

A Review of Electronic Structure Tuning in Bi_2Se_3 Topological Insulators

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ABSTRACT

Motivated by the discovery of quantum spin Hall systems, topological insulators constitute a class of quantum phase with insulating bulk and symmetry-protected metallic boundary modes, arising from nontrivial band topology. Among them, Bi_2Se_3 and its related substances are gradually known as the representative three-dimensional strong topology analyzer because of their large bulk energy gap, a Dirac cone on the surface and good chemical stability. In ideal theory, topological surface states have linear dispersion and anti-nonmagnetic scattering properties, so they are attractive in both basic research and application. However, in real materials, inherent defects will produce a lot of bulk carrier, which will lead to the increase of bulk conductivity, and it is difficult to see the contribution of “surface states” in transportation measurement. In order to solve this problem, various methods to adjust the electronic structure of Bi_2Se_3 are proposed. This review summarizes the latest progress of Bi_2Se_3 topology installers in electronic structure adjustment. We will focus on nonmagnetic doping and strain engineering in particular, and briefly discuss other methods, including electric-field control and interface engineering. By comparing various adjustment methods, we will explain their advantages and limitations, and expound the direction and prospect of better electronic control in the future.

Keywords: Topological Insulators; Bi_2Se_3 ; Electronic Structure Tuning; Doping; Strain; Topological Surface States

1. INTRODUCTION

Beyond the conventional band-theory description of electronic phases, topological insulating phases are a type of marveling quantum matter because of their unique physical properties. The bulk state has an insulating energy gap, but the surface states are gapless. These properties can be described by time-reversal symmetry. With these properties above, topological insulators are regarded as potential materials to make new-generation electronic devices, highly sensitive magnetic sensors, and study topological superconductors.

Research on topologically nontrivial systems began with the quantum hall effect and quantum spin hall effect. Two-dimensional insulators with quantum spin hall effect are also called two-dimensional topological insulators, whose topological properties of electronic bands are determined by a $\mathbb{Z}_2$ topological invariant ν which is related to the time-reversal symmetry. In 2006, the classification of two-dimensional topological insulators was theoretically extended to three-dimensional systems^[1]. Going to the three-dimensional system, topological properties are controlled by four $\mathbb{Z}_2$ invariant ($\nu_0; \nu_1\nu_2\nu_3$): when $\nu_0 = 0$, the system behaves as a weak topological insulator and can be viewed as a simple stacking of quantum spin hall effect systems; when $\nu_0 = 1$, it is a strong topological insulator, whose surface Fermi circle encompasses an even count of Kramers points, and a linear dispersion relationship is observed near the Dirac point. Fu and Kane further proposed a method for calculating the $\mathbb{Z}_2$ topological invariant of systems with inversion symmetry, and theoretically predicted that $\text{Bi}_1\text{-xSbx}$ and other substances are three-dimensional topological insulators^[2]. In 2008, the three-dimensional topological insulator of $\text{Bi}_1\text{-xSbx}$ was experimentally verified for the first time^[3]. However, because the surface state of $\text{Bi}_1\text{-xSbx}$ is quite complicated and the bulk energy gap is small, topological insulators with simpler surface state and larger bulk gap were being explored further. In 2009, materials such as Bi_2Se_3 were theoretically predicted^[4] and experimentally confirmed^[5] to be a new generation of three-dimensional topologically insulating systems. Compared with other topology installers (such as Sb), Bi_2Se_3 is an easier material to study. In particular, Bi_2Se_3 has only one Dirac cone, so the electronic structure is not complicated, and theoretical research and experiments are easy. Moreover, because the bulk band gap is large, it is easy to observe the conduction state of the surface. Because of its chemical stability and easy fabrication, Bi_2Se_3 has become a representative material for the study of topological physics. However, in practical use and experimental measurement, Bi_2Se_3 's topological surface state is often disturbed by bulk conduction, which is difficult to see directly in the transport experiment. This has also become a problem when using Bi_2Se_3 in practice^[6].

Adjusting the electronic structure can not only inhibit the annoying bulk conduction, but also make clear the conduction effect on the surface state. In addition, it is also a convenient place to study the new quantum state and increase the available scenarios. Therefore, in the review, our main purpose is to summarize various adjustment methods and their results, and discuss the adjustment that will use various methods in the future.

