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First-principles study of X/Bi_2Te_3(0001) surface (X = Ag, Ni, Ti)

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The influence of Ag, Ni and Ti on the electronic properties of Bi_2Te_3 has been analysed. The relaxation of clean Bi_2Te_3(0001) surface and relaxation of silver, nickel and titanium on clean Bi_2Te_3(0001) surface have been studied using *ab-initio* density-functional techniques. STM images of surface, the total density of states and the band structure of bismuth telluride were determined by using the Quantum-Espresso ab-initio simulation package based on pseudopotential method. The relaxation was performed on a 8×8×1 *k*-point mesh, whereas in the calculations of the density of states the 12×12×1 k-point mesh was used.

Key words: *semiconductor surface; narrow-band system; electron density of states; pseudopotential method*

1. Introduction

In the recent years electronic properties of Bi_2Te_3 compound have been experimentally and theoretically studied by various *ab-initio* methods [1–7]. Bismuth telluride is a narrow-bandgap semiconductor material which, because of its thermoelectric properties, plays an important role in thermoelectric devices. This semiconductor have one of the highest figures of merit at room temperature. Bismuth telluride and its alloys have been investigated since late 1950's (for details see [4]). Ab-initio calculations have shown that Bi_2Te_3 is a narrow-gap semiconductor and its gap structure strongly depends on spin-orbit coupling. In this paper, we focus on the calculation of band structure of Bi_2Te_3, relaxation and the calculations of density of states at clean (0001) Bi_2Te_3 surface and the same surface covered by a single layer of atoms (Ni, Ag, Ti). We also simulated STM images of these surfaces.

The paper is organized as follows: in Section 2, we describe the method of calculation, the results of calculation are presented in Section 3. Finally, a short summary is given.

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2. Method of calculation

The density of states and the band structure were calculated by plane-wave basis set method and pseudopotentials within the density functional theory. The local density approximation (LDA) with the Perdew–Zunger functional was used for exchange-correlation potentials [13]. All pseudopotentials excluding pseudopotential for nickel used in the slab calculations were norm-conserving scalar relativistic type. In the case of nickel we use the ultrasoft pseudopotential. For bulk calculation we use both scalar relativistic and full relativistic pseudopotentials. The calculations have been performed within the Quantum-Espresso package [8].

The density of states (DOS) for the bulk bismuth telluride were performed on 12×12×12 *k*-point mesh. The same calculations for slab materials were computed on 12×12×1 *k*-point mesh. The relaxation calculations were performed on the bismuth telluride hexagonal cell as the supercell using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [9–12]. For the relaxation we used 8×8×1 *k*-point mesh. The energy convergence was within 10^{-6} Ry.

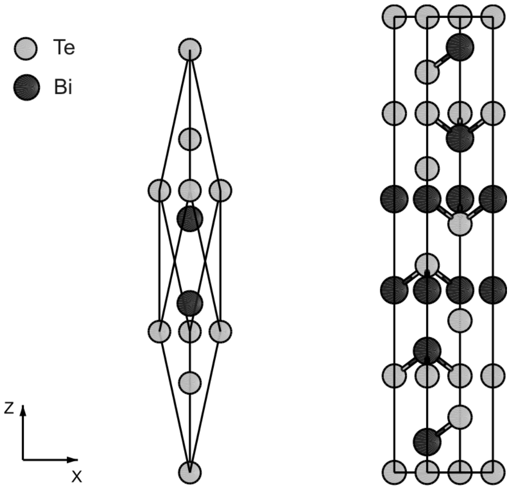

Fig. 1. Crystal structure of Bi_2Te_3: rhomboedral (left) and hexagonal (right) unit cell

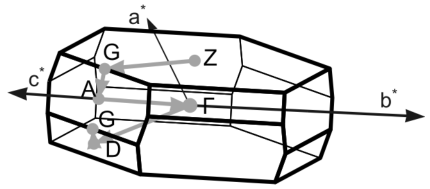

Fig. 2. The first Brillouin zone of Bi_2Te_3 for a rhomboedral unit cell showing symmetry points

Bismuth telluride has the rhomboedral crystal structure with the space group *hR*5 ($\bar{R}3m$) containing five atoms per unit cell (two bismuth atoms and three tellurium atoms). We can reduce the number of atoms to three inequivalent positions usually described as Bi, TeI and TeII. The unit cell parameters are: the lattice constant a = 19.79 a.u.

and cosα = 0.9124775. The atoms are located at: TeI (0, 0, 0), TeII ±(x, x, x) with $x = 0.212$ and Bi ±(y, y, y) with $y = 0.400$. In Figure 1, the unit cells, both rhomboedral and hexagonal are shown. Figure 2 presents the Brillouin zone for a rhomboedral unit cell.

