

# First-Principles Investigation on Electronic Structure of $\text{Bi}_2\text{Se}_3$ Thin Film and the Films Doped with Pb

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**Abstract:** First-principles calculations were performed to investigate the electronic structure of the  $\text{Bi}_2\text{Se}_3$  single quintuple layer thin film and the films doped with Pb. Their band structures and densities of states were explored. The results show that the main composition of the valence band and conduction band of these films is p-states, and their band-gap type can change from the direct to the indirect as  $\text{Bi}_2\text{Se}_3$  from block to film. For the  $\text{BiPbSe}_3$  film, the newly appearing Se(1') layer in its structure caused by the doped Pb has an impact on the electronic structures of the film, but for the  $\text{Pb}_{0.25}\text{Bi}_{1.75}\text{Se}_3$  thin film with the concentration of Pb ~5%, it has the similar band structure to the pristine film. This paper also discussed the modulation of Bi 6s orbital states at the valence band maximum and the concentration of carriers in doped films.

**Key words:**  $\text{Bi}_2\text{Se}_3$  film; Pb dopant; energy bands; density of states

Topological insulators (TIs)<sup>[1-3]</sup> are widely investigated not only because of their special electronic structures but also because of their potential for future applications in electronic devices<sup>[4,5]</sup>. They have an insulating gap in the bulk, while also possessing conducting states in their surfaces that are protected by time-reversal symmetry<sup>[6]</sup>. These conducting surface states in the materials were predicted by theoretical stimulation and then were confirmed experimentally on samples ranging from bulk to thin films<sup>[4]</sup>. Recently, the researches in this field have been strongly motivated by the discovery of several real compounds<sup>[7-10]</sup> and two-dimensional (2D) TIs that was first proposed and successfully realized in the HgTe/CdTe heterostructure<sup>[11]</sup>. Much work has been devoted to phases  $\text{Bi}_2\text{X}_3$  ( $X=\text{Se}, \text{Te}$ ), as one of the well-known TIs, and new finding showed that  $\text{Bi}_2\text{X}_3$  surface states consist of a single Dirac cone at the G point<sup>[12]</sup>.  $\text{Bi}_2\text{Se}_3$  is an important topological insulator among  $\text{Bi}_2\text{X}_3$  materials. It is chemically stable and easy to synthesize<sup>[13,14]</sup> and has a bulk band gap of about 0.3 eV, which is much larger than the others in room temperature<sup>[4]</sup>. Some stimulations have shown that  $\text{Bi}_2\text{Se}_3$  doped with Fe, Mn, Cr and Cu, could exhibit some interesting physical properties, such as ferromagnetism,

quantized anomalous Hall effect and superconductivity<sup>[15]</sup>. P. Larson et al<sup>[16]</sup> found that  $\text{Bi}_5\text{FeTe}_9$  ( $\text{Bi}_2\text{Se}_3$  doped with transition metal Fe) has the largest magnetic moment compared with the others; however,  $\text{Bi}_5\text{NiTe}_9$  ( $\text{Bi}_2\text{Se}_3$  doped with Ni) demonstrates a slightly lower magnetism than the average variations. L. B. Abdalla et al<sup>[11]</sup> pointed that the surface state of 2D  $\text{Bi}_2\text{Se}_3$  (111) could change as it was doped with Cr, Mn, Fe or Ni, especially doped Ni resulting in the surface conducting state destruction. For  $\text{Bi}_2\text{Se}_3$  thin films, H. Jin et al<sup>[17]</sup> found that magnetic-ion substitution opens a gap in the Dirac cone of a single surface and O substitutions at the surface layer that can move the energy level of a gapless surface state upward with a local magnetic field. Some other studies focused on the effect of mechanical strain on topological effects, showing that both spin-orbit coupling (SOC) and mechanical strain can largely influence the topological insulating phase<sup>[18]</sup>.

In the present paper, the first-principles calculations were carried out to study the electronic properties of  $\text{Bi}_2\text{Se}_3$  with Pb, which is the neighbor of Bi, having the similar electronegativity and atom radius with Bi. Electronic structures of  $\text{Bi}_2\text{Se}_3$  thin film doped with Pb are systematically

Received date: November 10, 2015

Foundation item: Fundamental Research Funds for the Central Universities (2013XK07)

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investigated, aiming at getting better understanding of the electrical properties of this type of doping.

