Physics Letters A 376 (2012) 768–772

Contents lists available at SciVerse ScienceDirect

Physics Letters A

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Effects of surface modification on the properties of topological surface states in Bi_2Se_3

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ARTICLE INFO

Article history:
Received 19 September 2011
Received in revised form 8 December 2011
Accepted 13 December 2011
Available online 17 December 2011
Communicated by R. Wu

Keywords:
Bi_2Se_3
Topological surface states
Surface modification
First principles

ABSTRACT

The effects of surface modification on the topological surface states in Bi_2Se_3 have been studied using first-principles calculations. Although surface modification cannot change the topological order, however, the spin polarization, dispersion of topological surface bands and the position of Dirac points are altered. All the studied surface modifications can push Dirac cone upwards effectively. Bi-capped surface can attract the quantum well states into bulk band gap, forming new Dirac cone at $\overline{M}$ point. Both Bi-capped and Se-removed surface can slightly enhance spin polarization of topological surface states, while flatten the energy dispersion of the topological surface bands above Dirac point.

1. Introduction

Topological insulators [1–6] are a kind of unique quantum matter, which possess gapless topological states on their boundaries while have a finite band gap in bulk. The spin-momentum locked topological surface state(s) (TSS) are protected by time reversal invariance; therefore, they are expected to be robust against non-magnetic perturbations, which do not break time reversal symmetry. The scanning tunneling microscope measurements indeed revealed the suppression of backscattering of TSS [7]. Meanwhile, the TSS are highly spin polarized. Accordingly, these states can be utilized in nondissipative spintronic devices [8]. When approaching superconductors, moreover, topological insulators can induce Majorana fermions in the interface, which are considered to be a feasible avenue to realize fault-tolerant quantum computation [9]. TSS are also found potential application in catalyzing [10].

Topological states have been observed in many semiconducting materials with strong spin–orbit coupling [11–13] soon after theoretical prediction, among which Bi_2Se_3 is the most promising one for its wide bulk energy gap [14] and simple surface states. Although TTS are supposed to be immune to non-magnetic perturbations, some recent experimental and theoretical works show that the TSS bands go through a considerable transformation with the impacts of non-magnetic adsorbents. Kong et al. [15] revealed the Bi_2Se_3 surface degradation upon oxidization using X-ray photoelectron spectroscopy (XPS) and transport measurements, confirming oxygen had great influence on the surface properties of Bi_2Se_3. Bianchi and coworkers [16] found that the TSS could coexist with conventional 2D electron gas in the surface due to the band-bending effect. Upon copper adsorption, the Dirac cone of Bi_2Se_3 could be rearranged, creating two new Rashba type Dirac cones [17]. Chang reported that the TSS of Bi_2Se_3 were susceptible to SiO_2 substrate. O-terminated SiO_2 could destroy the Dirac cone but the Si-terminated or H-terminated SiO_2 could not [18].

Although the topological order of topological insulator films is preserved under non-magnetic perturbation, the properties of topological surface states can change a lot, which will ultimately influence the topological transport property. In this Letter we use first-principles calculations to study the influence of general surface modifications on the topological surface states.

2. Calculation method

All of the calculations were realized employing first-principles calculation package Abinit [19,20]. The LDA approximation was used for the exchange-correlation potential in the framework of plane wave basis and pseudopotential. Existing results show that LDA is a good approximation for the present system [21,22]. The cutoff of kinetic energy was 400 eV. An $8 \times 8 \times 1$ Monkhorst–Pack k grid was used. Spin–orbit coupling effect was taken into account by using HGH type pseudopotential [23]. The lattice constant of Bi_2Se_3 were adopted from a previous study [24]. Zhang et al. [25] confirmed that when Bi_2Se_3 films were thinner than 6 quintuple layers (QL) there was a gap at Dirac point due to the

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0375-9601/$ – see front matter
doi:10.1016/j.physleta.2011.12.022

