
Chapter 7

First principle study of defect induced band structure in Cu substituted Bi_2Te_3 topological insulator

7.1 Introduction

Topological Insulator (TI) is a new branch of science that draws significant attention in the contemporary field of material science and technology. Although the observation of two-dimension (2D) TI was reported earlier, the invention of 3D TI brought a new vista in condensed matter physics[6]. Chalcogenides are the first investigated compound in 3D TI, and its most exciting feature lies in its novel electronic band structure[71]. The system shows a semiconducting bulk band (BB) and the metallic surface state (SS). After investigating chalcogenides compounds (Bi_2Te_3 , Bi_2Se_3 , Sb_2Te_3), a gamut of 3D TI along its doped compositions is extensively studied. The doped compositions of the 3D TI also exhibit some of the great features rooted in fundamental science, which are enormously useful in technological applications, viz. photodetector, magnetic device, field-effect transistor (FET), laser, and so on[154]. Earlier studies reveal that Cu substituted TI based on the chalcogenides compound shows fascinating features. The Cu intercalated Bi_2Se_3

shows superconducting behavior[65], the doping of Cu atom on the Te site in Bi_2Te_3 gives rise the defect-induced magnetic properties[62], and a tiny amount of Cu doping in the Bi site of Bi_2Te_3 can raise the p -type to n -type carrier transition[64]. Our study, too, reveals theoretically how the 5 at % of Cu doping in the various site of Bi_2Te_3 can raise a p -type and n -type compound. Interestingly, our theoretical analysis unfolds the inside view of recently observed hole-dominated metallic ground state configuration in Cu substituted Bi_2Te_3 compound[155]. In this paper, we have studied the bulk band structure of four different stages of Cu insertion: (i) the pristine one, (ii) 5 at. % of Cu substitution in Bi site, (iii) 8 at. % of Cu substitution in Bi site, with Te vacancy, to make the system carrier-compensated, (iv) 5 at. % of Cu intercalated in the Van der Waals gap of Bi_2Te_3 .

7.2 Methods

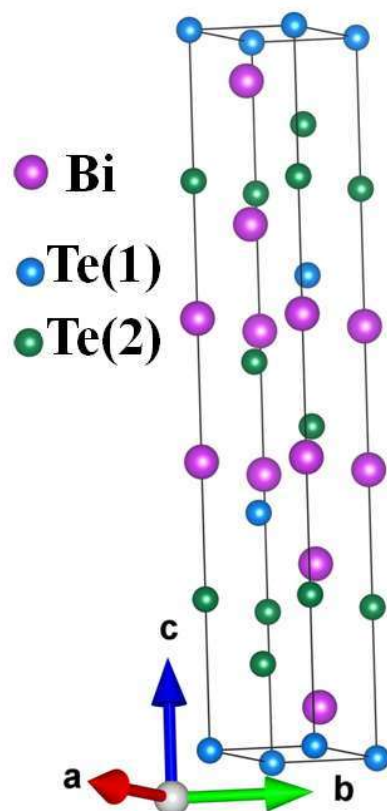


Figure 7.1: Unit cell of rhombohedral (space group: R-3m, 166) Bi_2Te_3 crystal.

7.2.1 Step by step procedure of unit cell preparation

To study the electronic structure, we have configured the unit cell as $2 \times 2 \times 1$ supercell. One unit cell of Bi_2Te_3 [FIG. 7.1] contains three formula units, and each formula unit contains two Bi atoms and three Te atoms. So, one unit cell of Bi_2Te_3 compound contains 6 Bi atoms and 9 Te atoms. If we make $2 \times 2 \times 1$ supercell, the size of a supercell becomes four times of the size of one unit cell. Such a supercell holds twelve 12 units containing 24 Bi atoms and 36 Te atoms. Now, for making the 5 at% of Cu doped in the Bi site of the Bi_2Te_3 crystal, we have to replace one Bi atom with one Cu atom. Such an arrangement takes the final form of a supercell containing one Cu atom, 23 Bi atoms, and 36 Te atoms. This supercell is equivalent to ~ 4.2 at% of Cu doping in the Bi site in the Bi_2Te_3 compound.

