applications, materials with metallic properties having spin-splitting near Fermi level are actually required. In this study we made an attempt to change electric properties and/or surface perfection of the (Bi,In)/Si(111) structures using one more chemical element. The choice of sodium for that was dictated by the following reasons. A deposited sodium atom is known to be able to donate its electron to the surface, that can change electronic properties of the surface from semiconductor to metallic (for example, Si(111) β - $\sqrt{3} \times \sqrt{3}$ -Bi to Si(111) $\sqrt{3} \times \sqrt{3}$ -(Bi,Na) [2]), or the surface can improve its metallic properties (e.g., Si(111) h - $\sqrt{3} \times \sqrt{3}$ -(Au,Na) [3]). In the case of the Si(111) h - $\sqrt{3} \times \sqrt{3}$ -(Au,Na) sodium atom modifies the surface-state band to spin-splitting of the metallic band [3]. On the other hand, sodium can decrease stress of a surface structure so that it gets rid of excess of domain boundaries to form smooth surface with large-size domains as in case of Si(111) h - $\sqrt{3} \times \sqrt{3}$ -(Au,Na) [3]. Adsorbed

sodium can also force atoms of a structure to change their positions keeping the structure periodicity (Si(111) $\sqrt{3} \times \sqrt{3}$ -(Bi,Na) [2]). Thus, we had assumed that sodium deposition onto the (Bi,In)/Si(111) structures possibly will improve the 2×2 -(Bi,In) or/and modify the bismuth–indium semiconductors’ structure to metallic with the spin-split metallic surface-state band feature.

The results of the present study of Na deposition onto the Si(111) 2×2 -(Bi,In) and Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surfaces have revealed that sodium atoms can integrate into those structure without breaking their initial periodicity. In the case of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surface, Na forms a new bismuth–indium–sodium $\sqrt{7} \times \sqrt{7}$ alloy, which is thermostable up to ~ 350 °C and can be formed in different ways, including codeposition of the metals onto Si(111) 7×7 surface followed by annealing. The plausible atomic model of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) has been constructed using density-functional-theory calculations. The $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) is not metallic, as it has been desired, but its structure possibly has, according to the atomic model calculation, the Rashba-type spin-splitting in the conduction band in the \bar{M} point with notable momentum splitting, but very small energy splitting.

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) 7×7 surfaces were

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prepared *in situ* by flashing to 1280 °C after the samples were first outgassed at ~600 °C for several hours. Bismuth was deposited from commercial HTEZ40 cell. Deposition rate of Bi was calibrated using Si(111) β - $\sqrt{3} \times \sqrt{3}$ -Bi surface (1 monolayer Bi [4]) as a reference by room temperature (RT) deposition of Bi onto Si(111) 7×7 followed by annealing at 500 °C. (1 monolayer (ML) = 7.83×10^{14} atoms/cm² 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) 4×1 -In surface containing 1 ML of In [5]. Sodium deposition was carried out from a commercial SAES chromate dispenser. Deposition rate of Na was calibrated using Si(111) $\sqrt{3} \times \sqrt{3}$ -(Bi,Na) (1/3 ML Na [2]) structure as a reference by RT deposition of Na onto Si(111) β - $\sqrt{3} \times \sqrt{3}$ -Bi surface. Annealing temperature of the samples in the range of 200–400 °C was measured by thermocouple.

Stability of the (Bi,In,Na)/Si(111) structural models was evaluated using the plane-waves total-energy calculations based on density functional theory (DFT) [6] with projector-augmented wave pseudopotentials [7] using Vienna Ab Initio Simulation Package (VASP) [8,9]. For the exchange and correlation functional, the generalized gradient approximation (GGA) [10] 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 according to Tersoff–Hamann approach [11].

3. Results and discussion

The (Bi,In)/Si(111) system has three stable structures, which can occupy the entire surface: 5×5 , $\sqrt{7} \times \sqrt{7}$, and 2×2 [1]. We have studied deposition of Na onto only two of them (viz. the $\sqrt{7} \times \sqrt{7}$ and 2×2), because the 5×5 -(Bi,In) structure has one structural drawback. Two mirror domain of the structure do not form a distinct domain boundary between each other, but one domain blends into the other so that the STM representation of the 5×5 -(Bi,In) seems as intricate tracery.

