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Two-dimensional bismuth–silver structures on Si(111)

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ABSTRACT

Using scanning tunneling microscopy (STM) observations, it has been found that deposition of 0.8–1.3 monolayer of Ag onto the mixed Si(111)$\alpha-\sqrt{3}\times\sqrt{3}/\beta-\sqrt{3}\times\sqrt{3}$-Bi surfaces followed by annealing at 150–250°C induces formation of new ordered and quasi-ordered (Bi,Ag)/Si(111) metastable structures, $\sqrt{19}\times\sqrt{19}$, 4×4, $2\sqrt{3}\times2\sqrt{3}$, and '$3\sqrt{3}\times3\sqrt{3}$'. Scanning tunneling spectroscopy has demonstrated that the $2\sqrt{3}\times2\sqrt{3}$ structure is semiconducting, while the $\sqrt{19}\times\sqrt{19}$ and 4×4 structures are metallic. Structural models of the $\sqrt{19}\times\sqrt{19}$ and 4×4 have been proposed based on placing a single Ag(111)1×1 layer with selected Ag atoms being substituted for Bi atoms onto the bulk-like Si(111)1×1 surface. The models have been proved with DFT calculations and comparison of simulated and experimental STM images. Calculated band structure of the Si(111)4×4 structure displays a spin–split metallic surface-state band with splitting of $\Delta k\approx0.002$ Å^{-1} and $\Delta E\approx10$ meV in the vicinity of the Fermi level.

1. Introduction

To design future spintronic devices, materials with controlled spin-polarization, capability to transport spin-polarized current and ability to work being an ultra-thin film or a nanoparticle are strongly demanded. The promising materials possessing such properties are surface reconstructions or surface alloys with the Rashba effect. Vivid examples of Rashba-effect materials are the Si(111)$\beta-\sqrt{3}\times\sqrt{3}$-Bi surface reconstruction and $BiAg_2$ surface alloy (Ag(111)$\sqrt{3}\times\sqrt{3}$-Bi structure) which demonstrate a giant spin–orbit splitting of surface-state bands [1–9]. However, the Si(111)$\beta-\sqrt{3}\times\sqrt{3}$-Bi structure is semiconducting and its spin–orbit splitting is located in the valence zone without crossing the Fermi level [1–3]. This means that it does not allow significant spin transport. In contrast, the other structure ($BiAg_2$) is a metallic surface structure which has an amazing giant spin–orbit splitting of its bands below and above the Fermi level [4,5,7–9]. However, the main drawback of this structure is that the substrate under the surface alloy is also metallic, while the substrate is preferred to be a semiconductor for using in spintronics. It is also desired that a new spintronic structure can be easily combined with current or perspective Si surface technologies. That is, the substrate should preferably be silicon.

Thus, the main goal of our investigation was to form an ultra-thin bismuth–silver structure directly on Si(111). We have found four new one-atomic-layer bismuth–silver structures, including the well-ordered 4×4 and $2\sqrt{3}\times2\sqrt{3}$, poorly-ordered $\sqrt{19}\times\sqrt{19}$, and quasi-ordered '$3\sqrt{3}\times3\sqrt{3}$'. Among them, the metallic 4×4 structure has been concluded to be an Ag(111) layer where several Ag atoms are substituted for Bi atoms. DFT calculations have confirmed that its band structure contains spin–split metallic surface-state band.