3. Results

3.1. Band structure

Calculations of the band structure were performed with and without taking into account the spin-orbit coupling. In the former case, pseudopotentials were of the scalar-relativistic type. Spin-orbit coupling calculations were performed with full-relativistic pseudopotentials. Calculated band structures without are shown in Fig. 3.

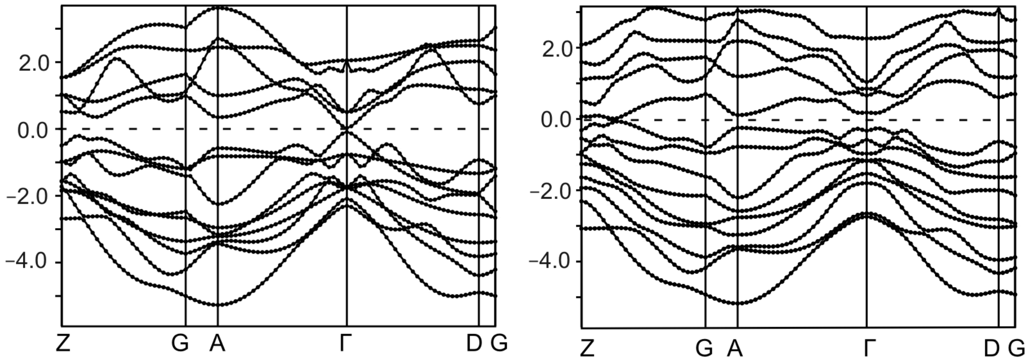

Fig. 3. Band structure of bismuth telluride without (left) and with (right) spin-orbit interaction, energy in eV, the dashed line is the Fermi level

It is seen that Bi_2Te_3 is a semiconductor with a narrow energy gap. The character of the gap strongly depends on the spin-orbit interaction. The spin-orbit coupling changes the shape of the bands and the character of the gap from a direct to indirect one. From the calculations of the total density of states we get the value of the energy gap. In both cases, these values are similar, and equal to 0.13 eV in a scalar-relativistic type and 0.1 eV in the case of full relativistic type of calculations. This value is close to the experimental one of 0.145 eV [14].

3.2. Electronic density of states for X/(0001)Bi_2Te_3 surface (X = Ni, Ag, Ti)

In this section, we present results of calculations of the relaxation, the density of states and the STM images. All results were obtained after ionic relaxation with the BFGS algorithm. First we calculated the relaxation of a clean surface. Then we added a single layer of a transition metal, in our case – silver, nickel and titanium (Fig. 4–7). The initial position of this layer was 2 Å above the tellurium layer in (0001)Bi_2Te_3 surface.