The 2×2 -(Bi,In) structure is metallic, but it forms small domains separated by wide dark domain boundaries oriented along the main Si(111) crystallographic directions. The domain is an array of honeycomb cells, which always incorporate inner defects (Fig. 1a) [1]. It was supposed that Na deposition onto the surface can decrease the number of defects

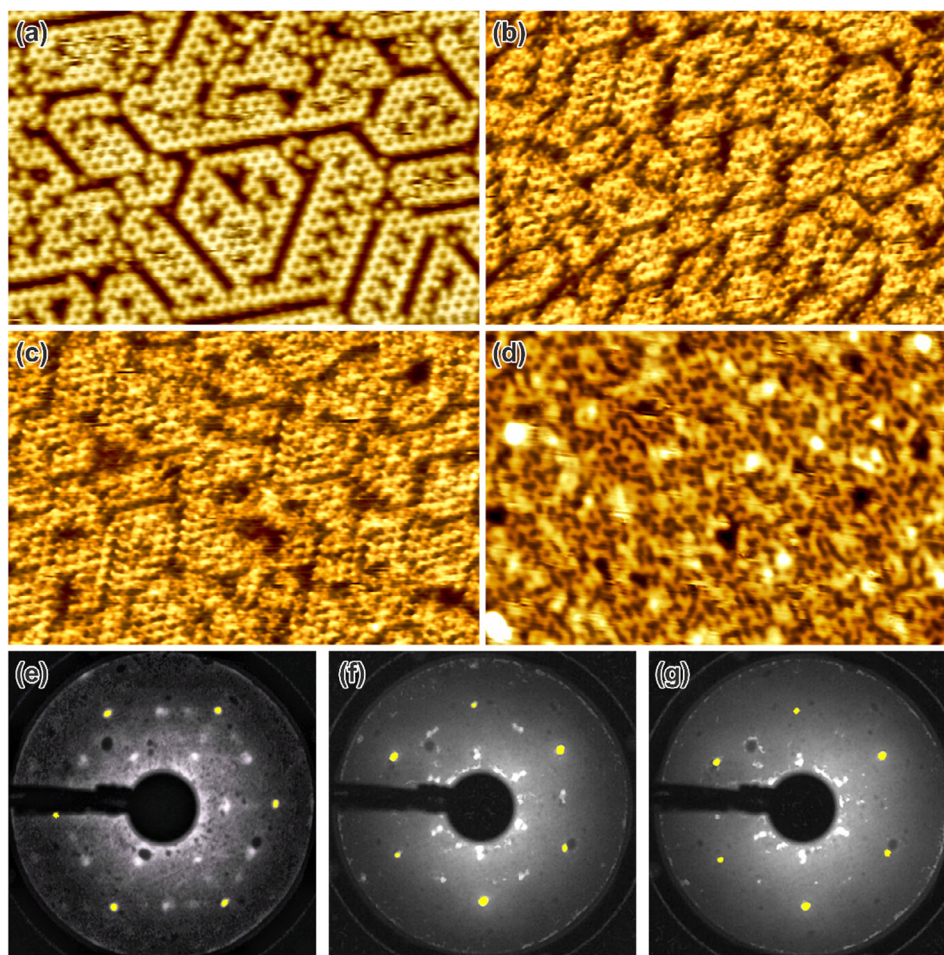


Fig. 1. $300 \times 200 \text{ \AA}^2$ filled-state (-1.0 V) STM images of the initial Si(111) 2×2 -(Bi,In) (a), after ~ 0.1 ML (b), ~ 0.2 ML (c), and ~ 0.4 ML (d) of Na deposition at RT. LEED patterns of the initial Si(111) 2×2 -(Bi,In) (e), after ~ 0.2 ML (f), and ~ 0.4 ML (g) of Na deposition at RT (1×1 reflections are marked with yellow color to guide the eye). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