## 1 Crystal Structure and Method

The  $\text{Bi}_2\text{Se}_3$  family of compounds form in the tetradymite crystal structure with a smallest unit cell with three inequivalent atoms in the rhombohedral ( $R\bar{3}m$ , No.166) structure with Bi in the 2c, Se(1) in the 2c and Se(2) in the 1a Wyckoff positions. The crystal structure can be seen as layers along the  $c$ -axis direction with alternating layers of Bi and Se in the order Se(1)-Bi-Se(2)-Bi-Se(1) to form “quintuple layer” (QL) [4]. The inter-layer bonding, dominated by the covalent, within the QLs is stronger than the bonding between the QLs because of the interaction of van der Waals binding [13]. The positions of the atoms in this symmetry, as shown in Fig.1, demonstrate that all atoms lie along the trigonal axis. We take Se (2) to be at the origin (0, 0, 0); then two Bi atoms at  $(\pm\mu, \pm\mu, \pm\mu)$  and two Se(1) at  $(\pm\nu, \pm\nu, \pm\nu)$ , defined in the unit of primitive translation vectors. The experimental lattice constants for  $\text{Bi}_2\text{Se}_3$  are  $a=b=0.4143$  nm,  $c=2.8636$  nm,  $\alpha=\beta=90^\circ$ ,  $\gamma=120^\circ$  and  $\mu=0.4008$ ,  $\nu=0.2117$ [19,20]. Surface states in  $\text{Bi}_2\text{Se}_3$  bulk and films were investigated using (111) slab model, which is the natural cleavage plane. The Pb doped film we choose is a single QL structure due to the limitations of the computing resources. A single QL is shown in the frame of Fig.2, and the thickness of the vacuum layer is about 1.5 nm, which can exclude the impact of the interaction between two QLs. Experimental results has shown that there can be a stable Pb-Se bond. Therefore, the doping model we used is the subsurface Bi atoms replaced by Pb, which is one form of the doping means.

First-principles calculations use the plane wave density functional theory (DFT) code Quantum-ESPRESSO (QE) with norm-conserving pseudopotentials[21-23]. The calculations have been performed within the DFT framework employing the Perdew-Burke-Ernzerhof (PBE)[24]—generalized gradient approximation (GGA) to the exchange-correlation functional.

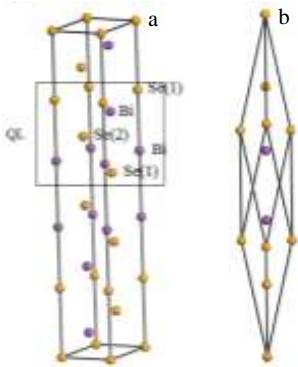


Fig.1 Crystal structure of  $\text{Bi}_2\text{Se}_3$ : (a) crystal structure of  $\text{Bi}_2\text{Se}_3$  consists of hexagonal layers of Bi and Se stacked alternating (a quintuple layer was indicated by the black square); (b) rhombohedral unit cell

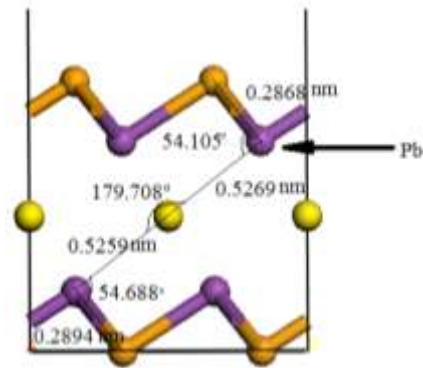


Fig.2 Structural model for the single-QL thin film and the parameters of the bond lengths and angles of doped film

For structural relaxation, the plane-wave kinetic energy cutoff was set to 140 Ry and the Brillouin zone was sampled with a  $8 \times 8 \times 8$   $k$ -point grid for block [25] and  $9 \times 9 \times 1$  for films to ensure the convergence. The BFGS quasi-newton algorithm method was used for relaxation, in which the atomic position parameters were relaxed for a set of constant lattice vector until forces had converged to less than  $10^{-3}$  eV/nm, while the block had a variable cell. The relaxation were done in a non-spin-polarized manner and self-consistent calculations were performed in a spin-polarized manner, since the SOC is important for the heavy elements considered here [26].

## 2 Results and Discussion

The structural model of the single-QL thin film doped with Pb and the parameters of the bond lengths and angles are shown in Fig.2. Compared with the parameters of the film before and after doping, obviously, the thickness becomes small (from 0.7078 nm to 0.7049 nm). In addition, the bond length of Pb-Se and Bi-Se is 0.2893 and 0.2868 nm in surface, respectively, but 0.5268 and 0.5269 nm in middle. The bond angles are still  $54.105^\circ$  shown in the figure. however, it can be sure that the lattice configuration of pristine film is wholly similar to that doped with Pb.

