A new topological insulator built from quasi one-dimensional atomic ribbons

Piet Schönherr\(^1\), Shilei Zhang\(^1\), Yuanqian Liu\(^1,2\), Patryk Kusch\(^3\), Stephanie Reich\(^3\), Terence Giles\(^4\), Dominik Daisenberger\(^1\), Dharmalingam Prabhakaran\(^1\), Yulin Chen\(^1\), and Thorsten Hesjedal\(^*1\)

\(^1\) Department of Physics, Clarendon Laboratory, University of Oxford, Oxford OX1 3PU, United Kingdom
\(^2\) University of Science and Technology of China, Hefei 230026, P.R. China
\(^3\) Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany
\(^4\) Diamond Light Source, Chilton, Didcot, Oxfordshire, OX11 0DE, United Kingdom

Received 13 November 2014, revised 8 December 2014, accepted 9 December 2014
Published online 18 December 2014

Keywords topological insulators, angle-resolved photoemission spectroscopy, nanowires, (Bi,Sb)\(_2\)Se\(_3\), orthorhombic structure

\(^*\) Corresponding author: e-mail t.hesjedal1@physics.ox.ac.uk

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

A novel topological insulator with orthorhombic crystal structure is demonstrated. It is characterized by quasi one-dimensional, conducting atomic chains instead of the layered, two-dimensional sheets known from the established Bi\(_2\)(Se,Te)\(_3\) system. The Sb-doped Bi\(_2\)Se\(_3\) nanowires are grown in a TiO\(_2\)-catalyzed process by chemical vapor deposition. The binary Bi\(_2\)Se\(_3\) is transformed from rhombohedral to orthorhombic by substituting Sb on ~38% of the Bi sites. Pure Sb\(_2\)Se\(_3\) is a topologically trivial band insulator with an orthorhombic crystal structure at ambient conditions, and it is known to transform into a topological insulator at high pressure. Angle-resolved photoemission spectroscopy shows a topological surface state, while Sb doping also tunes the Fermi level to reside in the bandgap.

1 Introduction

Topological insulators (TIs) are fascinating quantum materials which are characterized by an insulating bulk and a conducting surface state [1–3]. The topological surface state (TSS) is protected by time-reversal symmetry and it is robust against scattering from non-magnetic impurities [4]. A bandstructure with an odd number of Dirac cones residing in the bulk bandgap is the signature of TIs [5]. Their characteristic that the charge carriers of opposite spin have opposite linear momentum makes TIs ideal systems for a range of possible spin-based and low-power electronic applications. Nanowires in general have a high surface-to-volume ratio, enhancing the relative contribution of the TSS to the overall electric transport in TI nanostructures [6–9]. The synthesis of one-dimensional structures most commonly relies on an Au-catalyzed vapor–liquid–solid (VLS) growth process [10–13], in which the catalyst forms a liquid alloy with the vapor, and the crystal growth occurs at the liquid–solid interface. Unfortunately, the migration of the Au catalyst and the subsequent deterioration of the electronic properties of the nanostructures are fundamental limitations for device applications [14]. However, TI nanostructures can also be grown in a catalyst-free process with low yield [15], or by using TiO\(_2\) catalysts which do not incorporate into the nanostructures, yet yield high uniformity and density [16].

Since the first experimental demonstration of a two-dimensional TI in the form of HgTe/(Hg,Cd)Te quantum wells [17], and the three-dimensional TIs Bi\(_2\)Sb\(_2\)Te\(_4\) [18], Bi\(_2\)Se\(_2\) [19, 20], and Bi\(_2\)Te\(_2\) [20, 21], only a few more TIs were experimentally confirmed. In general, the search for novel TIs utilizes strain as a means to stabilize metastable phases as in case of Ag\(_2\)Te [22], or to open a bandgap in semimetals like α-Sn [23], and HgTe [24].