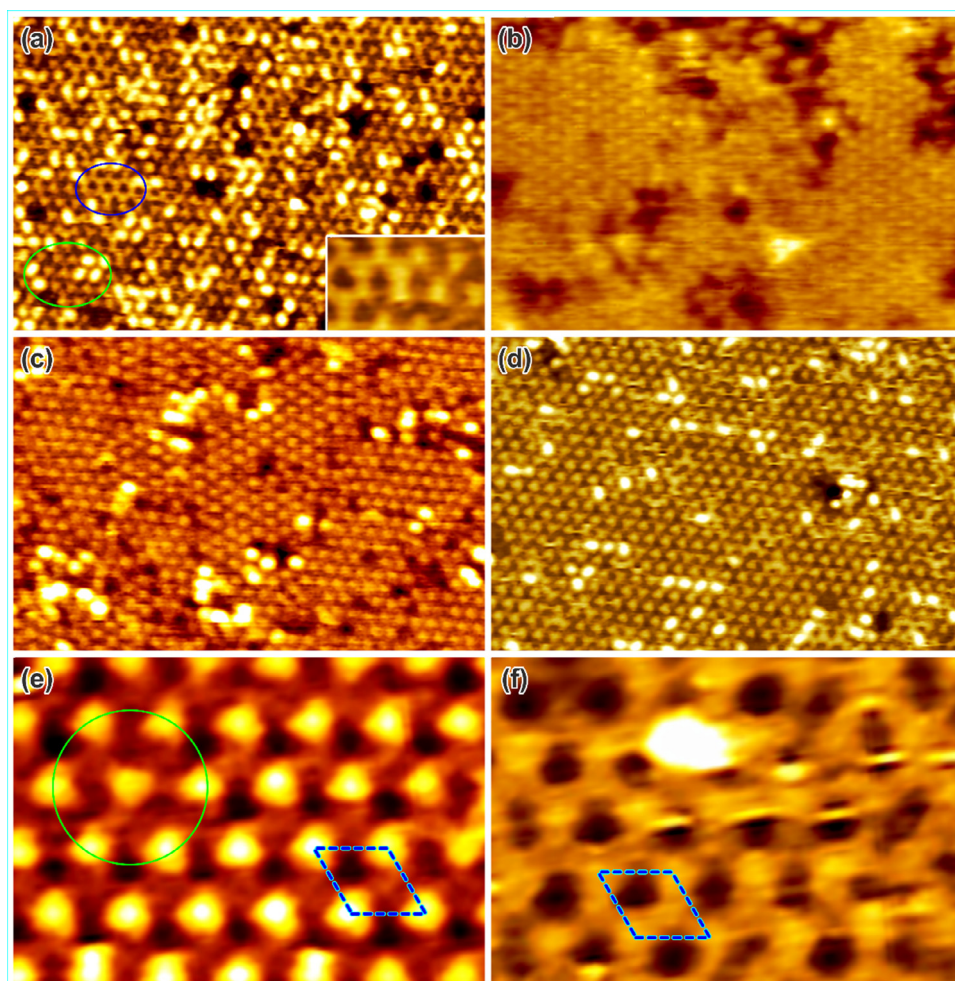


Fig. 2. (a) $300 \times 200 \text{ \AA}^2$ filled-state (-1.0 V) STM image of the initial $\text{Si}(111)\sqrt{7} \times \sqrt{7}\text{-(Bi,In)}$ after $\sim 0.1 \text{ ML}$ of Na deposited at RT, where blue and green lines outline areas of the $\sqrt{7} \times \sqrt{7}\text{-(Bi,In)}$ and new $\sqrt{7} \times \sqrt{7}\text{-(Bi,In,Na)}$ structures, respectively, while $42 \times 25 \text{ \AA}^2$ inset demonstrates $\sqrt{7} \times \sqrt{7}\text{-(Bi,In)}$ (left) to $\sqrt{7} \times \sqrt{7}\text{-(Bi,In,Na)}$ (right) transition. $300 \times 200 \text{ \AA}^2$ filled-state (-1.0 V) STM images of the $\sqrt{7} \times \sqrt{7}\text{-(Bi,In,Na)}$ surface prepared with the initial surfaces: $\text{Si}(111)7 \times 7$ (b), $\text{Si}(111)\alpha\text{-}\sqrt{3} \times \sqrt{3}\text{-Bi}$ (c), and $\text{Si}(111)\sqrt{7} \times \sqrt{7}\text{-(Bi,In)}$ (d). Enlarged ($65 \times 45 \text{ \AA}^2$) filled-state STM images (different areas) of the $\sqrt{7} \times \sqrt{7}\text{-(Bi,In,Na)}$ for -1 V (e) and -2 V (f) bias voltage. The $\sqrt{7} \times \sqrt{7}\text{-(Bi,In,Na)}$ unit cell is outlined in (e) and (f) by a blue dashed rhomb, the vertices of which are on the same surface positions in the both images. In (e) the green circle outlines the rotated bright small triangle and its surrounds (see the text for the details). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and increase size of the domains. These suppositions were based on the structural model of the $2 \times 2\text{-(Bi,In)}$. The structure consists of two layers: the lower one contains 4 atoms of In and the upper 3 atoms of Bi per unit cell, where each Bi atom is a part of the two near-neighboring conjugating trimers, which yield bright protrusions in the STM images. That is, the large number of inner defects in a domain of the structure is a result of lack of only a few Bi atoms [1]. Sodium atoms were assumed to take positions of the lacking Bi atoms or to redistribute the upper Bi atoms over the lower In layer so that they form a structure with large well-ordered domains.