For a better understanding of the electronic structures of single-QL  $\text{Bi}_2\text{Se}_3$  thin film, we firstly calculated the band structure and electronic density of states (DOS) of  $\text{Bi}_2\text{Se}_3$  block, as shown in Fig.3, which are consistent with the recent studies[27].

The calculated electronic band structure of single-QL thin film is shown in Fig.4a. Compared with the block, the position of Fermi level and the valence band maximum (VBM) shift. And the film performances as an indirect gap semiconductor with a narrow band gap of about 0.91 eV. The curve near the VBM is smoother than that near the conduction band maximum (CBM), which means that the VBM is dominated by a strong local atomic orbit, correspondingly the CBM being decided by the strong extended atomic orbits. In addition, the effective mass ( $m^*$ ) is completely determined by

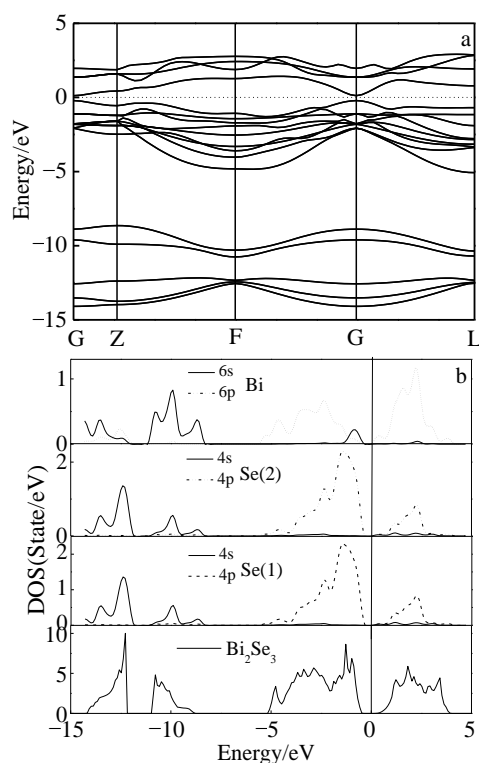


Fig.3 Energy bands (a) and corresponding density of states (DOS) (b) of  $\text{Bi}_2\text{Se}_3$  block

$d^2E/dk^2$  based on formula (1).

$$m^* = \left| \frac{\hbar^2}{d^2E/dk^2} \right| \quad (1)$$

where,  $m^*$ : effective mass of carriers;  $\hbar$ : planck constant;  $E$ : energy;  $k$ :  $k$  point in the reciprocal lattice, Obviously, the effective mass of the carriers at the VBM is bigger than that at the CBM. The quasi-classical formula  $F=m^*a$  illustrates that the carriers with small effective mass can get big acceleration in an external field. It can be deduced that the response of electrons in conduction band to external field is agile in the single-QL thin film.

Fig.4b is the electronic density of states (DOS) of the pristine film. The energy bands under Fermi level are divided into three parts: the deep level (-13 eV to -12 eV), intermediate level (-11 eV to -8 eV) and shallow level (-5 eV to 0 eV, valence band), among which the valence band broaden is the most and there is an apparent energy splitting phenomenon. On the other hand, Se(1) and Se(2) atoms in the structure display a distinctly different site projected DOS. Se(2) is situated at the center of the QL. Its 4p states have a larger contribution to the valence band, Se(1) 4p and Bi 6p coming second, moreover, Bi 6s having small contribution near the Fermi level. The energy region of conduction band is between 0 to 5 eV, whose low part and high part are composed of p states of Bi and Se(1) (they provide almost equal contribution to the low part) and 4p states of Se(2), respectively.

As one subsurface Bi atom replaced by Pb in the QL,

$\text{PbBiSe}_3$  thin film is obtained. As shown in Fig.4c, the CBM of the film is almost the same as before. But, the VBM is more flat relatively than that before, which is decided by the enhanced local orbit. The band gap belongs to indirect characteristics with a value of 0.89 eV, slightly decreasing compared with the pristine film and presenting a blue-shift effect. Displayed in Fig.4d, the DOS illustrates that in the vicinity of Pb, the arrangement of Se surface atoms takes a new pattern and is named as  $\text{Se}(1')$  layer, and that in the valence band, the most contribution comes from 4p states of  $\text{Se}(1')$ , 6p and 6d states of Pb accounting minority. What is different from the valence band is that the conduction band is mainly composed of Bi 6p states, the  $\text{Se}(1')$  4p states second. Therefore, the doped Pb atoms change the arrangement of Se atoms around so as to affect the energy band structure of the  $\text{PbBiSe}_3$  film material deeply.