7.2.2 Simulation methodology and software used

The Bulk-band structure is calculated using Projected Augmented Wave (PAW) method as implemented in the *Vienna Ab initio* Simulation Package (VASP) [156] within the generalized gradient approximation (GGA) [123], Perdew-Burke-Ernzerhof (PBE) scheme. We have configured the unit cell as $2 \times 2 \times 1$ supercell to study the electronic structure. During the Structure optimization, we use the experimental lattice parameters and relax the atom position only. Structure optimization is done until the residual forces are less than $0.01 \text{ eV}\text{\AA}^{-1}$. The electronic structures have been calculated using Monkhorst-Pack $2 \times 2 \times 1$ K-point mesh. The spin-orbit coupling (SOC) has been included during the Self Consistency Field (SCF) run. The basis set of plane wave with the kinetic energy cut off ($E_{\text{cut-off}}$) in the simulation is 300 eV [52].

7.3 Result and Discussion

7.3.1 The pristine one

The unit cell of the pure Bi_2Te_3 crystal is shown in Fig. 1. The crystal structure contains five monoatomic layers in a pattern of Te(1)-Bi-Te(2)-Bi-Te(1). The Van der Waals gap is

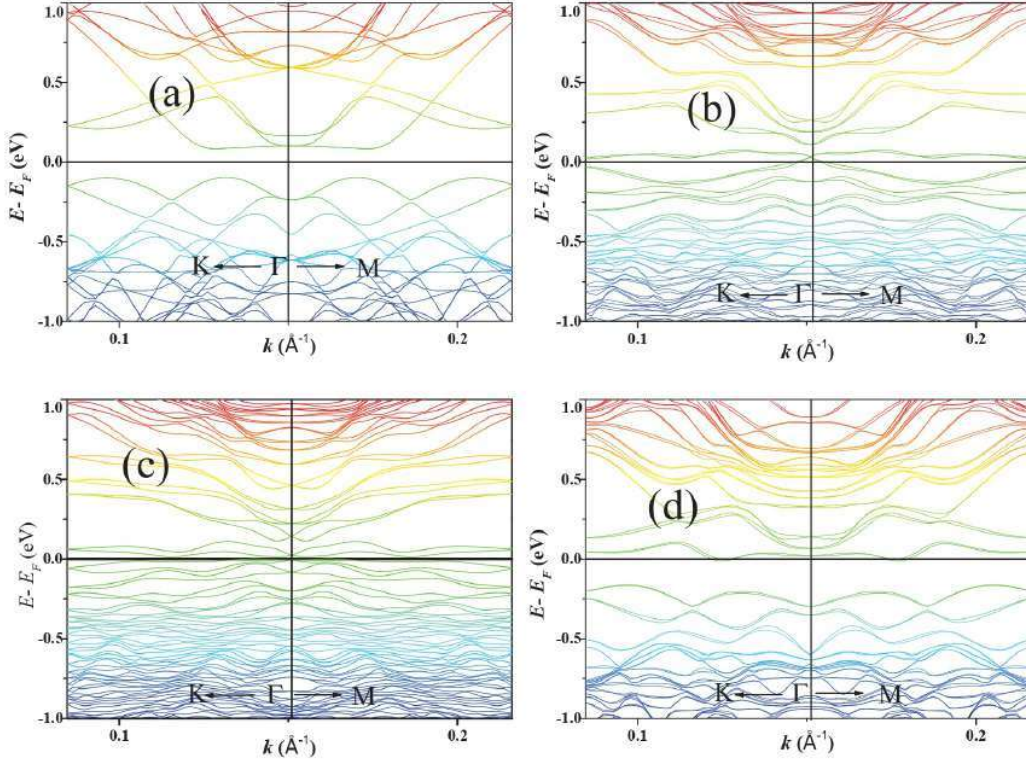


Figure 7.2: Simulated band-structure of the configurations: (a) pure Bi_2Te_3 compound, (b) Cu-substituted compound, (c) Cu-substituted with carrier neutral configuration and (d) Cu intercalated in the Van der Waal gap.