Bi\(_2\)Se\(_3\) is in the focus of much experimental work owing to its large bulk bandgap and relatively simple single Dirac cone surface bandstructure. However, the bismuth sesquichalcogenides such as Bi\(_2\)Se\(_3\) are plagued by chalcogen vacancies leading to intrinsic n-type doping, and thus to an increase of the Fermi level above the Dirac point. Sb doping was reported to suppress Se vacancies by substitution of Bi atoms in bulk samples [25], and MBE grown thin films [26]. Similar improvements are possible in nanowires grown using the VLS method [27]. In nano-sheets, an Sb\(_2\)Se\(_3\) guest lattice is formed at a doping level of 10% Sb and no further substitution on Bi sites is possible [28].
Bi$_2$Se$_3$ which has been grown at ambient conditions usually has a rhombohedral crystal structure (space group R$ar{3}$m) and at high pressure an orthorhombic crystal structure (space group Pnma) [29]. However, when quenching it from high-pressure growth conditions it remains metastable. The orthorhombic form of Bi$_2$Se$_3$ occurs naturally as well and is known as Guanajuatite [30]. Further, it has been reported that the orthorhombic phase can be induced by S and Sb doping [31, 32]. This is interesting in terms of TIs because of the reduced conductivity compared to the rhombohedral phase [33].

In contrast to the layered compounds of the Bi$_2$(Se,S,Te)$_3$ solid solution series, orthorhombic Bi$_2$Se$_3$ is characterized by a one-dimensional nanoribbon structure. The polymer-like [Bi$_x$Se$_y$]$_z$ chain is linked to four neighbors per unit via weak Bi–Se and Se–Se bonds [34]. Density functional theory simulations have shown an electronic quasi one-dimensional behavior as van Hove singularities are found in the density of states [35]. For orthorhombic Sb$_2$Se$_3$, it is reported that the surface of the (internal) nanoribbons, which are 0.2 nm thick and 1 nm wide, is virtually perfect due to the absence of dangling bonds [36].

Here, we present experimental evidence that orthorhombic (Bi$_{0.45}$Sb$_{0.55}$)$_2$Se$_3$ with its strong structural and electronic one-dimensional character is a topological insulator. Chemical vapor deposition (CVD) is used to grow high-density (Bi,Sb)$_2$Se$_3$ nanowires in a TiO$_2$ nanoparticle catalyst process. We use X-ray diffraction (XRD) and transmission electron microscopy (TEM) to unambiguously identify the crystal structure and angle-resolved photoemission spectroscopy (ARPES) to confirm the existence of a TSS in this material.

2 Experimental

2.1 Synthesis

Samples were grown in a horizontal, 60 cm long tube furnace (Nabertherm B180) equipped with a sealed, 22 mm inner diameter quartz tube. Substrates and precursor material were placed in quartz boats inside the tube. The precursor was prepared by grinding Sb-doped Bi$_2$Se$_3$ single crystals into a fine powder. Cleaned Si substrates were functionalized using the binding agent poly-L-lysine and a custom-made P-25 TiO$_2$ catalyst solution was applied [16]. Before loading the substrates the system was purged by repeated cycles of low vacuum pumping and dry N$_2$ flushing. Substrates were loaded under N$_2$ flow. N$_2$ was also used as the carrier gas and the flow rate was 150 sccm (standard cubic centimeters per minute). The furnace temperature in the center was ramped up to 585 °C for 60 min and held constant for 60 min. The substrates were placed approximately 25 cm away from the center in the upstream direction at gradually cooler spots. After the growth the furnace was switched off and allowed to cool down while keeping N$_2$ flowing.

2.2 X-ray characterization

Nanowires were carefully scraped from the substrate and placed onto the cuvet of a single crystal diamond for X-ray powder diffraction measurements on beamline 115 at Diamond Light Source. A pre-focused monochromatic beam ($E = 37.06$ keV) was collimated with a 30 µm pinhole. Powder diffraction patterns were recorded by a Perkin Elmer detector, integrated using Fit-2D [37], and analyzed using TOPAS [38].