$\text{Pb}_{0.25}\text{Bi}_{1.75}\text{Se}_3$  thin film has the concentration of Pb ~5%. It is found that the layer of  $\text{Se}(1')$  does not appear in the structure due to the low doping concentration. The band gap of the film takes a value of 0.75 eV, but the valence and conduction band structure is similar to those of the pristine film, as shown in Fig.4e.

Through analyzing the constitution of the VBM, we find that for  $\text{Bi}_2\text{Se}_3$  block, the contribution of Bi 6s state is about 6.5%, but it is only 3.2%, 2.1% and 1.2%, smaller than the half of 6.5%, for the single-QL  $\text{Bi}_2\text{Se}_3$ ,  $\text{PbBiSe}_3$  and  $\text{Pb}_{0.25}\text{Bi}_{1.75}\text{Se}_3$  thin film, respectively. So, we deduce that Bi 6s state should have a significant role in modulating the position of the VBM. For the block, the big contribution of Bi 6s state makes the VBM and CBM locate at the same point (G point) and maintains the characteristic of direct band gap semiconductor. For the thin films, the contribution of Bi 6s state declines significantly at the VBM because the periodic potential field changes. This weak modulation causes the VBM to deviate from the CBM with an indirect band gap accompanying this deviate. Otherwise, compared with the band gap value of the block (0.32 eV), that of the films changes multiply, which are 0.91 eV (pristine), 0.75 eV (low concentration doping) and 0.89 eV (high concentration doping). It should be also attributed to the significant adjustments of the periodic potential field in the films.

For the doped films, because their Fermi level moves down in the valence band near VBM, that moving will influence the concentration of the carriers. The conductivity of semiconductors is derived from formula (2), which depends on the concentration and mobility of carriers. For single-QL thin film of  $\text{Bi}_2\text{Se}_3$  doped with Pb, we can calculate the concentration of carriers based on their DOS. And the concentration of carriers in valence band is calculated by formula (3) and (4).

$$\sigma = nq\mu_- + pq\mu_+ \quad (2)$$

where,  $\sigma$ : conductivity of semiconductors;  $n$ : concentration of carrier with negative charge;  $p$ : concentration of carrier with positive charge;  $q$ : charge of carrier;  $\mu_-$ : mobility of negative carrier;  $\mu_+$ : mobility of positive carrier.

