Computational Materials Science 117 (2016) 76–82

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Topological electronic states of bismuth selenide thin films upon structural surface defects

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ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form 11 January 2016
Accepted 18 January 2016
Available online 8 February 2016

Keywords:
Topological insulators
Bismuth selenide
Electronic band structure
Surface states

ABSTRACT

A noticeable effort has been put into developing a consistent understanding of surface electronic structure of topological insulators. Of special interest has been a fundamental feature of their surface electronic states being insensitive to various types of defects and distortions. In the following paper, based on the density functional theory calculations, these topological states are investigated in asymmetric thin films of bismuth selenide with one surface modified by structural distortions. It is shown that the energetics and spatial localisation of the topological electronic states on the modified surface of the film evolve drastically as a consequence of their topological dangling bond nature. It is also shown that all the asymmetric slabs exhibit suppression of the thin film size effect and restoration of massless Dirac electrons on the undistorted surface of the film. The results are relevant for effective band gap engineering in thin films of topological insulators by means of chemical or physical functionalisation.

1. Introduction

A topological insulator (TI) can be simply described as a material that exhibits insulating bulk electronic structure while having a conductive surface [1–4]. This discovery has attracted considerable attention due mainly to the fact that the metallic surface states are topologically protected and as such insensitive to non-magnetic defects. It has already been envisaged how some of the nanoscale technologies, such as nanoelectronics, optoelectronics or quantum computing, could benefit from such attribute. The unanswered question remains, however, what are the boundaries of topological protection of the TI surface electronic structure. One aspect of this problem is investigated here for the surfaces of thin films of bismuth selenide. We focus on the evolution of the surface electronic structure of Bi_2Se_3 thin film distorted by asymmetric surface layers exfoliation.

The importance of the structural variations or modifications of TI surfaces lies in the ability to control the surface electronic properties of the material. This has mainly been studied in two aspects: (i) chemical, i.e. surface adsorption of magnetic and non-magnetic elements and films [5–15], and (ii) mechanical, such as stress and strain [16–19], as well as structural defects including variations in surface termination [20–29]. With respect to the latter, He et al. [20] have reported, based on low energy ion scattering measurements, that while Bi_2Se_3 usually terminates with Se, shortly after cleaving at room temperature the amount of Se atoms drops with time in favour of bismuth and leaves the system entirely Bi-terminated. This observation has been supported in [20] by the density functional theory calculations predicting that a bismuth bilayer on top of a clean Bi_2Se_3 is energetically favourable and the topological features of the system are preserved after Bi_2 deposition. The latter has been challenged by Govaerts et al. [21] who investigated the evolution of Bi related bands in the electronic structure of Bi_2 covered Bi_2Se_3 and showed that those states are Rashba-type split states. By contrast – as of the surface termination – dos Reis et al. [22] demonstrated, using low energy electron diffraction (LEED) and surface X-ray diffraction, that the surface of the cleaved Bi_2Se_3 crystal terminates with Se. This is partially in line with Hewitt et al. [23] who concluded that the observed termination depends on the sample preparation and that the Se and Bi atoms could coexist on a cleaved surface. Yan et al. [24] reported that the topologically protected surface states (TPSS) of Bi_2Se_3 may coexist with Se vacancies and that a large number of Se vacancies (leading towards full Bi termination) forces the TPSS to localise deeper within the structure.

Lin et al. [25] investigated experimentally and theoretically the cleaving process that exposed internal atomic planes of a clean Bi_2Se_3 system after 2 and 3 exfoliations. They introduced a term *topological dangling bond* (TDB) states to describe the complex band structure features that arise due to atomic layers exfoliations. Wang and Chiang [26] showed that for each atomic plane cleaved

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http://dx.doi.org/10.1016/j.commatsci.2016.01.024
0927-0256/

within Bi_2Se_3 there are topologically protected surface states in the bulk band gap, including multiple massless as well as massive Dirac electrons. The study of Wang and Chiang was performed for thick 60 monolayers (ML) slabs with the two surfaces (top and bottom) modified in the same manner to retain both the bulk properties and the spatial symmetry of the system.

In this contribution, we extend the work of Lin et al. [25] and Wang and Chiang [26] in less explored but important aspect. We investigate the evolution of the electronic structure of asymmetric thin films of Bi_2Se_3 distorted by systematic surface layers exfoliation on one side of the film for energetically most stable structures, i.e. the positions of all of the atoms in the slabs have been relaxed, as this effect has been neglected in previous studies [25,26]. We demonstrate that the electronic structure of the undistorted thin films, with the gap and massive Dirac electrons on both film surfaces transforms to the gapless surface electronic structure dominated by topological dangling bonds on all of the modified surfaces and the massless Dirac electrons on the pristine one. We show that the restoration of massless Dirac electrons on the undistorted side of asymmetric thin films occurs whenever the system's inversion symmetry is broken which quantitatively supports the model studies demonstrated by Shan et al. [30] for thin films of 3D TI. The reported results fall within the scope of fundamental knowledge on TPSS in thin films of TI and may be useful for effective band gap engineering in such systems via chemical or physical functionalisation.