2. THEORITICAL BACKGROUND

Bi_2Se_3 and its isostructural compounds, such as Sb_2Te_3 and Bi_2Te_3 , are rhombohedral crystal structures with five atoms in the primitive unit cell and belong to the space group $R\bar{3}m$. Fig.1 shows the structure of Bi_2Se_3 crystal. Units of a layer made up of five atoms named quintuple layer are stacked in the direction of the z-axis. Each layer has two groups of atoms of the same kind-se (Se1 and se1') and Bi (Bi1 and bi1')-and a different kind of Se atom (Se2). Because the atom of Se2 is located in the center of space inversion, the parity eigenstates can be obtained, and the topological invariant can be understood by having inversion symmetry.

In 2009, Zhang Haijun announced that Bi_2Se_3 is a three-dimensional topological insulator by using the first-principles calculations. With the addition of spin-orbit coupling, the energy gap of the body with band inversion can be generated at the γ point where the time reversal of Brillouin zone is constant, as shown in Fig. 2. The size of the gap is about 0.3 eV, which is much larger than the energy generated by heat at room temperature. By looking at this band inversion, we can see that the electronic structure of Bi_2Se_3 has unusual topological properties. Moreover, in the electronic structure of the surface of BiSe known in the calculation, there is a gapless Dirac state centered on the γ point. Because its node is located near Fermi energy, as shown in Fig.3, it is confirmed that this substance has unusual properties in topologic. These results show theoretically that BiSe has the representative properties of three-dimensional topological insulator.

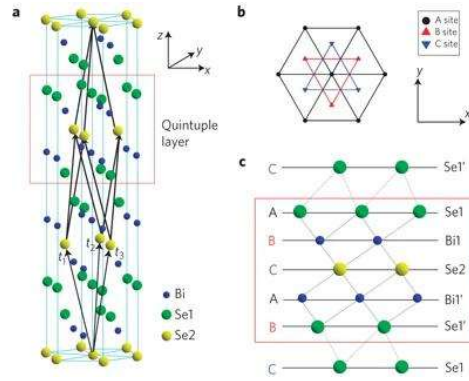


Figure 1. Crystal structure of Bi_2Se_3 [4].

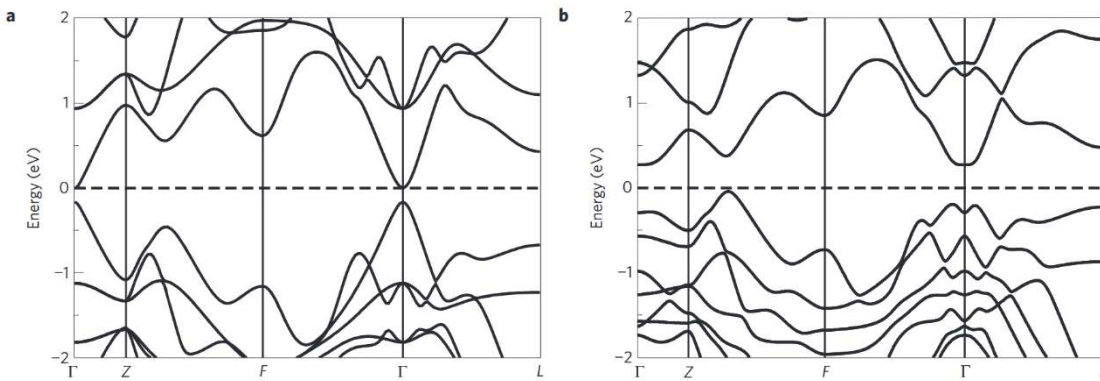


Figure 2. Band structure for Bi_2Se_3 in the absence (a) and presence (b) SOC [4].

