Weak Antilocalization Effect of Topological Crystalline Insulator Pb$_{1-x}$Sn$_x$Te Nanowires with Tunable Composition and Distinct {100} Facets

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Supporting Information

ABSTRACT: Pb$_{1-x}$Sn$_x$Te is a unique topological crystalline insulator (TCI) that undergoes a topological phase transition from topological trivial insulator to TCI with the change of Sn content and temperature. Meanwhile, the surface states properties of Pb$_{1-x}$Sn$_x$Te are strongly dependent on crystallographic plane orientation. In this work, we first reported controllable synthesis of rectangular prismatic Pb$_{1-x}$Sn$_x$Te nanowires by vapor deposition method. Rectangular prismatic Pb$_{1-x}$Sn$_x$Te nanowires exhibits distinct {100} surfaces. Furthermore, The Sn composition of Pb$_{1-x}$Sn$_x$Te nanowires can be continuously controlled from 0 to 1. Low temperature magnetotransport shows that PbTe nanowire exhibits weak localization (WL) effect, whereas Pb$_{0.5}$Sn$_{0.5}$Te and Pb$_{0.2}$Sn$_{0.8}$Te nanowires display pronounced weak antilocalization (WAL) effect. This transition is explained by the topological phase transform of Pb$_{1-x}$Sn$_x$Te from trivial to nontrivial insulator with Sn content ($x$) exceeding 0.38. Pb$_{1-x}$Sn$_x$Te nanowires synthesized in this work lay a foundation for probing spin-correlated electron transport and show great potentials for future applications of tunable spintronic devices.

KEYWORDS: topological crystalline insulator, weak antilocalization effect, Pb$_{1-x}$Sn$_x$Te nanowires, magnetotransport

Topological crystalline insulators (TCIs) are recently discovered topological phase in which gapless metallic surface states reside on highly symmetry crystal surface such as (001), (110), and (111).$^{1-4}$ The crystalline symmetry of TCIs warrants the topological protection instead of time-reversal symmetry.$^{5-12}$ Soon after the theoretical predication of topological states in SnTe$^{1}$ and its related alloys Pb$_{1-x}$Sn$_x$(Se/Te),$^{13,14}$ the Dirac-like dispersions are observed on their mirror symmetry surfaces by angle-resolved photoemission spectra (ARPES).$^{15}$ Interestingly, the electronic structure of Pb$_{1-x}$Sn$_x$(Se/Te) can be modulated by composition, electrical field, or elastic strain.$^{1,16}$ These unique physics properties of TCIs may bring us novel quantum mechanical phenomenon and lead to the applications of tunable electronic and spintronic devices.$^3$

Suppressing the transport of bulk carriers is essentially important to investigate topological surface transport of topological insulators (TIs).$^{10,17-21}$ One method is to grow low dimensional TIs with large surface-to-volume ratio. Indeed, for conventional TIs, the synthesis of their nanostructures such as Bi$_2$Se$_3$ nanoribbons,$^{19}$ few-layer Bi$_2$(Se/Te)$_3$ nanoplates,$^{18}$ and Ag$_x$Te nanowires,$^{22}$ have achieved great success by the vapor deposition method. As to TCIs, synthesizing their nanostructures with distinct surfaces is crucial for exploring unique topological nature since surface states of TCIs varies from one highly symmetry crystal surface to another.$^{14,23}$

and Zhang’s group have reported the synthesis of high-quality SnTe nanostructures with highly symmetrical facets by tailoring the experimental conditions in the chemical vapor deposition (CVD) process.$^{24-28}$ Furthermore, two-dimensional SnTe nanoplates with predominant (111) surfaces or (100) surfaces have been grown by Cha group.$^{29}$ Recently, we have reported the controllable synthesis of rectangular prismatic Pb$_{1-x}$Sn$_x$Se nanowires$^{30}$ and nanoplates$^{30}$ with distinct (100) surfaces. However, low-dimensional nanostructures of Pb$_{1-x}$Sn$_x$Te are not yet obtained, which seriously impedes the exploration of their intriguing topological properties and their potential applications as the low-dissipation electronic and spintronic devices as demonstrated in this work.

Pb$_{1-x}$Sn$_x$Te has a rock-salt crystal structure with a direct electronic bandgap ($E_g \leq 0.30$ eV). Similarly to Pb$_{1-x}$Sn$_x$Se, its band structure undergoes an inversion with Sn content reaching a critical value $x_c$. The temperature also induces the band inversion when it drops to gap-inversion temperature $T_{inv}$ in the samples with $x > x_c$. Intriguingly, recent theoretical studies and ARPES experiments have confirmed Pb$_{1-x}$Sn$_x$Te transforms from topological trivial insulator to topological nontrivial insulator accompanying with the band inversion.$^{13,15}$

Received: December 26, 2014  
Revised: February 26, 2015  
Published: March 2, 2015
Above features of Pb₁₋ₓSnₓTe suggest that composition or temperature can be applied to adjust its electronic properties. Meanwhile, the tunable topological nature of Pb₁₋ₓSnₓTe makes it highly important to perform the growth of Pb₁₋ₓSnₓTe nanowires with tunable composition and distinct facets.