2. Method

The calculations have been performed using the relativistic – including spin–orbit coupling (SOC) – and non-relativistic (non-SOC) density functional theory (DFT) as implemented in the ABINIT software package with plane waves basis set and Hartwigsen–Goedecker–Hutter (HGH) pseudopotentials [31–36]. The exchange–correlation potential has been calculated with the local density approximation (LDA); the XCrySDen program has been used for structures visualisations [37].

Bulk Bi_2Se_3 belongs to the rhombohedral 166th crystallographic symmetry space group. The system consists of chemically bonded stacked Bi and Se monolayers in the order of Se–Bi–Se–Bi–Se. Such structural unit is referred to as a quintuple layer (QL). An isolated QL is chemically inert and QL in the bulk crystal interact with each other via van der Waals forces. The structural data used to generate all the slabs within this work have been adopted from Nakajima [38]. The slabs containing 15, 20 and 40 atomic monolayers corresponding to 3, 4 and 8QL have been employed to describe the Bi_2Se_3 films. As the intention is to model a film instead of the surface of a quasi semi-infinite system, the positions of all of the atoms within the slabs have been optimised within the 1×1 surface unit cell (i.e. surface reconstruction is neglected) using the Broyden–Flet cher–Goldfarb–Shanno (BFGS) algorithm [39]. An exception was the 8QL slab in which only five topmost/bottommost ML have been relaxed. The convergence criteria for the optimisation runs have been selected for the total energy and the force gradients with the corresponding threshold values of 10^{-8} Ha and 10^{-7} Ha/Bohr, respectively. The kinetic energy cut-off of 18 Ha and the Monkhorst–Pack k-points mesh of $8 \times 8 \times 1$, giving 32 points within the irreducible surface Brillouin zone (SBZ), have been employed in all of the total energy calculations.

The deformations of the films have been introduced into pristine QL by simply removing the first and subsequent ML. After each removal the whole system has been reoptimised. The electronic structure calculations have been performed for structurally optimised systems at 216 k-points uniformly distributed along the high symmetry K–Γ–M directions in the SBZ (see right inset in Fig. 1c). An important aspect in studying electronic properties of thin films is determination of spatial localisation of the electronic states of the system. This property was calculated by sampling the wave function (its squared module) on 432 x–y planes along the cell height (coordinate z perpendicular to the film's surface). The squared modules of the wave functions for each plane have been numerically integrated with respect to x and y and plotted as a function of the distance (z) from one surface of the film to the other. The charge/probability density calculated this way shows the spatial localisation of the states in real space within the unit cell. For the sake of consistency it has been assumed that if the 65% or more of a state's overall charge/probability density is localised within the first (top/bottom) QL – the state is qualified as a surface state of the film, otherwise it is a bulk state.

3. Results

3.1. Reference systems

In order to study the evolution of the electronic properties between two films of Bi_2Se_3 with two pristine Se-terminated surfaces, the atomic and electronic properties of the initial and final systems need to be determined first. According to our convergence study, the minimal slab thickness necessary to properly represent the TPSS of bismuth selenide should consist of more than 4QL (20 ML). This means that the surface electronic structure of the 4QL thick film of Bi_2Se_3 has all typical features induced by a size effect. The details of the optimised geometry of the 4QL slab are presented in Table 1 and the surface electronic structure is shown in Fig. 1.

The data in Table 1 show that the z distances between monolayers for both sides of the clean 4QL slab are symmetric, and the van der Waals (vdW) gaps (marked in bold in Table 1) separating the QL are equal to 2.347 Å in the outer layers, which is smaller than the bulk value of 2.579 Å [38]. It is also considerably smaller than the value obtained by Liu et al. [40] for the 4QL slab by using GGA-PBE including vdW correction – reaching almost 2.9 Å. Therefore, an error associated with the LDA approach should be kept in mind. The corresponding relativistic and non-relativistic electronic band structures shown in Fig. 1a and c, respectively, are in agreement with previous reports, see e.g. [25,26]. The shaded areas on both figures represent the bulk band structure of an infinite Bi_2Se_3 crystal projected onto the (1 1 1) plane along K–Γ–M directions. The main difference between the non-SOC and SOC surface electronic structures of the 4QL film is the presence of the surface states in the latter, marked in the figure by the red squares. A linear dispersion of these states around the Γ point in the vicinity of the Fermi level leads to the formation of the Dirac cone (DC) and the Dirac point (DP) located at −0.15 eV below the Fermi level. Zooming up the band structure around DP reveals a tiny gap of 0.0023 eV which is very small with respect to that seen in the corresponding non-SOC band structure of Fig. 1c. Clearly, as DC is missing in the latter, this feature in the relativistic surface band structure represents the topological properties of the system. Apart from the DC, there is also a surface-related Rashba splitting at the energy of −0.82 eV.

A spatial localisation of a Dirac surface state at the Γ point is shown in Fig. 1b. As there is no DP in gapped band structure of Fig. 1a, the charge distribution is plotted for the upper DC band only. The density peaks are localised on both sides of the slab. It should be noted that as the undistorted 4QL slab is symmetric, it contains two equivalent Se-terminated surfaces and, while all the surface states are energetically degenerate, they have different spatial localisation.