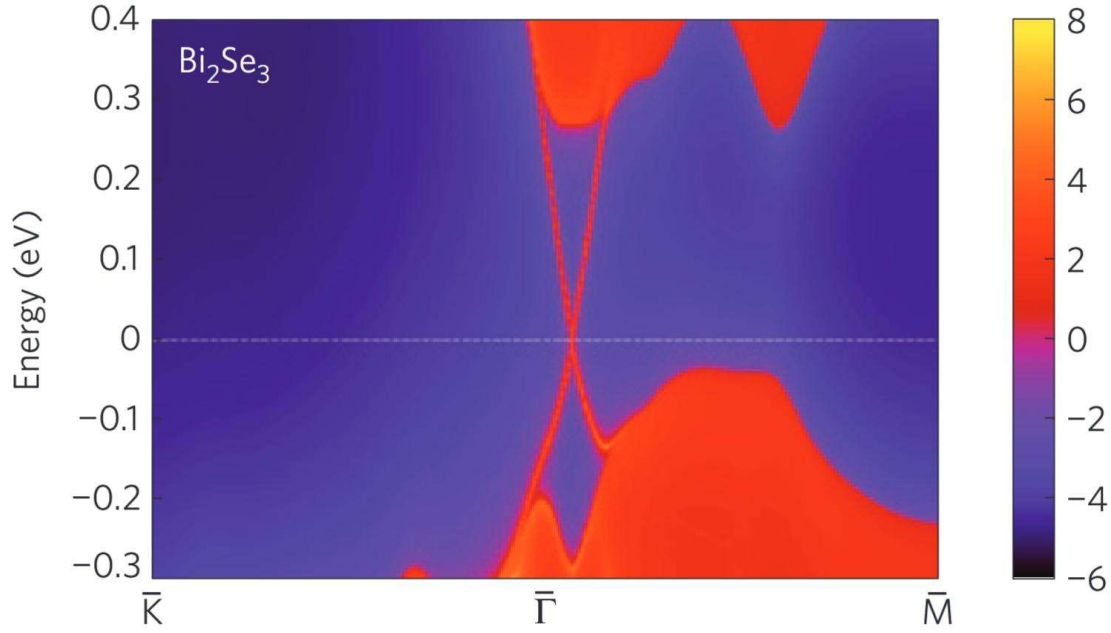


Figure 3. Surface state of Bi₂Se₃ on the (111) surface [4].

However, it is important that the calculation just now shows the electronic structure of Bi₂Se₃ in an ideal state. In practical matter, there are inevitable lattice imperfections such as vacancies of Se and anti-site defects of Bi/Se. For these reasons, Fermi energy level tends to deviate from the ideal Dirac point conduction band, which obviously shows bulk conduction. Moreover, the influence of environment such as surface oxidation will also produce excess charge carriers, further hiding the contribution of surface state. Therefore, it is considered theoretically that the surface state dominates the electron transport, but it is often observed in experiments that the bulk state dominates the transport [6]. The deviation between theoretical prediction and experimental results is a big obstacle to the practical application of topological insulators, and it is also an opportunity to improve the research of electronic structure by doping, strain engineering, external field and interface modulation.

3. TUNING METHODS

3.1 DOPING

Doping is one of the most effective methods to adjust the electronic structure of Bi₂Se₃-based topological insulators. Doping can be roughly divided into two types: non-magnetic and magnetic according to whether the dopant produces magnetic moments. The main purpose of non-magnetic doping is to eliminate N-type carriers generated by Se vacancies, thus inhibiting bulk conduction and adjusting the position of the Fermi level. Among various methods, Ca doping is one of the most representative and in-depth research methods.

In 2009, Hor researchers found in the study of Ca-doped Bi_{2-x}Ca_xSe₃ that the role of Ca as acceptor dopant can greatly reduce the number of electrons produced by Se vacancies. Therefore, the original N-type Bi₂Se₃ can be made close to electric neutrality, and it can even be changed to a P-type region. They use the angle-resolved photoemission spectroscopy (ARPES). When $x = 0.02$, the Fermi level is roughly less than 400 meV compared with the undoped sample, and the resistivity results are correct. These results show that the bulk carrier density has been effectively controlled. This study has laid an important foundation for both basic research and applied research of topological insulators [7].

It is understood that after adding about 1.2% Ca, both electron-type and hole-type can effectively inhibit the carrier density of sample to about 10 cm. This corresponds to the kinetic energy of about 25 meV under the action of heat [8]. In 2011, Hor and his partners further discovered in bi.ca.se that Fermi level can be adjusted to be close to Dirac point. Moreover, they also found that superconductivity can occur in Bi₂Se₃ by inserting Cu atoms, which created an important experimental site for the study of topological superconductors [9].