The results of sequential of the Na deposition at RT onto $\text{Si}(111)2 \times 2\text{-(Bi,In)}$ surface are present in Fig. 1. One can see that after $\sim 0.1 \text{ ML}$ of Na almost all the inner defects seem to be disappeared so that the domains are more like arrays of honeycomb cells according to the $2 \times 2\text{-(Bi,In)}$ structural model (Fig. 1b). Additionally, the domain boundaries start to be covered by bright protrusions, getting less observable in the filled-state STM images. It looks like sodium atoms try to gloss over the defects of the $2 \times 2\text{-(Bi,In)}$ surface. Subsequent Na deposition (totally $\sim 0.2 \text{ ML}$) leads to more essential smoothing of the domain boundaries so that they become poorly identifiable in the STM images (Fig. 1c). Moreover, the surface starts to rearrange, several components of a new structure appear on the surface. But the full reconstruction of the sur-

face takes place at $\sim 0.4 \text{ ML}$ of Na. In the filled-state STM images the new surface looks like a fixed-thickness bright line, which runs over the entire surface forming various hexagonal-type dark elements (Fig. 1d).

Such kind of changing of the STM images supposes possible reconstruction of the surface, but LEED observation shows absence of an essential reconstruction (Fig. 1e–g). A LEED pattern of the origin $\text{Si}(111)2 \times 2\text{-(Bi,In)}$ surface has elongated or even split $\frac{1}{2}$ reflections (induced by forming of the small domains with wide domain boundaries) and $\frac{1}{4}$ reflections (as a result of self-assembling of defects into an ordered linear structure with doubled $2a$, i.e., with $4a$, where a is the $\text{Si}(111)1 \times 1$ surface lattice constant, periodicity) (Fig. 1e). One can see that the split $\frac{1}{2}$ reflections remain in the LEED patterns after $\sim 0.2 \text{ ML}$ (Fig. 1f), as well as $\sim 0.4 \text{ ML}$ (Fig. 1g) of Na deposition, but they are weaker in the last case. That is, two suppositions can be done: the lower In layer does not change and the domain boundary, containing only In atoms, has atomic structure different from the $2 \times 2\text{-(Bi,In)}$ lower indium layer. If the boundary and the lower In layer of the $2 \times 2\text{-(Bi,In)}$ structure had the same atomic structure, then the top sodium–bismuth alloy formed the same structures on the both surface and the LEED pattern does not have splitting of the $\frac{1}{2}$ reflections.

Because of appearance of small islands on the surface after $\sim 0.4 \text{ ML}$ of Na deposition at RT, further possible ordering of a surface structure of

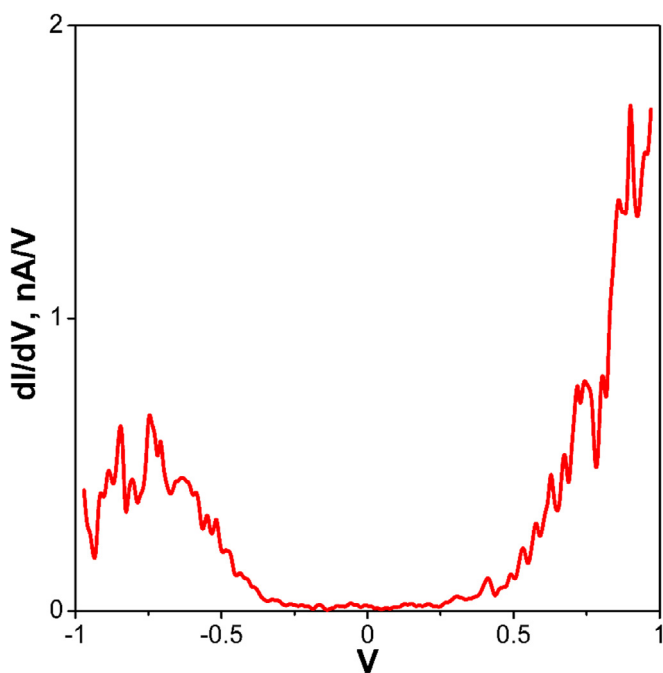


Fig. 3. STS spectrum of the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure.

sodium-bismuth alloy on the indium layer was assumed to be achieved using a low-temperature annealing. But even a 100 °C temperature annealing results into complete disordering of a structure on the surface. The surface is covered by various atomic agglomerations and disordered alloys of the metals' atoms.