present between the two quintuple layers gaps. The electronic band structure of the pure Bi_2Te_3 is shown in FIG. 2 (a). We have observed that the bulk band structure of the pure compound acts as an intrinsic semiconductor with a shallow bandgap (170 meV)[157].

7.3.2 The Cu substitution in Bi site

To make 5 at.% of Cu doping in Bi site, we have replaced one Bi atom with one Cu atom in the supercell. In pristine Bi_2Te_3 , the Bi and Te atoms have 3^+ and 2^- ionic states. Replacing one Bi atom with one Cu atom makes the system hole-doped (as the Cu atom has a 2^+ ionic state). Such doping makes the structure a p -type compound [FIG. 7.2]. From FIG. 7.2(b), it is also shown that the Fermi level of the compound lies deep in the valence band, indicating the hole-mediated metallic phases of the compound. Such a result unfolds the origin of the bulk metallic phase of the same compound in the recently published

article[155].

7.3.3 The Carrier neutral configuration

One formula unit of the Bi_2Te_3 compound contains 2 Bi atoms and 3 Te atoms. Bi and Te atoms form Bi^{3+} and Te^{2-} ionic state; that means in one formula unit 2 Bi atom gives total 6 electrons to fulfill its octet and 3 Te atoms take these 6 electrons (to achieve its octet). Now, the Cu atom can form a Cu^{2+} ionic state. If we replace one Bi atom with one Cu atom, 5 electrons (3 from Bi and 2 from Cu) are donated to fulfill the octet of one Bi and one Cu atom in one formula unit. These 5 electrons are taken by 3 Te atoms in that particular formula unit. But as the Te atom is in Te^{2-} ionic state, 3 Te atoms need 6 (instead of 5) electron to complete its octet. Such arrangement causes one electron crisis in the Te site and makes the system hole-doped. To make the system carrier-neutral, we have replaced two Bi atoms with two Cu atoms and created one Te vacancy. One formula unit (out of 12 formula units in the supercell) contains only two Cu and two Te atoms for this arrangement. In such a scenario, 4 electrons are exchanged from the Cu site to the Te site, and the system becomes carrier-neutral. This structure contains 2.7 at% of Te vacancy with 8.3 at% of Cu doping in Bi site. The bulk band of such a configuration shows a *p*-type nature [FIG. 7.2 (c)]. During making the configuration, we have confirmed that all vacancy and substitution are created from the same quintuple layer (one quintuple layer is equivalent to one formula unit in Bi_2Te_3 crystal); otherwise, it can act as an isolated defect in the crystal[52].

7.3.4 The Cu intercalation in the Van der Walls gap

For our last assumption, we have placed one Cu atom between the two quintuple layers of the compound (5 at.% Cu intercalation). In this case, the Cu atom acts as an electron donor. FIG. 7.2 (d) shows that the Fermi level of such a configuration lies very close to the bottom edge of the conduction band, making an *n*-type ground state. Such *p*-type to the *n*-type evolution of the bulk band in the presence of a Cu atom is a widespread phenomenon observed experimentally[64].

7.4 Conclusion

We can conclude that the substitution of Cu in the pristine Bi_2Te_3 compound can harvest different carrier densities depending upon the position of the Cu atom in the crystal lattice. Our result unravels that BB of the Cu-substituted Bi_2Te_3 has an enormous role in transport phenomena apart from the topologically trivial SS. Importantly, our study simulates the two most promising experimental features, *viz.*; carrier type transition[64] and metallic ground state configuration[155] in the Cu substituted Bi_2Te_3 system.