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Crystals growth of topological insulators in $Bi_2(Se_xTe_{1-x})_3$ system

D. Dimitrov [a,*], V. Marinova [a], V. Tomov [b], P. Rafailov [b], M. Gospodinov [b]

[a] *Institute of Optical Materials and Technologies, Sofia 1113, Bulgaria*
[b] *Institute of Solid State Physics, Sofia 1723, Bulgaria*

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Topological insulator single crystals of $Bi_2(Se_xTe_{1-x})_3$ and doped Bi_2Se_3 are prepared by modified Bridgman technique. The crystals are with high quality as confirmed by XRD and Raman spectroscopy measurements. These new materials are of great importance for the research on devices and technologies based on topological insulator properties.

Keywords: topological insulators, Bi_2Se_3, single crystals

INTRODUCTION

Topological insulators (TIs) have generated a great interest in the fields of condensed matter physics, chemistry and materials science. The topological insulator is an insulator in the bulk, while it conducts on the surface like a metal. Topological insulators occur as two-dimensional (2D) – also called quantum spin Hall state – and three-dimensional (3D) versions. They have a full energy gap in the bulk, but host topologically protected gapless edge (2D) or surface (3D) states.

The first TIs was predicted in 2006 and experimentally realized in 2007 in HgTe quantum wells. Shortly later, three well-known binary chalcogenides, Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3, were predicted and observed to be TIs with a large bulk gap and a metallic surface state consisting of a single Dirac cone. The discovery of these topological materials opened up the exciting field of topological insulators. Extensive experimental and theoretical efforts are devoted to synthesizing and optimizing samples, characterizing the topological states, transport measurements, device fabrications, and searching for new material candidates [1].

The most promising 3D system is currently Bi_2Se_3, which is known to have a large bandgap and a single surface Dirac cone [2]. Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 have rhombohedral crystal structures [3] and the surface Brillouin zone of the (001) surface is hexagonal. The combination of spin polarization and extreme robustness of the surface states on the TIs makes these materials promising for practical device applications. However, in order to achieve conduction from the surface states alone the chemical potential needs to be placed inside the bulk band gap, something which requires careful control of the amount of bulk defects in these materials. In reality, this has proven difficult in the stoichiometric Bi_2Se_3 due to a large number of Se vacancies which render the materials *n*-doped, placing the Fermi-level in the conduction band [4]. The surface state transport accessing in as-grown Bi_2Se_3 remains challenging. There are several possible strategies [5] to reduce the bulk conduction: reducing the thickness of the crystal; adding more Se during growth to reduce Se vacancies; growing mixed crystals with large bulk resistivity (low bulk carrier density) ; growing crystals with compensating dopants (e.g., Sb or Ca) to reduce bulk doping. Employing one or more of such strategies is considering important to prepare TI materials for transport studies and device applications of TI surface states.

In this paper growth and characterization of $Bi_2(Se_xTe_{1-x})_3$ mixed crystals and Bi_2Se_3 crystals doped with Ca, Cu and Mn are reported.

EXPERIMENTAL DETAILS

Single crystals of 3D topological insulators in the system $Bi_2(Se_xTe_{1-x})_3$, where x= (0.5; 0.75; 1) as well as crystals in the Bi_2Se_3-based system doped with Ca, Cu, Co and Mn are grown by a modified Bridgman technique.The starting materials with high purity as follows Bi -99.999%, Se - 99.999%, Te 99.9999%, Cu (99.99 %),Ca (99.99 %), Co(99.99 %) and Mn (99.99%) are mixed according to the desired compositions of $Bi_2(Se_xTe_{1-x})_3$ or doped Bi_2Se_3 and placed in

* To whom all correspondence should be sent:
E-mail: ddimitrov@iomt.bas.bg

encapsulated quartz ampoules with diameter 10 mm-50 mm.. The possible reaction between Ca and quartz during the crystal growth of doped Bi_2Se_3 is prevented by covering the inside surface of the quartz ampoule with pyrolytic graphite. The $Bi_2(Se_xTe_{1-x})_3$ crystals are grown with a speed of withdrawing of quartz ampoule of 0.2mm/h, after being heated to 800 C and kept at a constant temperature. The ampoule rotation speed was 25 rot/min. Doped Bi_2Se_3 crystals were grown by melting the stoichiometric mixtures at 850°C overnight in sealed evacuated quartz tubes. The crystal growth took place via slow cooling from 850 °C to 620°C and then quenching in cold water.

The polarized Raman spectra were measured from (100) cubic surfaces with a triple T64000 spectrometer equipped with microscope. The crystal structure characterization of as-grown topological insulators was performed by X-ray single crystal analyses. The data are collected at room temperature on SuperNova (Oxford Diffraction) diffractometer with Mo radiation (λ = 0.071073 nm).