Deposition of Na onto Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surface results in formation of a new Bi–In–Na surface compound with $\sqrt{7} \times \sqrt{7}$ periodicity. Formation of this new structure can be done in different ways. At first, the structure was observed at RT Na deposition onto $\sqrt{7} \times \sqrt{7}$ -(Bi,In) (Fig. 2a). The filled state STM representation of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surface is an array of large bright triangles, corners of which join in small bright triangles so the large and small triangles form a honeycomb structure [1] (Fig. 2a, area outlined by blue line). After RT Na deposition onto the $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surface the large triangles disappeared in the STM images, but the small bright triangles remained in the original positions (Fig. 2a, area outlined by green line). In a more detail, coexisting of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In) and new $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) is shown in inset of Fig. 2a. The $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) is so stable that it can be formed with codeposition of Bi, In, and Na onto the initial Si(111) 7×7 followed by annealing. If the annealing temperature is 300–330 °C, then the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) takes a small part of the surface (several percent at 300 °C and about 20–30% at 330 °C). While the 350–360 °C annealing leads to ~80% occupancy of the surface by the structure (Fig. 2b). However, further increasing of the temperature does not increase the occupancy, because at 400 °C all sodium atoms leave the surface in any case, including from the already formed structure.

Another way to form the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) over the entire surface is an attempt to use a Bi or In structure with zero coverage of Si, preliminary formed on the surface as an initial layer. The most suitable of this kind of structures are Si(111) α - $\sqrt{3} \times \sqrt{3}$ -Bi (nominally 1/3 ML of Bi [4]) and Si(111) β - $\sqrt{3} \times \sqrt{3}$ -In (nominally 1/3 ML of In [12]). After deposition onto these initial surfaces additional desired quantity of Bi, In, and Na, followed by 300 °C annealing, almost the entire surface becomes covered by the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na). However, the surface contains small domains of the structure delimited by defective areas, as shown in Fig. 2c for the case of the initial Si(111) α - $\sqrt{3} \times \sqrt{3}$ -Bi surface. There is one peculiarity for the initial α - $\sqrt{3} \times \sqrt{3}$ -Bi surface. If the initial surface contains small areas of the Si(111) β - $\sqrt{3} \times \sqrt{3}$ -Bi structure

(nominally 1 ML of Bi [4]), even of only 5% or more, then after the annealing the occupancy of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) is dramatically lower than if the initial surface does not contain the β - $\sqrt{3} \times \sqrt{3}$ -Bi. Portion of sodium atoms is assumed to desorb from the surface of the β - $\sqrt{3} \times \sqrt{3}$ -Bi. On the other hand, usage of this method has helped us to estimate the experimental coverages of the metals: ~0.45 ML for each of Bi and In, and ~0.15 ML of Na, i.e., 3 atoms of Bi, 3 atoms of In, and 1 atom of Na per the unit cell.

The best way of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) formation over the entire surface is to use the $\sqrt{7} \times \sqrt{7}$ -(Bi,In) structure as the initial surface. Deposition of ~0.15 ML of Na onto this surface heated at 300 °C results in formation of large domains of the structure with a small density of defects (Fig. 2d). The $\sqrt{7} \times \sqrt{7}$ -(Bi,In) structure contains the necessary coverage of Bi (~0.43 ± 0.03 ML), but excess coverage of In (0.85 ± 0.06 ML) [1]. Nonetheless, sodium ousts superfluous indium, which possibly agglomerates into large In islands located far from each other. For all of the formation methods essential excess of the deposited Na, additional 50% or more of the needed coverage for the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na), always leads to formation disordered structures and metals' alloys on the surface, while the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) formation does not occur. It is possible that there is formation of an indium-sodium alloy, because without In on the surface this kind of formation has not observed. The method of using the initial $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surface also has some drawbacks. Main of them are as follows: some difficulty to form the $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surface without the other (Bi,In)/Si(111) structures; defects on the structure like bright protrusions in the filled-state STM image, which are assumed to be Si adatoms [1]. After formation of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure these drawbacks do not disappear from the surface (Fig. 2d).