Checkelsky and Hor et al. further carried out a systematic investigation of the transport behavior of Ca-doped Bi_2Se_3 by combining temperature-dependent and gate-voltage-controlled measurements. Under sufficiently large gate-voltage modulation, the Hall coefficient underwent a sign change. The experimental results can be interpreted in terms of two parallel transport channels: a bulk transport channel requiring a thermal activation energy of roughly 50 meV, and a high-mobility metallic channel prevailing at low temperatures, which is attributed to topologically protected surface states. However, the study also pointed out that due to the relatively small activation energy, realizing devices dominated by surface-state transport at room temperature remains challenging ^[10].

In addition to Ca, other non-magnetic dopants, such as Ag, Sb, Te, and Sn, have also been reported to optimize the electronic structure of Bi_2Se_3 to varying extents, for example by tuning the Fermi level, reducing bulk carrier density, or improving material stability, thereby providing more possibilities for future device applications ^[11-13]. In contrast, magnetic dopants (e.g., Fe and Mn) are mainly employed to break time-reversal symmetry and explore phenomena such as the quantum anomalous Hall effect. Since their research objectives differ from the present focus on suppressing bulk conduction and enhancing surface-state transport, magnetic doping is not discussed in detail in this review.

3.2 STRAIN

Besides chemical doping, strain engineering, as a “clean” method, has also attracted many people’s attention. This is because the method of changing the electronic structure of Bi_2Se_3 -based topological insulators will not cause excessive impurity scattering. Because Bi_2Se_3 is a layered crystal structure, its lattice constant and interlayer distance are very sensitive to the externally applied strain. Strain changes the electronic structure by changing the mixing of atomic orbitals or the intensity of spin-orbit interaction, thus affecting the topological phase of materials.

Theoretical research shows that applying strain in Z direction can effectively adjust the degree of energy band inversion of Bi_2Se_3 near γ point. Young et al. found from the first-principles calculation that the band gap stress related to Z-axis strain is much larger than that caused by in-plane strain in five planes, and the influence of interlayer interaction on band gap is more obvious than that of in-plane interaction. In addition, when uniaxial strain in Z-direction increases to about 7%, topological phase transition occurs near γ point. They also calculated the band gap corresponding to Bi_2Te_3 . The size of lattice of bite is about 6% larger than that of bise, and bite cannot be simply the same as that of bise which accepted chemical strain ^[14].

From the experimental point of view, Segura et al. reported that when the applied pressure rises to 8 GPa, the optical band gap of Bi_2Se_3 will expand from 0.17eV to 0.45eV. This means that when pressure is applied, the band gap of bulk will also increase at the same time. In addition, we also found that high pressure will promote the 3D electron trapping process to reduce the number of electrons in bulk ^[15]. On this basis, Flötotto achieved the maximum elastic tensile strain of 2.1% through Bi_2Se_3 film, and it was observed that when the tensile strain in the X-axis direction became larger, Dirac point moved to a lower energy direction ^[16].

Generally speaking, strain engineering is an important method to refine the band structure of topology generator using Bi_2Se_3 by changing the symmetry and orbital hybridization of lattice. Compared with chemical doping, strain control fundamentally avoids the influence of chaos caused by impurity mixing, but the adjustable range and stability of actual equipment are still limited by manufacturing conditions. Therefore, the combination of strain with other methods such as doping and electric-field control is widely regarded as a promising direction to realize high-performance topological devices.

3.3 OTHER TUNING METHODS

In addition to chemical doping and strain engineering, external field and interface engineering are also important methods to change the electronic structure of topology analyzer using Bi_2Se_3 .

The control of electric-field is generally carried out by using the structure of gate, and the Fermi level can be changed little by little without adding excess impurities. Checkelsky et al. successfully changed the chemical potential by using the device of thin film whose Bi_2Se_3 is back-gated, and observed the activation energy of bulk transportation of about 50meV. In this way, the influence of the topological surface state is more obvious ^[10]. In addition, Kim et al. also found that in a very thin Bi_2Se_3 file, the equipment with the field-effect transistor with the back cover can effectively suppress the batch carriers. This will be an efficient experimental approach to study the transport properties of topological surfaces ^[17].

On the other hand, Magnetic-field and magnetic control will destroy the symmetry of time reversal and produce energy gap at the “Dirac” point of “topological surface state”. In the ARPES measurement of Bi_2Se_3 with Fe, it is found that there

is an energy gap in Dirac node. This is the experimental evidence that magnetic doping will destroy the symmetry of time reversal and change the topological surface states^[18]. This will be a way to create quantum anomalous Hall state and other topologies, but it will also weaken the mechanism of topological protection.