RESULTS AND DISCUSSION

High-quality $Bi_2(Se_xTe_{1-x})_3$, and Bi_2Se_3 doped with Co, Mn, Ca (shown in Fig.1a) and Cu (shown in Fig.1b) single crystals were synthesized by modified Bridgman technique. Bi_2Se_3 is a direct band gap semiconductor. Compared to other topological insulator compounds it has a relatively large (300 meV) bulk band gap and the Dirac point lies well above the valence band maximum. The crystal structure is solved by direct methods using

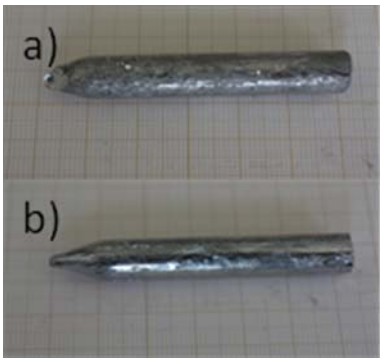

Fig. 1. Bi_2Se_3 doped with Ca (a) and Cu (b) crystals.

SHELXS-97 and refined by the full matrix least-squares procedure on F2 with SHELXL-97. The crystal is rhombohedral and can be presented as stacks of quintuple Se-Bi-Se-Bi-Se layers where the Bi and Se order hexagonally. The quintuple layers are bonded together with weak van der Waals force. Due to the weak Van der Waals bonds the crystal cleaves easily. Figure 2 shows an example of cleaved Bi_2Se_3 crystals. The prepared crystals are in single phase as confirmed by XRD patterns shown in Figure 3 for some representative crystal samples. The lattice constant as determined from the powder X-ray diffraction measurements (not shown) are as follows: Bi_2Se_3 (a = 4.137 Å and c = 28.679 Å); $Bi_2Se_{2.25}Te_{0.75}$ (a = b=4.211Å and c = 29.331 Å); Cu-doped Bi_2Se_3 (a = 4.136 Å and c = 28.626 Å); Mn-doped Bi_2Se_3 (a = 4.106 Å and c = 28.563 Å).

Fig. 2. Cleaved Bi_2Se_3 single crystal.

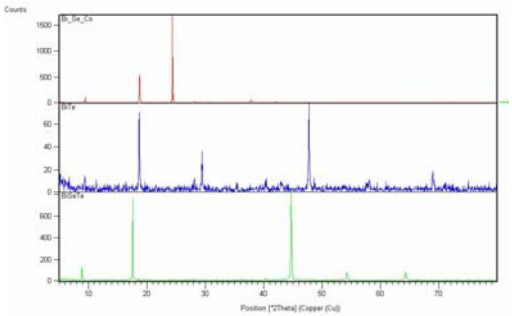

Fig. 3. X-ray diffraction (XRD) pattern of Bi_2Te_3, BiSeTe and Cu- doped Bi_2Se_3 crystals.

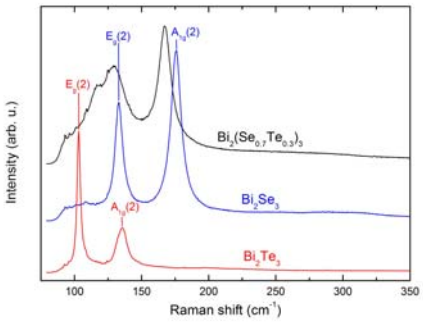

Fig. 4. Raman spectroscopy spectra.

The lattice structure of the prepared single crystals was further investigated by Raman spectroscopy. Some representative Raman spectra are shown in Fig.4. The spectra obtained with 633 nm, 515 nm, 488 nm, or 458 nm excitation were observed to be practically the same. Raman peaks for the characteristic lattice vibration modes A_{1g}^2 and E_g^2 are detected.

It is known that Bi_2Se_2Te is stable, bulk topological insulator suitable for studying massive Dirac Fermions, with a (111) cleavage-surface derived Dirac point isolated in the bulk band gap at the Fermi energy, with a spin texture alterable by layer chemistry [6]. The potential use of these new materials as a 3D – topological insulator device requires control over the bulk resistivity, therefore the development of high-quality materials is of utmost importance.

CONCLUSIONS

Crystals of 3D topological insulators: - $Bi_2(Se_xTe_{1-x})_3$ and Cu, Ca, Co and Mn –doped Bi_2Se_3 were grown by modified Bridgman method. They were characterized by X-ray diffraction and Raman spectroscopy. The frequencies of the vibrational modes in the different samples were compared and their shifts depending on the changes in stoichiometry and composition as well as the lattice parameter analyzed. Both single-mode and two-mode behavior are observed in the mixed crystals. In view of the recently discovered topological-insulator states in these compounds, studies of the variation of their mechanical and electronic properties with composition and the doping concentration are highly important for their future applications.

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ИЗРАСТВАНЕ НА КРИСТАЛИ ОТ ТОПОЛОГИЧНИ ИЗОЛАТОРИ В СИСТЕМАТА $BI_2(SE_XTE_{1-X})_3$

Д. Димитров [a], В. Маринова [a,], В. Томов [b], П. Рафаилов [b], М. Господинов [b]

[a] *Институт за оптични материали и технологии, София 1113, България*
[b] *Институт по физика на твърдото тяло, София 1723, България*

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(Резюме)

Монокристални топологични изолатори от $Bi_2(Se_xTe_{1-x})_3$ и дотиран Bi_2Se_3 са получени с модифициран метод на Бриджмен. Получените кристали са с високо качество което е потвърдено с изследвания по методите на рентгеновата дифракция и Раманова спектроскопия. Тези нови монокристални материали са от съществено значение за изследването и разработването на нови технологии и устройства основаващи се на топологичните свойства.