2.3 Raman

A Horiba T64000 Raman spectrometer system in combination with an HeNe laser ($\lambda = 633$ nm) was used for lower wavenumbers and a titanium–sapphire laser ($\lambda = 800$ nm) for higher wavenumbers. The backscattered light was collected through a 100× objective lens and dispersed by a triple grating spectrometer with a spectral resolution of 1 cm$^{-1}$. In this configuration we were able to study individual nanowires. The polarization of the light was parallel to the nanowire axis to maximize the intensity. All measurements were carried out at room temperature. The spectrometer was calibrated using a Ne standard.

2.4 ARPES

Micro-ARPES measurements were conducted at the spectromicroscopy beamline at Elettra Synchrotron Radiation Laboratory in Italy on a single nanowire, with energy resolution at 70 meV and angle resolution 0.5°. The surface of the sample was cleaned by several cycles of Ar-sputtering.

3 Results

Figure 1 shows scanning electron microscopy (SEM) images of the growth results as a function
of substrate temperature. High purity and density (Bi$_{0.62}$Sb$_{0.38}$)$_2$Se$_3$ nanowires, which are the main focus of this investigation, grow at a substrate temperature of 450 °C. The furnace temperature was 600 °C for all growth experiments. Above a substrate temperature of 450 °C, sparsely distributed larger wires with a lower Sb concentration are found. For lower temperatures, less Bi is incorporated leading to the growth of Sb$_2$Se$_3$ nanowires and the appearance of Sb crystals. The Sb concentration is measured by SEM energy-dispersive X-ray spectroscopy (EDS) with an error of ~10 at%. A typical EDS spectrum is shown in the Supporting Information, Fig. S1. The nanowire growth depends on the catalyst particle size as can be seen in Fig. 1b, where large TiO$_2$ flakes have not catalyzed any material deposition. Below we present the study of the nanowires grown at 450 °C to determine the crystal structure and the electronic properties.

Pure Bi$_2$Se$_3$ has a rhombohedral lattice structure with space group R$3\bar{m}$ at ambient conditions. In high pressure experiments a metastable orthorhombic phase was observed [39], which has the same crystal structure as Sb$_2$Se$_3$ (orthorhombic space group Pnma). Lattice-resolved TEM images (Fig. 2a) show that an orthorhombic phase forms upon Sb incorporation in Bi$_2$Se$_3$ nanowires. The interplanar spacings for (Bi$_{0.62}$Sb$_{0.38}$)$_2$Se$_3$ are $d_{110} = 0.8$ nm and $d_{001} = 0.4$ nm and compare to 0.828 nm and 0.398 nm, respectively, for pure Sb$_2$Se$_3$ nanowires [40].

An ensemble of nanowires was investigated by X-ray powder diffraction at beamline I15 at Diamond Light Source (Didcot, Oxfordshire, England). The reader is referred to the Supporting Information for details on the crystal structure analysis. The dominating phase for (Bi$_{0.62}$Sb$_{0.38}$)$_2$Se$_3$ is the orthorhombic phase which was identified in the diffraction pattern using the Rietveld method. Small amounts of the rhombohedral phase and Si are also present in the ensemble since the nanowires were obtained by scratching from a Si substrate. The fit to the data is presented in Fig. 3. Since the Sb concentration is not high enough to form pure Sb$_2$Se$_3$ structures to such a high percentage, we conclude that (Bi$_{0.62}$Sb$_{0.38}$)$_2$Se$_3$ forms...
an orthorhombic lattice. Bi atoms occupy Sb sites in the orthorhombic Sb$_2$Se$_3$-type lattice as we will see in the Raman spectrum.