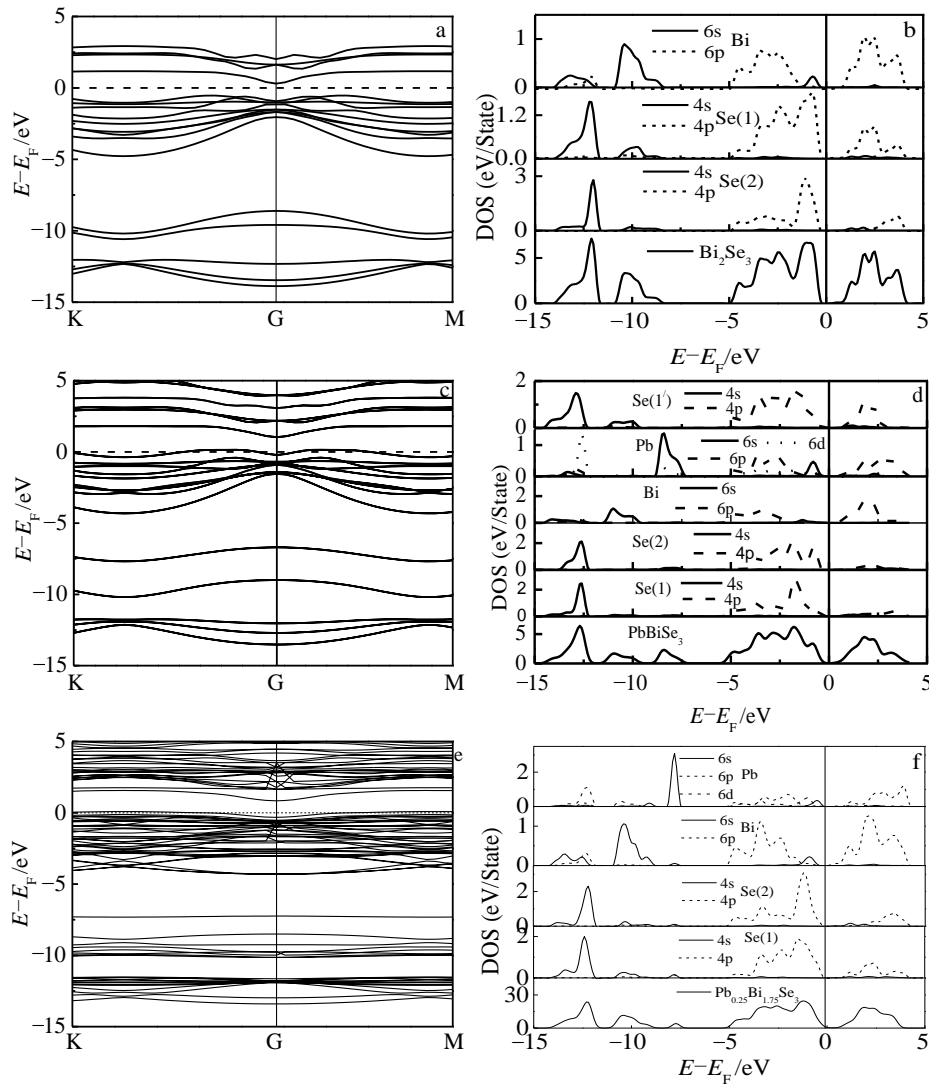


Fig.4 Energy bands of single-QL thin film of  $\text{Bi}_2\text{Se}_3$  (a),  $\text{PbBiSe}_3$  (c), and  $\text{Pb}_{0.25}\text{Bi}_{1.75}\text{Se}_3$  (e) along high symmetry directions of the first Brillouin zone, and their corresponding density of states (DOS) of single-QL thin film of  $\text{Bi}_2\text{Se}_3$  (b),  $\text{PbBiSe}_3$  (d), and  $\text{Pb}_{0.25}\text{Bi}_{1.75}\text{Se}_3$  (f)

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \quad (3)$$

where,  $f(E)$ : fermi function;  $E$ : energy;  $E_F$ : energy of Fermi;  $k_B$ : Boltzmann constant;  $T$ : temperature.

$$P_0 = \frac{1}{V} \int_{-\infty}^{E_+} (1 - f(E)) N_+(E) dE \quad (4)$$

where,  $P_0$ : concentration of hole;  $V$ : volume;  $E_+$ : energy of valence band top;  $f(E)$ : Fermi function;  $N_+(E)$ : density of states. The results show that the  $\text{Pb}_{0.25}\text{Bi}_{1.75}\text{Se}_3$  film takes the concentration of carriers about  $3.45 \times 10^{20} \text{ cm}^{-3}$ , while  $1.13 \times 10^{21} \text{ cm}^{-3}$  in  $\text{PbBiSe}_3$  film. The conductivity is enhanced.

### 3 Conclusions

1) The main composition of the valence band and conduction band of these films is p-states, and their band-gap type can change from the direct to the indirect as  $\text{Bi}_2\text{Se}_3$  from block to film.

2) The band structures are the similar between the pristine film and the  $\text{Pb}_{0.25}\text{Bi}_{1.75}\text{Se}_3$  film, but in  $\text{BiPbSe}_3$  film, the arrangement of Se surface atoms in the vicinity of Pb is changed and presents a new pattern, which greatly affects its energy band structure. The 6s states of Bi (Pb) have a certain modulation on the morphology of the valence and conduction band, which controls the block to be a direct band gap semiconductor, but the single-QL thin films show an indirect gap.

3) The concentration of carriers in  $\text{PbBiSe}_3$  and  $\text{Pb}_{0.25}\text{Bi}_{1.75}\text{Se}_3$  is calculated as  $1.13 \times 10^{21}$  and  $3.45 \times 10^{20} \text{ cm}^{-3}$ , respectively.

**Acknowledgements:** We are grateful to the Advanced Analysis and Computation Center of CUMT for the award of CPU hours to accomplish this work.

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## Bi<sub>2</sub>Se<sub>3</sub> 薄膜及 Pb 掺杂电子结构变化的第一性原理

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**摘要:** 利用第一性原理平面波赝势方法, 研究 Bi<sub>2</sub>Se<sub>3</sub> 从块体到薄膜的电子结构变化特性。通过分析材料的原子位置以及电子间相互作用, 具体探讨块体、双层和单层薄膜及单层 Pb 掺杂薄膜的能带结构、态密度等。计算结果表明, 这几种材料的价带和导带主要由原子的 p 态构成, 同时由于 Bi (Pb) 的 6s 轨道态对价带顶的影响, 它们的带隙类型随着材料结构的变化, 发生从直接带隙到间接带隙的转变, 此外 Pb 掺杂单层薄膜后产生的 Se(1')层对其电子结构的变化有重要影响。

**关键词:** Bi<sub>2</sub>Se<sub>3</sub> 薄膜; 能带; 态密度; 电子结构

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