Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Structural and transport properties of iridium-doped Bi₂Se₃ topological insulator crystals



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ARTICLE INFO

Article history: Received 14 May 2016 Received in revised form 29 September 2016 Accepted 1 October 2016 Available online 3 October 2016

Keywords: Topological insulators Magnetoresistance Structural properties

1. Introduction

Topological insulators (TIs) have metallic boundary states that originate from topological invariants and are protected by timereversal symmetry (TRS), while their bulk states remain insulating due to a finite energy band gap [1–4]. Theoretical calculations and experimental results have shown that 3D topological insulators such as Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ doped with transition metal elements will become magnetically ordered, which can break the TRS and open a gap around the original Dirac point [2,5]. In Codoped Bi₂Se₃ [6], Mn-substituted Bi₂Te₃ single crystal [7], Cr-doped and V-doped Sb₂Te₃ thin film [8–10], ferromagnetism has been found. The magnetic elements doped into TIs may lead to many exotic phenomena and the tuning of surface states as well. Thus they may have potential application in spintronics and faulttolerant quantum computing [11–13]. It was also reported that doping with Ca or Cd in Bi₂Se₃ crystals produced p-type semiconductor [14,15]. However, doping with 5d transition metals, which have many exotic properties such as strong spin-orbit coupling, Ir-doped Bi₂Se₃ crystals have never been reported. Among 5d transition metals, iridium is of particular interest, due to

ABSTRACT

Iridium doped Bi₂Se₃ crystals have been prepared by self-flux method. Their crystalline, morphological, Raman spectra, and transport properties were investigated. The obtained crystals have typical topological insulator characteristics. Same layered structure was confirmed for all samples. The lattice parameter *c* first decreased and then increased with increasing Ir content. All samples showed two characteristic Raman peaks of Bi₂Se₃ with one of them blue-shifting as the Ir content increased. The magnetoresistance as well as the resistivity increased first and then decreased with increasing Ir content. The doping mechanism was considered that Ir atoms mainly occupied Bi sites when doped content was lower but they tended to intercalate into atomic layers and van der Waals gap at higher doping content. © 2016 Elsevier B.V. All rights reserved.

its versatility in oxidation states [16]. In this article we report the preparation of iridium doped Bi₂Se₃ samples. Also structural and morphological characterizations will be analyzed. Raman spectroscopy and magneto-resistance measurements will be used to explore the intrinsic properties of the Ir doped Bi₂Se₃.

2. Experimental

Single crystals of $Bi_{2-x}Ir_xSe_3$ (x = 0, 0.01, 0.03, 0.05 and 0.07) were prepared from the reaction of stoichiometric mixture of highpurity (99.999%) bismuth, selenium and iridium powders. The mixed powders were grinded, pressed into small rounds in a glove box with an argon atmosphere, and sealed in evacuated quartz tubes. The tubes were heated up to 860 °C, then slowly cooled to 620 °C and kept at that temperature for 8 h. Finally, the samples were quenched in cold water.

The obtained Bi_{2-x}Ir_xSe₃ crystals can be easily cleaved into small pieces with flat and shiny surfaces. All samples for test were prepared via mechanical exfoliation. The crystal structure was studied by x-ray diffraction (XRD, X'Pert Panalytical) at 300 K. The morphology was characterized by Field Emission Scanning Electron Microscope (FESEM, JSM-7001F) equipped with an energy-dispersive spectroscopy (EDS) instrument, which was conducted at room temperature. Transport properties were performed by using Physical Property Measurement System (PPMS, Quantum



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Design), where the standard four-probe method was used for resistivity measurements. A Laser Raman Spectrometer (HORIBA, France) was used for Raman spectroscopy. Samples were excited with laser light $\lambda = 532$ nm at 300 K. The exposure time was 10 s and laser intensity was set to 0.5 mW. Energy dispersion relations were studied by angular resolved photoemission spectroscopy (ARPES) with a SES 200 hermispherical analyzer using 52eV photos under the temperature of 10 K.

3. Results and discussion

The obtained $Bi_{2-x}Ir_xSe_3$ crystals have been experimentally confirmed to have typical topological characteristics through ARPES measurement. No band gap can be observed, which is common in non-magnetic doped Bi_2Se_3 [2]. Typical ARPES intensity map for $Bi_{2-x}Ir_xSe_3$ crystal (x = 0.05) is shown in Fig. 1. The APRES band map shows a single Dirac cone with the Dirac point located at 0.375 eV below the Fermi level, indicating a clear TI surface state.

The XRD patterns of $Bi_{2-x}Ir_xSe_3$ samples are shown in Fig. 2. All samples exhibit the rhombohedral layered structure. Only the (00L) diffraction peaks are observed. All of these peaks shift to the right side with increasing Ir concentration up to x = 0.05, then shift to the left side for x = 0.07. As an example, the (006) peak in the inset of Fig. 2 shows this trend, which suggests that the lattice constant *c* decreases with increasing Ir content between x = 0 and x = 0.05, but increases after x > 0.05.