2. Experimental and calculation details

The experiments were carried out with Omicron STM operated in an ultrahigh vacuum (~7.0×10^{-11} Torr). Atomically-clean Si(111)7×7 surfaces were prepared in situ by flashing to 1280 °C after the samples were first outgassed at ~600 °C for several hours. Ag and Bi were deposited from commercial cells HTEZ40. Deposition rate of Ag was calibrated by formation of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface containing 1 monolayer of Ag [10]. (1 monolayer (ML) = 7.83×10^{14} atoms/cm^2 for Si(111).) Deposition rate of Bi was calibrated using Si(111)$\beta-\sqrt{3}\times\sqrt{3}$-Bi surface (1 ML Bi [11]) as a reference by room temperature (RT) deposition of Bi onto Si(111)7×7 followed by annealing at 470–500°C. Additional checking of the Bi deposition rate was done with Si(111)$\alpha-\sqrt{3}\times\sqrt{3}$-Bi (1/3 ML Bi [11], prepared by Bi desorption from the $\beta-\sqrt{3}\times\sqrt{3}$-Bi) to which Bi was deposited at RT followed by 270 °C heating to convert it to the $\beta-\sqrt{3}\times\sqrt{3}$-Bi structure. The checking proved that there is no apparent Bi desorption at 470–500°C. The details of the mixed $\alpha-\sqrt{3}\times\sqrt{3}/\beta-\sqrt{3}\times\sqrt{3}$-Bi surface preparation are given in Section 3. Annealing temperature of the samples in the range of 100–600°C was measured by thermocouple.

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Structural models of the (Bi,Ag)/Si(111) surface structures were calculated using the plane-waves total-energy calculations based on density functional theory (DFT) [12] with projector-augmented wave pseudopotentials [13] using Vienna Ab Initio Simulation Package (VASP) [14,15]. For the exchange and correlation functional, the generalized gradient approximation (GGA) [16] 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–Ag layer 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. The Hamiltonian contains the scalar relativistic correlations, and the spin–orbit interaction was taken into account by the second variation method as has been implemented in VASP [17]. Simulated STM images of the relaxed models were generated from local density of states (DOS) according to Tersoff–Hamann approach [18].

3. Results and discussion

In the beginning it is worth noting that coadsorption of Ag and Bi onto Si(111) surface does not always lead to the formation of the new (Bi,Ag)/Si(111) surface structures. Say, RT codeposition of Bi and Ag onto Si(111)7 × 7 followed by annealing results in the surface which contains domains of √3 × √3-Ag and β − √3 × √3-Bi (for Ag coverage less than 1 ML) or the √3 × √3-Ag surface with Bi islands (for larger Ag coverage). The former surface (mixture of √3 × √3-Ag and β − √3 ×√3-Bi domains) develops also when Bi is deposited onto the Ag/Si(111) surface which comprises the mixture of √3 × √3-Ag and 6 × 1-Ag phases, while the latter surface (√3 × √3-Ag with Bi islands) develops when Bi is deposited onto the √3 × √3-Ag surface followed by annealing. Note that this is contrasted to (Sn,Ag)/Si(111) system, where the new Si(111)2 × 2-(Sn,Ag) structure appears after RT Sn deposition onto the √3 × √3-Ag followed by annealing [19].

Thus, Si(111)7 × 7 and Ag/Si(111) surfaces did not prove to be suitable templates for growing 2D (Bi,Ag) alloys on Si(111) and we paid the main attention to the Bi/Si(111) surfaces. Remind that Bi induces two one-atomic-layer structures on the bulk-like Si(111) surface, α − √3 × √3-Bi and β − √3 × √3-Bi with 1/3 and 1 ML Bi, respectively [11]. The β − √3 × √3-Bi can be formed directly by RT deposition of 1 ML Bi onto Si(111)7 × 7 surface followed by annealing. The α − √3 × √3-Bi can be prepared only by Bi desorption from the β − √3 × √3-Bi. The main defects of the α − √3 × √3-Bi structure are substitutional Si atoms, which substitute, according to our STM observations, up to ~10–12% (~0.033–0.04 ML) of Bi atoms. The β − √3 × √3-Bi is free of such defects.