The Raman spectrum of a single (Bi$_{0.62}$Sb$_{0.38}$)$_2$Se$_3$ nanowire in Fig. 4 resembles qualitatively the spectrum of Sb$_2$Se$_3$ [41]. All vibrational modes that involve Sb atomic sites are shifted to lower frequencies $\nu$, since the atomic mass $m$ of Bi ($Z = 83$) is higher than that of Sb ($Z = 51$) and $\nu \sim m^{-1}$. Therefore, the spectrum can be explained by substitution of Bi by Sb atoms in the orthorhombic lattice. A peak broadening on the high frequency side of the Bi–Se peak is observed as well. For comparison, the Bi–Se peak of pure Bi$_2$Se$_3$ is located at 131 cm$^{-1}$ and the Sb–Se peak of Sb$_2$Se$_3$ at $\sim 190$ cm$^{-1}$ [41]. No peak was observed above 180 cm$^{-1}$, thereby ruling out the existence of Sb$_2$Se$_3$ in our sample.

Our structural analysis shows that Sb-doped Bi$_2$Se$_3$ has an orthorhombic crystal structure in which the Sb substitutes on Bi sites. It is characterized by quasi one-dimensional bands, both structurally and electronically, much different from the layered structure known from pure Bi$_2$Se$_3$. The fundamental question is whether or not it is a topological insulator, keeping in mind that orthorhombic Sb$_2$Se$_3$ is not a TI.

An ARPES (angle-resolved photo emission spectroscopy) spectrum of the bandstructure along the K–Γ–K direction of a single (Bi$_{0.62}$Sb$_{0.38}$)$_2$Se$_3$ nanowire shows a single Dirac cone on the surface in Fig. 5. The feature resides in the gap above the bulk valence band similar to 3D bulk Bi$_2$Se$_3$ [4], confirming that orthorhombic (Bi,Sb)$_2$Se$_3$ is a TI. The V-shaped dispersion is from the surface state band (SSB), and the apex of the V-shaped dispersion indicates the Dirac point. The bandgap of the sample from the experiment is $\geq 200$ meV, and the Fermi level $E_F$ of the sample resides at the very bottom of the bulk conduction band, indicating a very low doping level.

4 Discussion and conclusions The incorporation of Sb into Bi$_2$Se$_3$ leads to an orthorhombic crystal structure (space group Pnma). Sb enters the crystalline matrix by replacing Bi, as concluded from the shift of the vibrational modes in the Raman spectrum. The amount of Sb doping can be controlled via the substrate temperature during
CVD growth. Instead of Au, we employed TiO\textsubscript{2} nanoparticles as a catalyst [16]. We explored the entire temperature range in which doping was possible, starting from Sb-free, binary Bi\textsubscript{2}Se\textsubscript{3} at 550 °C down to the lowest temperature (400 °C) at which Sb starts to crystallize out. The Sb doping concentration (in % of the Bi sites) ranges from 0 to 55. Our study focused on the 38% Sb-doped sample. The nanowires are pure, dense, and uniform, which allowed us to study ensembles by X-ray powder diffraction which unambiguously confirms the orthorhombic crystal structure of the nanowires. Previous work found a maximum doping concentration of 10% and the formation of an Sb\textsubscript{2}Se\textsubscript{3} guest lattice [27, 28] which was absent in our study in both the TEM and XRD data. In micro-ARPES measurements on an individual nanowire we found a TSS. The bulk bandgap is ≥200 meV. The Fermi level resides above the Dirac point and no further surface doping was required to make the TSS visible.

The interesting question is why Sb-doped Bi\textsubscript{2}Se\textsubscript{3} with its peculiar quasi one-dimensional sheet structure is a topological insulator, while the end member of the doping series, orthorhombic Sb\textsubscript{2}Se\textsubscript{3}, is not. A possible reason could be the strain resulting from Sb doping. Starting from the topologically trivial, orthorhombic Sb\textsubscript{2}Se\textsubscript{3} structure, the insertion of Bi\textsuperscript{3+} ionic radius 117 pm, as compared to 90 pm for Sb\textsuperscript{3+} will lead to an expansion of the lattice, similar to the application of pressure [42, 43]. In the future, density functional theory calculations are planned to better understand the occurrence of the TSS in one-dimensional structures which are very much different from the layered structure of the vast majority of all experimentally confirmed TIs.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-428739.