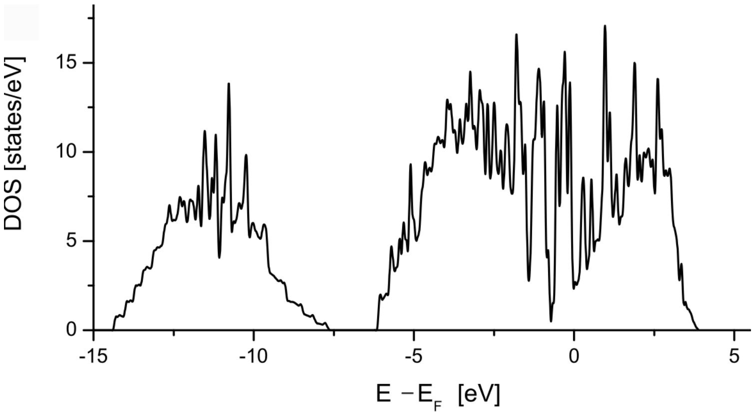

Fig. 4. Total density of states for clean (0001) Bi_2Te_3 surface

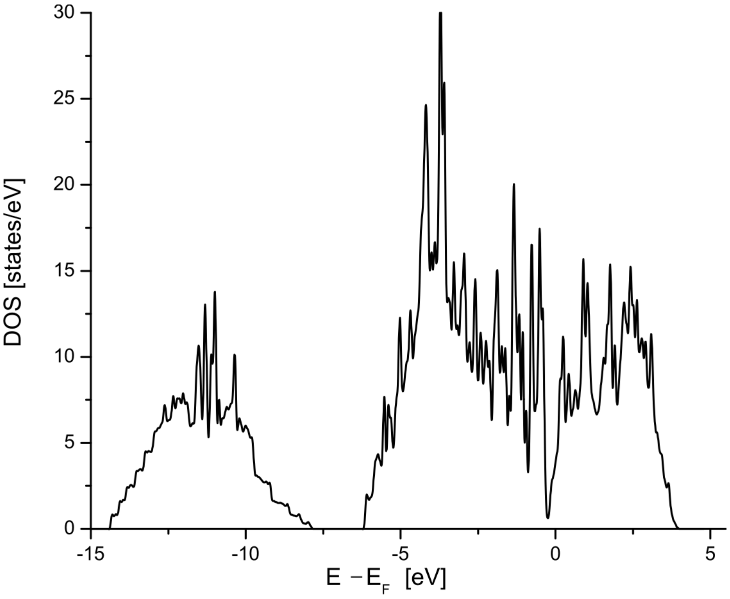

Fig. 5. Total density of states for silver relaxed on (0001) Bi_2Te_3 surface

The partial DOS calculations indicate that main contribution in clean (0001)Bi_2Te_3 surface to the total density of states in the valence band and lowest conduction band comes from tellurium and bismuth p states. After relaxation of a clean surface, the gap is very small (ca. 0.01 eV). It is probably caused by inaccuracy of the DFT method (see, e.g. [15] and references therein). When we added one layer of the transition metal, the total DOS was modified in all cases. From the total DOS calculations, we see that the energy gap vanished. From the partial DOS calculations we know that the modification of the total DOS comes from d states in of Ni, Ag and Ti atoms.