Deposition and annealing of Ag on the "monopolistic" β − √3 × √3-Bi surface results in formation of the high Ag islands with flat tops, i.e. again no 2D (Bi,Ag) alloys develop. However, when Ag is deposited onto the "monopolistic" α − √3 × √3-Bi surface at RT (as well as after following annealing at ~250 °C), a maze-like structure forms (Fig. 1a), where Ag atoms take adsorption sites without destroying the underlying α − √3 × √3-Bi structure. This maze structure accumulates about 1.0 ML Ag weakly bonded to the surface, hence it appears to be sensitive to the electric field of the STM tip. As an example, Fig. 1 shows a set of STM images acquired successively from the same surface area. Empty-state image (Fig. 1a) shows the surface completely covered by the maze structure. However, when the bias polarity is changed and filled-state image is acquired (Fig. 1b), the most of Ag layer is removed baring the underlying α − √3 × √3-Bi surface. The left fragments of the maze structure are believed to be anchored to the substitutional Si defects. Assumption is based on the observation that the Si-defect density at the denuded regions is noticeably less than that at the original the α − √3 × √3-Bi surface (~3% versus ~12%). This could be accounted to the fact that while Bi atoms in α − √3 × √3-Bi structure have lone electron pairs (hence, are chemically inert) while substitutional Si atoms have unsaturated dangling bonds (hence, are chemically active). When the bias polarity is changed back and empty-state images are acquired, the maze structure gradually recovers (Fig. 1c and d). Thus, the maze structure can be thought as an Ag adlayer on α − √3 × √3-Bi surface. Note that adatom manipulation by tip-generated electric field is a well-known phenomenon. Its mechanism was understood in terms of interaction of dipole associated with adsorbate atom and nonuniform electric field under the STM tip [20,21]. Depending on the tip bias polarity, the static dipole is either attracted towards the region of the maximum field strength (i.e., underneath the tip apex) or repelled away from it. The vivid examples were given by STM-induced manipulations of In on Si(111) [22] or Tl on Si(100) [23]. In the present study, removal of Ag atoms with positive tip bias and their recovery with negative tip bias imply that the negative charge is transferred from adsorbed Ag atom to the substrate.

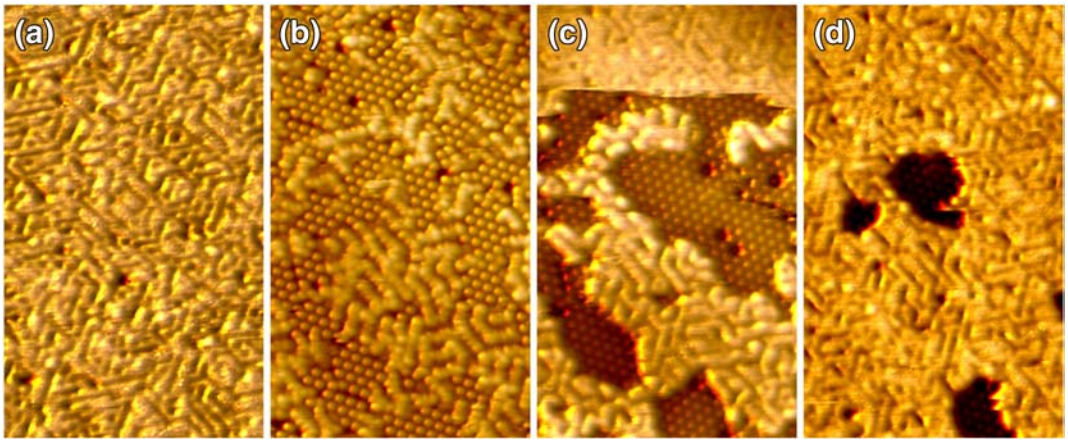

Fig. 1. Sequence of 150 × 250 Å^2 STM images of the maze structure successively recorded from the same area with changing the sample bias voltage. (a) Empty-state image ($V_s = +1.5$ V) of the initial maze structure. (b) Successive filled-state image ($V_s = -1.5$ V). (c) and (d) Successive empty-state images ($V_s = +1.5$ V) recorded after (b).