Acknowledgements We thank the Research Complex at Harwell for their hospitality, J. Holter for help with electron microscopy, and essential feedback from A. A. Baker. We acknowledge the Diamond Light Source for beamtime on beamline I15 (EE8608). PS acknowledges funding from EPSRC, Corpus Christi College (Oxford), and the Studienstiftung des deutschen Volkes (GER). This publication arises from research funded by the John Fell Oxford University Press (OUP) Research Fund.

References

[1] L. Fu, C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 98, 106803 (2007).
[2] M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. 82, 3045–3067 (2010).
[3] G. Brumfiel, Nature 466, 310–311 (2010).
[4] Y. L. Chen, J.-H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H.-H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen, Science 329, 659–662 (2010).
[5] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Phys. 5, 438–442 (2009).
[6] H. Peng, K. Lai, D. Kong, S. Meister, Y. Chen, X.-L. Qi, S.-C. Zhang, Z.-X. Shen, and Y. Cui, Nature Mater. 9, 225–229 (2010).
[7] J. H. Bardarson, P. W. Brouwer, and J. E. Moore, Phys. Rev. Lett. 105, 156803 (2010).
[8] S. Matsuo, K. Koyama, K. Shimamura, Y. Arakawa, Y. Nishihara, D. Chiba, K. Kobayashi, T. Ono, C.-Z. Chang, K. He, X.-C. Ma, and Q.-K. Xue, Phys. Rev. B 85, 075440 (2012).
[9] J. J. Cha, K. J. Koski, and Y. Cui, Phys. Status Solidi RRL 7, 15–25 (2013).
[10] K. W. Kolasinski, Curr. Opin. Solid State Mater. Sci. 10, 182–191 (2006).
[11] M. E. Messing, K. Hillierich, J. Johansson, K. Deppert, and A. D. King, Gold Bulletin 42, 172–181 (2009).
[12] D. Kong, J. C. Randel, H. Peng, J. J. Cha, S. Meister, K. Lai, Y. Chen, Z.-X. Shen, H. C. Manoharan, and Y. Cui, Nano Lett. 10, 329–333 (2010).
[13] Y. Yan, Z.-M. Liao, Y.-B. Zhou, H.-C. Wu, Y.-Q. Bie, J.-J. Chen, J. Meng, X.-S. Wu, and D.-P. Yu, Sci. Rep. 3, 1264 (2013).
[14] J. B. Hannon, S. Kodambaka, F. M. Ross, and R. M. Tromp, Nature 440, 69–71 (2006).
[15] L. Fang, Y. Jia, D. J. Miller, M. L. Latimer, Z. L. Xiao, U. Welp, G. W. Crabtree, and W.-K. Kwok, Nano Lett. 12, 6164–6169 (2012).
[16] P. Schönherr, D. Prabhakaran, W. Jones, N. Dimitratos, M. Bowker, and T. Hesjedal, Appl. Phys. Lett. 104, 253103 (2014).
[17] M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L. W. Molenkamp, X. L. Qi, and S. C. Zhang, Science 318, 766–770 (2007).
[18] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature 452, 970–974 (2008).
[19] D. Hsieh, Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, N. P. Ong, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature 460, 1101–1105 (2009).
[20] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature Phys. 5, 398–402 (2009).
[21] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z.-X. Shen, Science 325, 178–181 (2009).
[22] A. Sulaev, P. Ren, B. Xia, Q. H. Lin, T. Yu, C. Y. Qi, S. Y. Zhang, M. Y. Han, Z. P. Li, W. G. Zhu, Q. Y. Wu, Y. P. Feng, L. Shen, S. Q. Shen, and L. Wang, AIP Advances 3, 032123 (2013).
[23] A. Barluss, L. Dudy, M. R. Scholz, H. Roth, P. Höfner, C. Blumenstein, G. Landolt, J. H. Dil, N. C. Plumb, M. Radovic, A. Bostwick, E. Rotenberg, A. Fleszar, G. Bihlmayer, D. Wollerton, G. Li, W. Hanke, R. Claessen, and J. Schäfer, Phys. Rev. Lett. 111, 157205 (2013).
[24] C. Brüne, C. X. Liu, E. G. Novik, E. M. Hankiewicz, H. Buhmann, Y. L. Chen, X. L. Qi, Z. X. Shen, S. C. Zhang, and L. W. Molenkamp, Phys. Rev. Lett. 106, 126803 (2011).
[25] J. G. Analytis, R. D. McDonald, S. C. Riggs, J.-H. Chu, G. S. Boebinger, and I. R. Fisher, Nature Phys. 6, 960–964 (2010).