A filled-state STM representation of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure depends on the bias voltage. At –1 V the structure looks like an array of small bright triangles, which are rotated by 10–15° relative to an imaginary line linking the nearest-neighbor triangles (Fig. 2e). The unit cell of the structure consists of bright, light and dark areas. At –2 V the STM representation is different. The array of the structure changes from hexagonal to honeycomb type (Fig. 2f). The unit cell at –2 V bias contains two bright conjugated large triangles and a dark area. One of the triangles is on site of the bright small triangle of the –1 V bias STM image, but rotated by 180°. The $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) surface has a feature, when 5–10% percent of the bright triangles (in the –1 V STM image) are rotated by 180° (Fig. 2e, inside green circle). These rotated triangles are always surrounded by only light areas, while the ordinary triangle is usually surrounded by three light and three dark areas. In the –2 V STM image this feature looks like a bright large triangle (also rotated by 180° relative to the rotated small triangle) surrounded by dark area (no STM image presented).

In order to characterize electronic properties of the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure, we conducted scanning tunneling spectroscopy measurement on the structure (Fig. 3). One can clearly see that the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) is semiconductor with band-gap about 0.5–0.6 eV. Meanwhile, the original Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In) structure has a wider band-gap, ~0.8–0.9 eV [1]. However, in the process of the structure spectrum recording it was note, that the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) surface had a slight change, because a small part of sodium atoms possibly left their positions under the tip-field effect. That is also a reason of trouble to get a bearable empty-state STM image of the structure. This fact suggests that the presented STS spectrum is probably not to be quite correct, especially for the positive bias part.

Among the Na/Si(111) 2×2 -(Bi,In) and Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) surfaces, only for the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure it is possible to propose a tentative model of its atomic arrangement. The model is based on the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In) structural model [1] because of their excellent conjugation on the surface, where similar elements of the both structures form arrays on the surface, and easiness of transformation from the first structure to the studied one by simple sodium deposition even at RT. As it was mentioned above, the estimated composition of

