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Exceptional surface states and topological order in Bi_2Se_3

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ABSTRACT

Topological insulators possess time reversal symmetry protected metallic surface states over the insulating bulk, where these surface states are expected to be immune to small disorder, chemical passivation of the surface or temperature change. However, significant discrepancy from such behavior has been found experimentally in various materials. Here, we review some of our recent results on the electronic structure of a typical topological insulator, Bi_2Se_3. Both, the band structure results and high-resolution angle resolved photoemission data reveal significantly different surface electronic structure for different surface terminations. Furthermore, oxygen impurity on Se terminated surface exhibits an electron doping scenario, while oxygen on Bi terminated surface corresponds to a hole-doping scenario. The intensity of the Dirac states reduces with aging indicating fragility of the topological order due to surface impurities.

1. Introduction

Insulators are materials having an energy gap between the highest occupied band (valence band) and the lowest unoccupied band (conduction band). Topological insulators are a special type of such materials, which possess gapless states with novel electromagnetic properties protected by time reversal symmetry at the surface of bulk insulators [1,2]. The speciality of these surface states is that they are protected from backscattering due to the time reversal symmetry as such processes in the presence of time reversal symmetry requires a spin-flip, which is different from a typical two-dimensional surface states. Thus, the electric current due to the topologically ordered states is expected to be non-dissipative. The topologically ordered energy bands exhibit linear dispersion forming a Dirac cone. The formation of such states requires strong spin–orbit coupling and breaking of inversion symmetry.

Topological insulators have been theoretically predicted [3] and presumably for the first time, experimentally observed in HgTe [4]. Since then enormous research has been carried out as these materials are expected to bring immense technological advances and new possibilities in the fields of spintronics, quantum computation, dissipationless charge transfer, etc. [2]. Several materials have been discovered exhibiting surface states with topological order along with significant deviation from the theoretical predictions for such systems. For example, the bulk electronic structure of almost all the materials studied exhibits large density of states at the Fermi level [5]. Experiments show contrasting scenarios often with instability of the topologically ordered states. Thus, finding of an ideal topological insulator as per the definition continues to be an outstanding puzzle.

In this paper, we review some of our recent works on the stability of the topologically ordered surface states of an archetypical topological insulator, Bi_2Se_3 [6,7]. Bi_2Se_3 forms in a layered structure as shown in Fig. 1 with the quintuple layers of Se1-Bi-Se2-Bi-Se1 (Se1 and Se2 are the two non-equivalent Se atoms) stacked together by Van der Waals force [8]. The surface electronic structure of Bi_2Se_3 exhibits topological order with the apex of the Dirac cone, called the Dirac point (DP) appearing far away from the Fermi level, E_F due to the charge carrier doping arising from impurities, imperfections, etc. [9–11]. These states often show instability with time and complex time evolutions [5,12], which has been attributed to different phenomena such as relaxation of the Van der Waals bond [13], the surface band bending [5], dangling surface states [14], etc. Some observations indicate formation of two dimensional electron gas (2DEG) and Rashba states with time that has been explained employing impurity induced band bending scenario [15–17]. In order to reveal microscopic details underlying such complex electronic properties, we calculated the electronic band structure for both surface and bulk of the material employing density functional theory, and carried out high-resolution photoemission measurements with angle resolution and varied bulk

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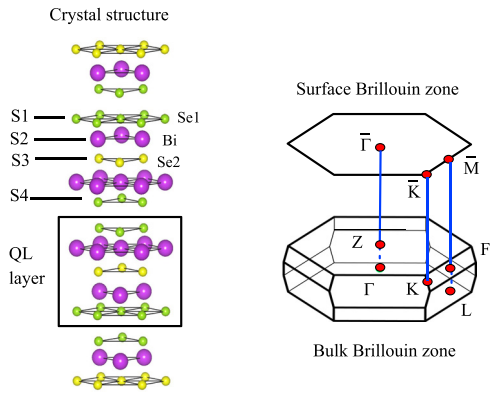

Fig. 1. Crystal structure of Bi_2Se_3 (left panel) and its Brillouin zone (right panel). Se1 and Se2 are two non-equivalent Se atoms. S1, S2, S3 and S4 are the surface layers for different surface terminations. The square box shows the quintuple layer.

sensitivity. The experimental results show exceptional behavior of the surface states due to different terminations and aging, which could be corroborated well by band structure calculations.

2. Experimental and theoretical details

Photoemission measurements were carried out on single crystalline Bi_2Se_3 samples grown by Bridgemann method and characterized by X-ray diffraction, Laue diffraction, etc. Hard X-ray photoemission (HXP) measurements were carried out using 5947.9 eV photon energy at the P09 beamline of Petra III, Hamburg, Germany and Phoibos analyzer (energy resolution = 150 meV). For angle resolved and conventional X-ray (Al $K\alpha$; $h\nu = 1486.6$ eV) photoelectron spectroscopy (ARPES and XPS), a Gammadata Scienta R4000 WAL analyzer and monochromatic photon sources were used with energy resolution 10 meV and 380 meV, respectively and an angular resolution of about 0.1°. The pressure of the photoemission chamber was maintained at about 5×10^{-10} torr during the measurements with the photon sources on. The sample was cleaved in situ using a top post glued on top of the sample. The cleanliness of the cleaved sample surface was checked using XPS & HXP wide scans and the surface crystallinity was verified by sharp & intense low energy electron diffraction (LEED) spots. All the data presented here are collected at temperature below 30 K using an open cycle He cryostat.