[26] Y. Zhang, C.-Z. Chang, K. He, L.-L. Wang, X. Chen, J.-F. Jia, X.-C. Ma, and Q.-K. Xue, Appl. Phys. Lett. 97, 194102 (2010).

[27] S. S. Hong, J. J. Cha, D. Kong, and Y. Cui, Nature Commun. 3, 757 (2012).

[28] C. H. Lee, R. He, Z. Wang, R. L. J. Qiu, A. Kumar, C. Delaney, B. Beck, T. E. Kidd, C. C. Chancey, R. M. Sankaran, and X. P. A. Gao, Nanoscale 5, 4337–4343 (2013).

[29] H. Okamoto, J. Phase Equilibria 15, 195–201 (1994).

[30] J. W. Earley, Am. Mineral. 35, 337–364 (1950).

[31] V. G. Kuznetsov and K. K. Palkina, Russ. J. Inorg. Chem. 8, 624–632 (1963).

[32] G. Neumann and R. Scheidegger, Helv. Phys. Acta 40, 293–300 (1967).

[33] L. F. Vereshchagin, E. S. Itskevich, E. Ya. Atabaeva, and S. V. Popova, Sov. Phys. – Solid State 6, 1763–1764 (1965).

[34] N. J. Cook, C. L. Ciobanu, T. Wagner, and C. J. Stanley, Can. Mineral. 45, 665–708 (2007).

[35] R. Caracas and X. Gonze, Phys. Chem. Minerals 32, 295–300 (2005).

[36] R. Vadapoo, S. Krishnan, H. Yilmaz, and C. Marin, Nanotechnol. 22, 175705 (2011).

[37] A. P. Hammersley, FIT2D: An introduction and overview, ESRF Internal Report, 1997.

[38] Bruker AXS (2009): Topas V4.2, 2009.

[39] J. Zhao, H. Liu, L. Ehm, D. Dong, Z. Chen, and G. Gu, J. Phys.: Condens. Matter 25, 125602 (2013).

[40] T. Zhai, M. Ye, L. Li, X. Fang, M. Liao, Y. Li, Y. Koide, Y. Bando, and D. Golberg, Adv. Mater. 22, 4530–4533 (2010).

[41] Z. G. Ivanova, E. Cernoskova, V. S. Vassilev, and S. V. Boycheva, Mater. Lett. 57, 1025–1028 (2003).

[42] I. Efthimiopoulos, J. Zhang, M. Kucway, C. Park, R. C. Ewing, and Y. Wang, Sci. Rep. 3, 2665 (2013).

[43] W. Liu, X. Peng, C. Tang, L. Sun, K. Zhang, and J. Zhong, Phys. Rev. B 84, 245105 (2011).

**Supporting Information** Additional supporting information may be found in the online version of this article at the publisher’s website.