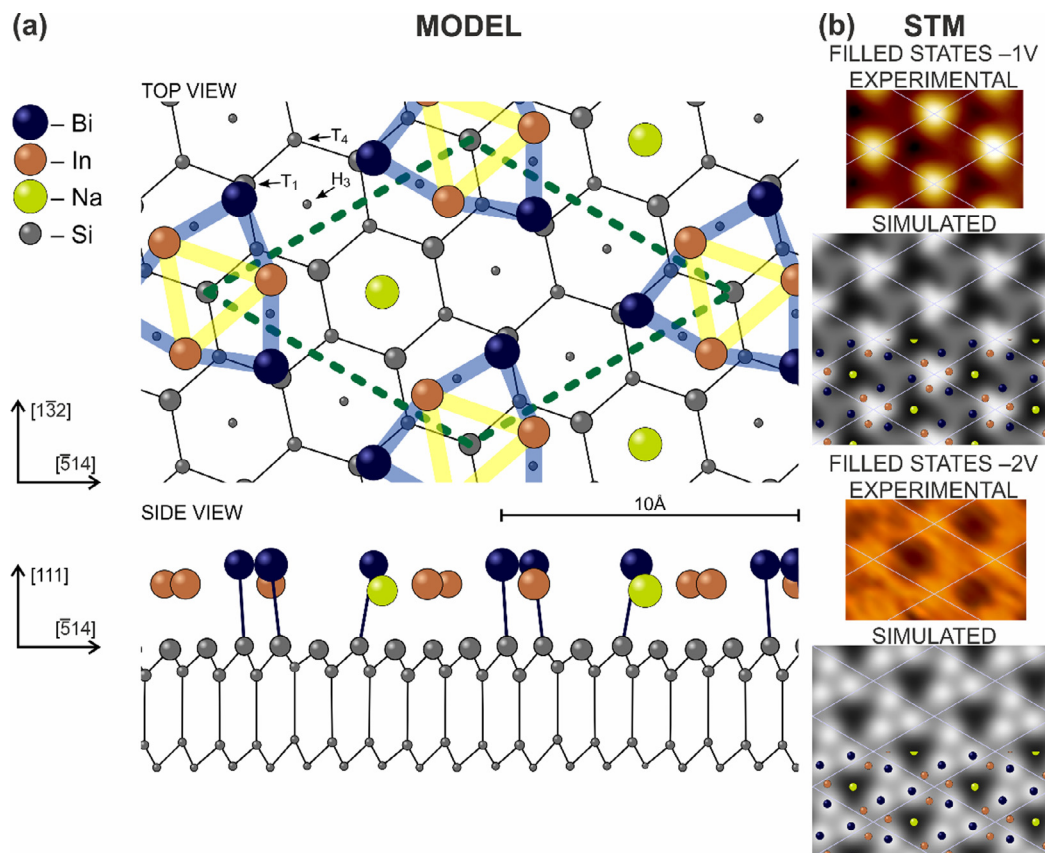


Fig. 4. (a) Atomic model of the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure (top and side views). Bi, In and Na atoms are shown by blue, orange and yellow circles, respectively, while Si atoms are represented by small gray circles. The In-In bonds within trimers are shown by yellow lines, while the Bi-In bonds denoted by blue lines. The $\sqrt{7} \times \sqrt{7}$ unit cell is outlined by the green dashed line. (b) Experimental and simulated STM images of the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) surface. In the lower half of simulated STM images, the model structure is superposed on the image. The $\sqrt{7} \times \sqrt{7}$ 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.)

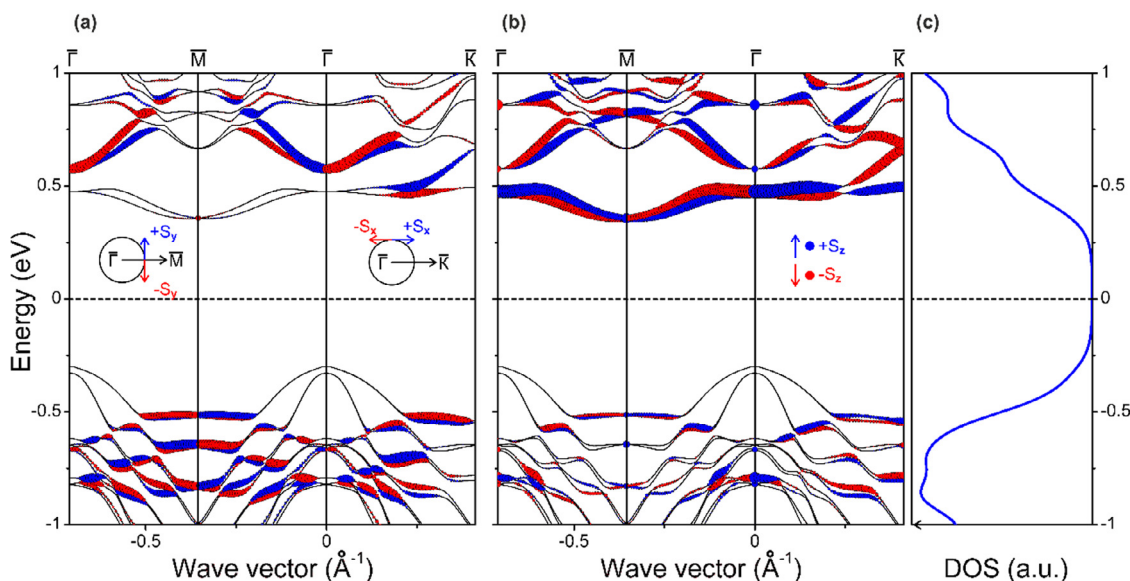


Fig. 5. Energy-band dispersions including spin-orbit coupling, which illustrate the in-plane (a) and out-plane (b) spin polarization components and total DOS (c) for the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) atomic model. The diameter of the circles in (a) and (b) is depended on the spin polarization at the surface layer. Different colors demonstrate opposite spin polarizations according to the schemes, where S_x and S_y components have near zero value at Γ -M and Γ -K directions, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure is 3 atoms of Bi, 3 atoms of In and 1 atom of Na. Because the small bright triangle is common for the both structures, then the tentative model for the DFT calculation contained bismuth and indium trimers locating on the same positions as for the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In) (T_4 and T_1 , respectively), and one Na atoms being between them on H_3 position (all of the positions are indicated in the top view of Fig. 4a by corresponding signs). The relaxed model of the structure is presented in Fig. 4a. Atoms of the Bi trimer are moved apart so that they together with atoms of the In trimer formed a convex triangle, where the Bi atoms are vertexes near T_1 positions, while the indium atoms are in some bridge sites between T_4 and H_3 . The sodium atom has not changed its initial H_3 position. The thickness of the metal Bi–In–Na layer is 0.87 Å, Bi atoms cap the layer, while Na atoms are its base. Indium atoms are higher than Na atoms by 0.22 Å. Comparison of the simulated and experimental STM images reveals a fairly good agreement (see Fig. 4b).