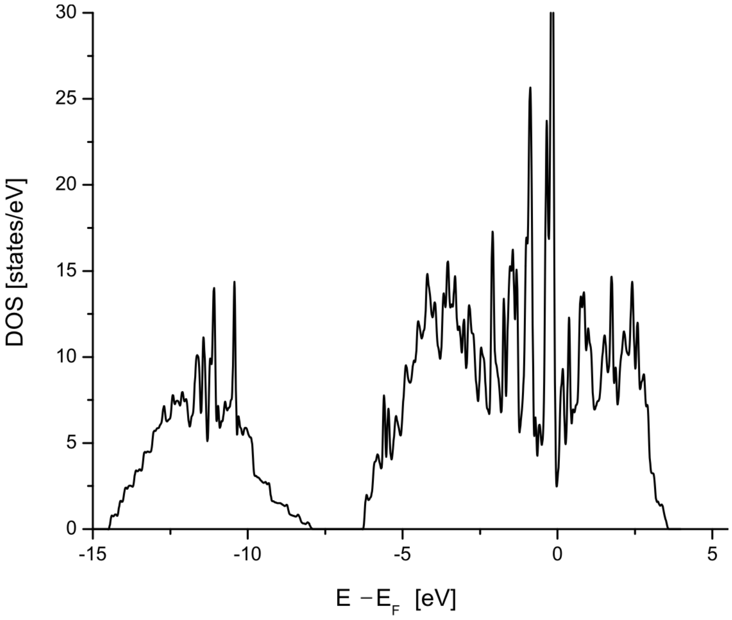

Fig. 6. Total density of states for nickel relaxed on (0001) Bi_2Te_3 surface

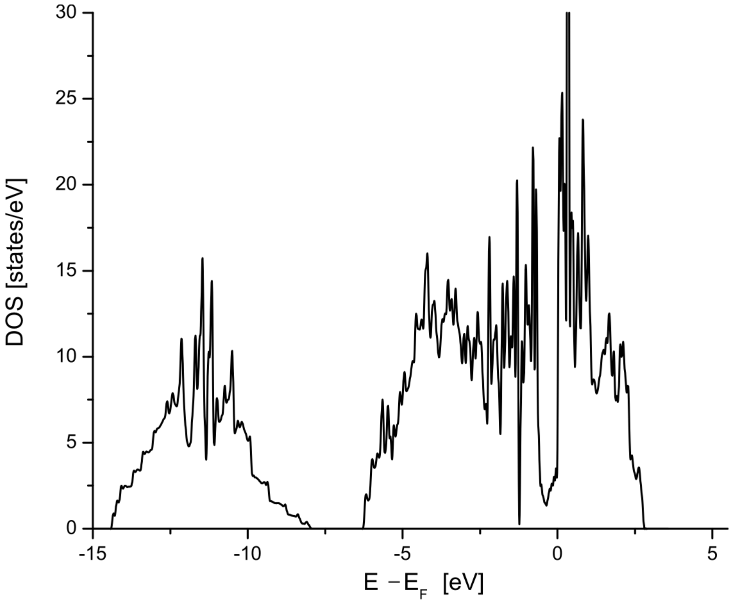

Fig. 7. Total density of states for titanium relaxed on (0001) Bi_2Te_3 surface

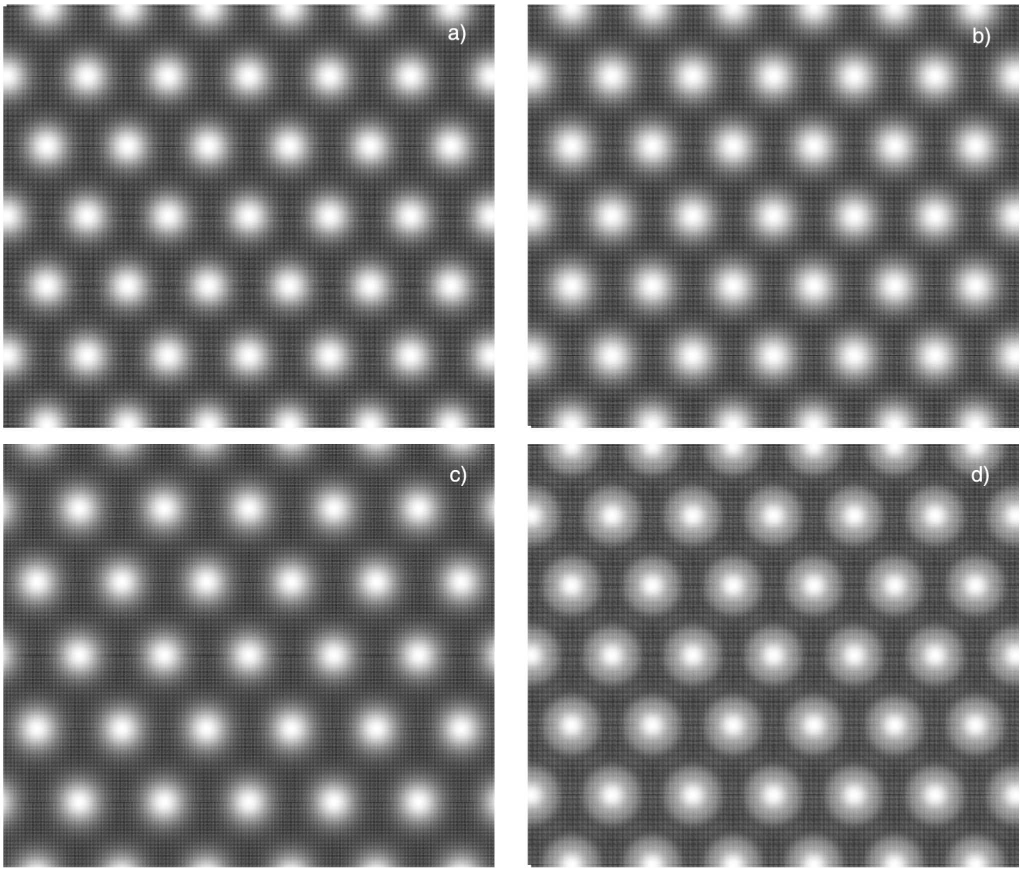

Fig. 8. Simulated STM images of (0001) bismuth telluride surface: a) clean and covered with: b) silver, c) nickel, d) titanium, bias voltage –1.0 V

Figure 8 presents the STM maps computed by *ab-initio* methods from the local DOS calculation after ionic relaxation with BFGS algorithm. In this algorithm, the displacements of atoms on the surface were very small, thus all surfaces look similar. Clean (0001)Bi_2Te_3 surface is presented in Fig. 8a with tellurium atoms visible in the picture. Figures 8b–d show the same surface covered with silver, nickel and titanium, respectively. In all cases the bias voltage was –1.0 V.

4. Summary

In the paper, we presented some results of first principle calculations for the bismuth telluride. We used *ab-initio* pseudopotential method. The method gives similar results as more exact methods like LAPW [5, 16], LMTO-ASA [3], or the tight-binding method [16]. From the calculations we see that Bi_2Te_3 is a semiconductor with a narrow energy gap. The Fermi level lies in the energy gap. A clean surface of bismuth telluride covered by one atom layer of metal changes the electronic structure of this material.

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