Recently, the efforts of interface and heterostructure have received a lot of attention. By creating topological insulator/superconductor heterostructures, the Cooper pair correlation can be moved to the surface state through proximity effect, thus generating superconducting gap. This will be the experimental site for topological superconductivity and Majorana bound states^[19, 20]. However, these methods have very harsh conditions in terms of interface advantages and material compatibility, and there are still some difficulties in the reproducibility of experiments and the stability of devices.

3.4 SUMMARY OF TUNING METHODS

By investigating the previous research paper, we can find that the electronic structure based on Bi_2Se_3 has its own advantages and disadvantages. Chemical doping is one of the most perfect and effective methods at present by making up for the original shortcomings and making the carrier density in it very small. However, scattering will inevitably be caused by impurities, which will have a negative impact on the mobility of surface state.

Strain engineering, as a “clean” method that does not introduce chemical disorder, enables continuous tuning of topological properties by modulating band inversion strength and the bulk band gap. Its theoretical feasibility has been confirmed by multiple first-principles calculations, but experimental implementation remains constrained by achievable strain magnitude and sample stability.

External-field control offers high reversibility and dynamic tunability, making it well suited for device-level functional design, yet it generally cannot fundamentally suppress bulk conduction. Interface engineering provides a unique platform for realizing novel topological quantum states, but the complexity of fabrication and stringent experimental requirements limit its current practical application.

Consequently, recent research has increasingly focused on the synergistic use of multiple approaches. For example, combining chemical doping with electric-field or strain control is regarded as a promising pathway to achieving low bulk carrier densities while maintaining surface-state-dominated transport^[7].

4. CONCLUSION AND OUTLOOK

This review has systematically summarized researches on the electronic structure regulation of Bi_2Se_3 -based three-dimensional topological insulators. As one of the most extensively studied three-dimensional topological insulators, Bi_2Se_3 provides an ideal platform for exploring topological phenomena owing to its simple surface-state dispersion, substantial bulk band gap, and favorable material stability. In theory, the combination of bulk insulation and time-reversal-symmetry-protected surface-state conduction provides an ideal platform for dissipationless transport, spintronics, and topological superconductivity.

However, a large number of experimental studies show that in the real Bi_2Se_3 sample, due to the original defects such as Se vacancy, the inside part is also very electrified. Therefore, the influence of surface state becomes invisible in handling measurement. The difference between theory and experiment has become a big problem that hinders the progress of basic research and equipment application of topological insulators. In order to solve this problem, various methods have been developed to reduce the number of carriers inside, adjust Fermi level and make the surface state clearer according to the nature of handling.

This review focuses on two representative methods: chemical doping and strain engineering. It is understood that non-magnetic doping (such as Ca, Sb) can well balance the increase of too many operating companies due to original defects. Moving “Fermi level” to “band gap” or even to “Dirac point” makes “bulk resistivity” very large. On the other hand, “strain engineering” adjusts the band inversion and size of the contour by changing the length and orbital hybridization of the grid. Teach you how to adjust continuously without creating chemical confusion. In addition, there are some special advantages in making external-field control, interface engineering and heterostructure, especially when looking for equipment to simplify thin-film and new quantum state. The above methods will slightly reduce the current of ontology, but there are still great shortcomings in various methods. Chemical doping often intensifies confusion and scattering. Strain engineering is limited to the range of strain that can be given in the experiment. Electric-field control is very dependent on the thickness of samples and the manufacture of equipment. These results show that only one method can not completely suppress the main body conduction without retaining the high-quality topological surface state.

Considering the future, it is expected that the research on adjusting the electronic structure of topological insulators based on Bi₂Se₃ will develop in several directions. First, combine multiple methods. For example, if externally applied strain or electric fields are matched with light chemical doping, the Fermi energy level and carrier distribution may be finely adjusted. The second is the technological progress in making high-quality films and heterostructure. In this way, a more stable place for interface engineering and proximity effect research can be obtained. Third, we should constantly shift the research from investigating the properties of substances to the research at the device level. Under the conditions of actual use, it is necessary to seriously investigate the stability and easy adjustment of topological surface states. The research on improving the electronic structure is more and more in-depth, and the theoretical expectation and experimental results are in better agreement. In the fields of quantum transport, spintronics, topological superconductor device, it is better to use the topological insulator technology.

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