With the knowledge of the atomic model of the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure, we have calculated its electron band structure and density of states, which are presented in Fig. 5. One can see that the band structure of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) has no bands which cross the Fermi level, i.e., the structure is a semiconductor. The band structure is seemed to be a set of mainly poorly dispersion bands, but there is a great Rashba-type spin-orbit splitting in \bar{M} point in the conduction band. The band with spin-splitting is in ~ 0.35 eV above the Fermi level, it has notable momentum splitting $\Delta k \approx 0.057 \text{ \AA}^{-1}$, but very small energy splitting $\Delta E \approx 8.5$ meV (in the band minimum). For example, the Si(111) β - $\sqrt{3} \times \sqrt{3}$ -Bi structure has giant splitting with $\Delta k = 0.105 \text{ \AA}^{-1}$ and $\Delta E = 120$ meV [13], another Bi-bearing structure, the Si(111) $\sqrt{3} \times \sqrt{3}$ -(Bi,Na), has the $\Delta k = 0.044 \text{ \AA}^{-1}$ and $\Delta E = 210$ meV splitting [2]. As for the calculated DOS spectrum (Fig. 5c), it demonstrates good similarity to the experimental STS spectrum presented in Fig. 3. The calculated spectrum has about 0.45 eV band gap near Fermi level, that is really close to the 0.5–0.6 eV value got experimentally with STS. Additionally, the DOS has two peaks at about -0.7 and -0.85 eV, which are similar to peaks in the experimental STS, and as well as the $+0.8$ eV peak above the Fermi level, which is close enough to the experimental $+0.75$ eV peak.

4. Conclusions

Using STM observations, it was found that Na deposition at RT onto Si(111) 2×2 -(Bi,In) and Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In) results in reconstruction of the surfaces. In the first case, sodium atoms initially “restore” and “conceal” defects and domain boundaries so that they cannot be recognized in the STM images. But at ~ 0.4 ML of Na the upper bismuth layer is reconstructed in a very poorly ordered bismuth-sodium structure with hexagonal elements, while the lower indium layer is unaltered. This bismuth-indium-sodium structure is temperature unstable so it destroys to an amorphous surface already at $100 \text{ }^\circ\text{C}$ annealing. In contrast, Na deposition onto the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surface leads to formation of the new Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure, which is thermostable up to $\sim 350 \text{ }^\circ\text{C}$, but destroyed by $\sim 400 \text{ }^\circ\text{C}$ annealing. This structure can be formed in several ways, including codeposition of the

metals onto the Si(111) 7×7 surface followed by $\sim 350 \text{ }^\circ\text{C}$ annealing, but it can be formed most ordered by ~ 0.15 ML of Na deposition onto the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In) surface heated at $\sim 300 \text{ }^\circ\text{C}$. The new $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) contains ~ 0.45 ML for each of Bi and In, and ~ 0.15 ML of Na, or 3 atoms of Bi, 3 atoms of In, and 1 atom of Na per the unit cell. Using DFT calculations, plausible atomic model of the Si(111) $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure has been proposed. The structure is bismuth-indium convex triangle, 3 Bi atoms are on the vertexes, 3 In atoms are on the sides, and 1 Na atom located in the center between three this kind of convex triangles. The metals’ atoms form single layer in 0.87 \AA thickness. According to the STS data, the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) structure is semiconductor with ~ 0.5 eV band-gap, that is lower than the original $\sqrt{7} \times \sqrt{7}$ -(Bi,In) structure has (~ 0.8 eV [1]). The band-gap and semiconductor properties of the $\sqrt{7} \times \sqrt{7}$ -(Bi,In,Na) are also corroborated by calculations of DOS and band structure of the atomic model. The band structure has Rashba-type spin-orbit splitting in the conduction band in the \bar{M} point with notable momentum splitting $\Delta k \approx 0.057 \text{ \AA}^{-1}$, but very small energy splitting $\Delta E \approx 8.5$ meV. Deposition of Na onto the (Bi,In)/Si(111) structures did not result in formation of large-size and defect-free domains of the 2×2 -(Bi,In) structure, or did not modify the semiconductor $\sqrt{7} \times \sqrt{7}$ -(Bi,In) structure to metallic with the spin-split metallic surface-state band feature near the Fermi level, as it was assumed, but we found the new thermostable sodium-containing structure on the Si(111) surface, which is stable up to $\sim 350 \text{ }^\circ\text{C}$.

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