A structural schematic diagram of undoped Bi₂Se₃ is shown in Fig. 3(a). A quintuple layer (1QL) consists of five individual atomic layers in the order of Se₁-Bi-Se₂-Bi-Se₁. There are three possibilities of doped Ir atoms: substituting Bi (Fig. 3(b)), inserting into individual atomic layers (Fig. 3(c)) or inserting into the van der Waals gap between QLs (Fig. 3(d)). Among the three possibilities, only the Bi-substitution would lead to a shrinkage of lattice constant, due to apparently shorter chemical bond between Ir and Se compared with the bond between Bi and Se. Based on previously reported. Ir–Se single bond length (2.45 Å) [17] and the Bi–Se bond length in Bi₂Se₃ (2.84 Å for Se₁–Bi and 3.04 Å for Se₂–Bi) [18], the contribution of each Bi-substituting Ir atoms on the decrease of lattice parameter *c* could be roughly estimated. Between x = 0 and x = 0.05, the majority of Ir atoms doped into Bi₂Se₃ have replaced Bi atoms in the crystal structure, causing the decrease of c value. However, when the Ir content x > 0.05, a certain amount of Ir atoms



Fig. 1. ARPES intensity map along the K-r-K direction for typical $Bi_{2-x}Ir_xSe_3$ crystal (x = 0.05). The bulk conduction band (BCB), bulk valence band (BVB), the surface state band (SSB) and the Dirac point are indicated.



Fig. 2. X-ray diffraction patterns of Bi_{2-x}Ir_xSe₃. Inset: the (006) peaks of Bi_{2-x}Ir_xSe₃.

might be at interatomic space within a QL or between QLs. Residing between QLs are more likely because the Se–Se link between QLs is week van der Waals bonds [19]. Ir atoms with a van der Waals radius of 2.3 Å [20] inserting between QLs will significantly expand the spacing between QLs, as well as the lattice constant along *c* axis.

In the Raman spectra of Bi_{2-x}Ir_xSe₃ (Fig. 4(a)), two characteristic peaks can be identified to be E_g^2 and A_{1g}^2 modes, which is in agreement with other reports of Bi₂Se₃ [21,22]. No other Raman scattering peaks is observed, indicating the overall crystal structures of doped samples are the same as pure Bi₂Se₃, which is consistent with the XRD results. The E_g^2 and A_{1g}^2 peaks are around 131 and 174 cm⁻¹ but also shift with different Ir contents (Fig. 4(b)). For the A_{1g}^2 mode, a blue shift (from 173 to 175 cm⁻¹) occurs as the Ir content increases from x = 0.00 to x = 0.07, while the E_{2g}^2 mode is more sensitive to the Ir content than the E_{2g}^2 mode, which is characteristic for the Raman spectra of this kind of compounds [23].

Blue shift of Raman peaks usually suggests lighter atoms and/or stronger chemical bonds between atoms. The atomic weight of Ir is slightly smaller than that of Bi, and more importantly the Ir–Se bond length is considerably shorter than Bi–Se bond length. Both factors can account for the blue shift of A^2_{1g} mode, and also prove that doped Ir atoms have substituted Bi atoms. The increasing blue shift with increasing Ir content indicates that the amount of Bisubstituting Ir atoms is constantly increasing along with doped Ir content. The XRD results show the same trend except x = 0.07. Combining with XRD and Raman scattering results, it can be concluded that at x = 0.07, the majority of doped Ir atoms are still substituting Bi atoms, with only a small fraction inserting between QLs. The inter-layer Ir atoms would have negligible effect on the Raman spectra, but are likely to significantly increase the lattice constant *c*.

SEM micrographs of Bi_{2-x}Ir_xSe₃ samples are shown in Fig. 5. Distinct layered structures can be seen for all samples and their surfaces are flat and smooth. The EDX results in Table 1 show the actual atomic percentage of Bi, Se, Ir, which is close to the nominal ratio.

The transport properties measurements (Fig. 6) show that all samples exhibit similar ρ -*T* curves under zero filed. Resistivity increases with increasing temperature, indicating weak metallic behaviors. For samples with different Ir contents, the electrical resistivity increases first and then decrease with increasing Ir contents. This phenomenon may be related to the competition between two doping mechanism: Ir atoms occupying Bi sites versus intercalating between Bi₂Se₃ layers. At first Ir atoms are mostly replacing Bi atoms, causing distortion of the lattice and introducing disorder that contributes to the increase of resistivity. Then at higher Ir concentration, some Ir atoms residing between layers are

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