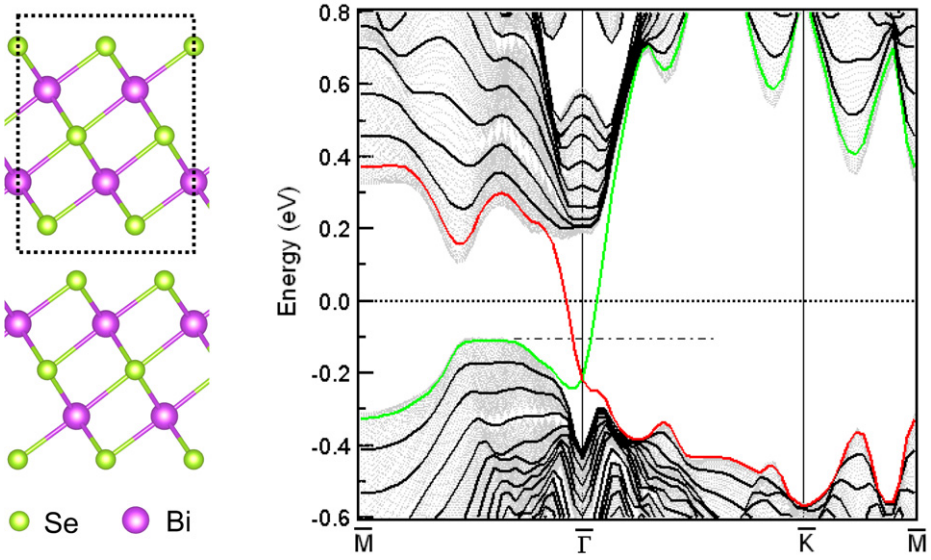

Fig. 1. Left panel: Ball-and-stick model of pristine Bi_2Se_3 slab, only 2 QLs are depicted. The dotted rectangle shows one QL along z direction of a 2×2 surface cell. The light green balls represent Se atoms; the light purple balls represent Bi atoms. Right panel: Band structure of pristine 10 QL Bi_2Se_3 slab. The gray regions represent the bulk band continuum projected on the 2D surface Brillouin zone. The solid lines mean quantum well states. The topological surface bands are highlighted with green and red lines. The dotted line indicates the midpoint of bulk band gap. The dash-dotted line indicates the position of Fermi level of 10 QL Bi_2Se_3 slab. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

entanglement of the TSS on top and bottom surfaces. We used a 10 QL Bi_2Se_3 slab so the interaction between surface states on opposite surfaces was negligible. Meanwhile, the distance between neighboring image slabs was no less than 15 Å, so the model was a good approximation to the free standing Bi_2Se_3 film. The atoms in the outermost QL were thoroughly relaxed before band structure calculation, while the interior atoms were fixed.

3. Results and discussion

For the convenience of studying the electronic structure difference after modification introduction, we first calculate the band structure of pristine 10 QL Bi_2Se_3 slab. The band structure is presented in Fig. 1. It well reproduces the existing results, suggesting that our calculation is reliable. The shaded regions in the band structure plot are bulk band continuum projected onto the 2D surface Brillouin zone. The bulk band gap is 0.3 eV, reasonably consistent with previous measurement [24]. The zero energy is set at the midpoint of bulk band gap, as the dotted horizontal line shown. The dash-dotted line represents the Fermi level of pristine 10 QL Bi_2Se_3 slab. The Fermi level is just on the top of bulk valence band continuum. The black solid lines represent quantum well states. Because electrons are confined in a 2D geometry, the continuous bulk bands transform into isolated quantum well bands. These quantum well bands are double degenerated for the symmetric structure of Bi_2Se_3 slab. At the same time, these bands are spin degenerated. The topological surface bands are highlighted with red line and green line. The topological surface bands are also bidegenerated because of the inversion symmetry of Bi_2Se_3 slab, while the Dirac point is four-degenerated due to Kramer's degeneracy [26]. The Dirac point locates at 0.12 eV below the Fermi level. To compare the effects of surface modification on the spin polarization of topological surface states the spin polarization of TSS along $\bar{\Gamma}$–$\bar{M}$ direction is also calculated. Spin polarization $\langle S_y \rangle$ ranges from 0.6 to 0.45 for the states on the upper branch of Dirac cone and decreases monotonically with the increase of momentum. At the edge of bulk conduction band it is 0.4, then it decreases to zero when the states transform into quantum well states. For the lower branch of Dirac cone it is about 0.65. Due to the spin–orbit entanglement the spin polarization is much less than ideal 100%.

Although nowadays high quality topological insulator films are usually prepared with molecular beam epitaxy (MBE) method, however, it is still possible that the redundant atoms adhere to the surface and change the topological surface properties. Measurements demonstrated that the deposition of Fe [27], K [28] and Cu [17] could dramatically change the surface properties. In view of this fact we calculate the band structure of monolayer bismuth-capped Bi_2Se_3 slab. Because the interaction between Se atoms is fairly weak, therefore, we haven't considered the perturbation of Se. In order to make band structure simple we calculate a symmetric model, namely, both surfaces are covered with Bi. After fully optimization the adsorbed Bi atom moves to the top of Se hole as in the bulk case, rather than directly attaching onto the top of Se atoms, as shown in Fig. 2 left panel. The band structure is shown in Fig. 2 middle panel. Two TSS bands are indicated with red line and green line, respectively. In contrast to the band structure of pristine Bi_2Se_3, the present one changes a lot. The first is that there are some new-generated surface bands residing in the bulk band gap except the TSS bands indicated with color lines. The second prominent change is that the position of the Dirac point at $\bar{\Gamma}$ moves upwards a lot, from below the top of bulk valence bands to above it 0.1 eV. Meanwhile, the Fermi level also moves up by 0.13 eV, see the dash-dotted line. The movement of Fermi level is easy to understand. When Bi is deposited onto the surface, Bi atoms will transfer electrons to Se atoms, so Bi_2Se_3 becomes n-type doped and the Fermi level is raised.

Besides the Dirac cone at $\bar{\Gamma}$, there are other two band crossings at $\bar{M}$ point. Because there are three symmetry-equivalent $\bar{M}$ points within the first surface Brillouin zone, so there are three-additional Dirac cones in the first surface Brillouin zone. The mechanism of the formation of the Dirac cone at $\bar{M}$ is quite clear. There is no band crossing at $\bar{M}$ point in the pristine case, as we can see in Fig. 1. When Bi is deposited onto the surface, Bi atoms transfer electrons to surface Se atoms and build a local electric field at the surface. Due to the effect of this electric field the lowest edged conduction quantum well states transform into surface states and subject to the Rashba effect. In Fig. 1, there are ten conduction quantum well bands including the tail of topological surface bands