The electronic band structure calculation of Bi_2Se_3 was carried out using full potential linearized augmented plane wave method [18]. The bulk electronic structure was calculated using the lattice constants, $a = b = 4.18$ Å, $c = 28.7$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$ obtained from Ref. [19]. In order to investigate the surface electronic structure, we considered the lattice in a 'slab' configuration with at least 5 quintuple layers within the unit cell – the total number of layers varies for different surface terminations. Calculations were carried out for the surface terminations, S1 (Se1 terminated), S2 (Bi terminated), S3 (Se2 terminated) and S4 (one Se1 layer over the quintuple layer) as defined in Fig. 1. We calculated the electronic structure for both the pristine surface and a layer of oxygen over it. The exchange and correlation potential was included using the generalized gradient approximation (GGA) [20] and the spin–orbit interaction was included for Bi and Se atoms. The energy convergence was achieved using $10 \times 10 \times 1$ k points mesh.

3. Results and discussions

We studied the electronic band structure for four different surface terminations, S1, S2, S3 and S4 as shown in Fig. 1. The energy bands near ϵ_F consist primarily of Se 4p and Bi 6p characters. The

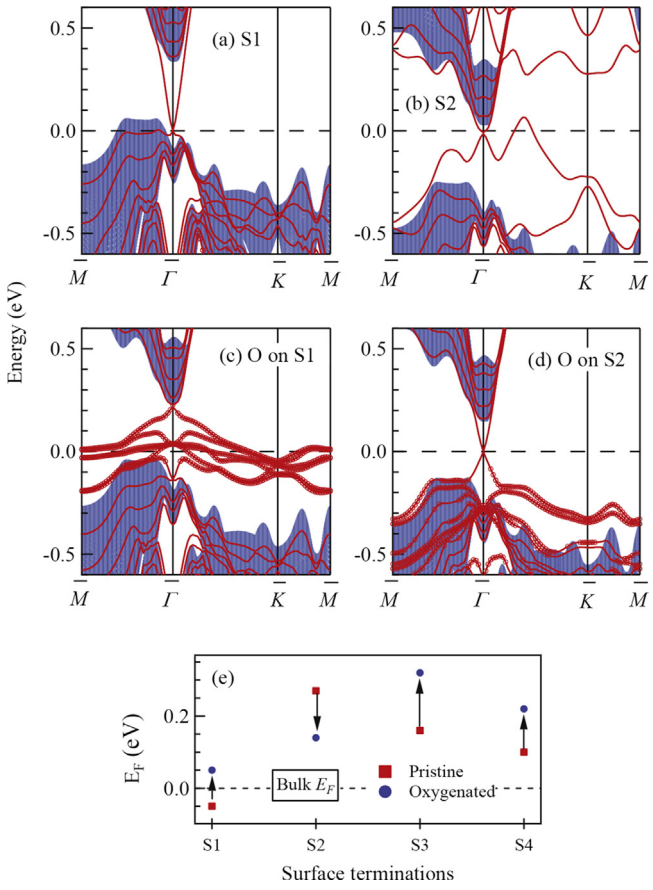

Fig. 2. Band structure results for (a) Se1 (S1-case) and (b) Bi (S2-case) terminated surface. The band structure for one layer oxygen deposited on S1 ans S2 terminations are shown in (c) and (d). (e) The Fermi level position with respect to the Bulk Fermi level.

results for all the surface terminations exhibit the surface bands crossing the Fermi level between surface projected time reversal invariant momenta (TRIM), $\bar{\Gamma}$-$\bar{M}$ odd number of times implying that the material belong to a strong topological insulator class [2,7]. However, the signature of Dirac cone was observed only for Se1, Se2 and Bi terminated surfaces denoted by S1, S2 and S3, respectively. The S4 case (one Se1 layer over the quintuple layer) exhibits two-dimensional surface states with no signature of the Dirac cone.

The calculated results [6] for experimentally observed surfaces, S1 and S2 terminations, are shown in Fig. 2. The lines show the results of the slab calculation and the shaded region represents the projected bulk bands (PBB). The inclusion of spin–orbit coupling in the calculation led to the Dirac cone like structure in the bands. The Dirac cone like structure in the energy band dispersion with DP at E_F is evident for both the surface terminations. DP appears close to the top of the valence band for Se terminated surface (S1 case) and in the vicinity of the bottom of the conduction band for Bi-terminated surface (S2 case).

Surface/bulk impurities and/or defects play an important role in the electronic structure leading to charge carrier doping, disorder induced local character to the charge carriers, etc. [21–23] Since we observed signature of oxygen impurities on the sample surface with aging, we have calculated the electronic structure considering one monolayer (ML) oxygen on the surface. The presence of 1 ML oxygen on the S1 and S2 surfaces changes the bands near E_F drastically as shown in Fig. 2(c) and (d). The thick lines show the energy bands with at least 50% contribution from O 2p. On Oxygen deposition, the DP on S1 shifts to higher binding energy and the O 2p contribution appears at the Fermi level. For S2 case,