In this work, we first grow highly single crystalline Pb₁₋ₓSnₓTe nanowires by chemical vapor deposition method on silicon (Si) with gold (Au) as the catalyst. Pb₁₋ₓSnₓTe nanowires exhibit typical rectangular prismatic morphology with highly symmetry {100} facets. Meanwhile, the Sn content can be continuously adjusted from 0 to 1. Magnetotransport measurements demonstrate that PbTe nanowire shows weak localization (WL) effect while Pb₀.₅Sn₀.₅Te and Pb₀.₂Sn₀.₈Te nanowires exhibit weak antilocalization (WAL) effect, which would be explained by the topological phase transition of Pb₁₋ₓSnₓTe from trivial to nontrivial insulator when Sn content (x) exceeds 0.38 at 2 K. Phase coherent length lₚ and the numbers of independent carrier valleys l₂αl (α = 1/2 per valley) of Pb₀.₅Sn₀.₅Te nanowire are estimated to be 41 nm and 0.64, respectively according to Hikami–Larkin–Nagaoka (HLN) model. Deviation of l₂αl from positive integer suggests coupling of multiple transport channels from both surface and bulk states.

Figure 1a shows a unit cell of cubic crystal structure of Pb₁₋ₓSnₓTe. The Pb₁₋ₓSnₓTe nanowires were synthesized by means of reaction between PbTe and SnTe (with a purity of 99.999%) in quartz tube furnace as shown in schematic diagram of Figure 1b. The source temperature and substrate temperature were set to be 800−900 °C and 500−600 °C respectively. An 8 nm gold (Au) layer was deposited on Si substrates before the synthesis. The growth of Pb₁₋ₓSnₓTe nanowires follows the vapor–liquid–solid (VLS) mechanism. More experimental details are described in the Supporting Information. The growth conditions for Pb₁₋ₓSnₓTe nanowires with different Sn content (x) maintain unchanged except the mole ratio of PbTe to SnTe. The shape and size of Pb₁₋ₓSnₓTe nanowires have been analyzed by scanning electron microscopy (SEM). Figure 1c−f are the SEM images of Pb₁₋ₓSnₓTe nanowires, showing that the nanowires are of typical rectangular prismatic morphology. The length distributes in 20−30 μm and the diameter ranges from 150 to 200 nm. High magnification images from top and bottom of a single Pb₁₋ₓSnₓTe nanowire in Figure 1e and f inform that (1) Au nanoparticle terminates the growth of the nanowire, and (2) the nanowires are covered by distinct {100} facets as demonstrated by the following transmission electron microscopy (TEM) analysis. Pb₁₋ₓSnₓTe nanowire with distinct {100} surfaces will allow special study of topological nature on {100} surfaces.

To characterize the crystal structure and composition of Pb₁₋ₓSnₓTe nanowire, we have executed TEM experiments on single Pb₁₋ₓSnₓTe nanowire. As shown in Figure 2a−e, elemental mapping clearly demonstrates the uniformity of spatial distribution of Pb, Sn, and Te. Strong Au signals at the top of nanowire further demonstrate the VLS growth model of our Pb₁₋ₓSnₓTe nanowires. To clarify the crystalline structure in more details, high-resolution TEM images (HRTEM) images and the corresponding selected area electron diffraction (SAED) patterns were taken from the nanowire as shown in Figure 2f and g. The Pb₁₋ₓSnₓTe nanowires are perfect single crystalline as indicated by clear lattice spacing of (200) crystal planes. The SAED pattern exhibits regular cubic structure, indicating the Pb₁₋ₓSnₓTe nanowires are terminated by high-symmetry {100} surfaces, which are topologically protected. The composition of Pb₁₋ₓSnₓTe nanowires was monitored by energy-dispersive X-ray spectroscopy (TEM-EDX) analysis as shown in Figure 2h, further demonstrating Pb₁₋ₓSnₓTe nanowires are composed of Pb, Sn, and Se. Signals of Cu and Ni originates from copper grid used for TEM character-
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Figure 2. Composition and crystal structure of Pb_{1−x}Sn_{x}Te nanowires. (a) Bright-field TEM image of an individual Pb_{1−x}Sn_{x}Te nanowire. (b–e) Elemental mapping of the same region of nanowire indicating even elemental distribution of Pb, Sn, and Te, strong Au signals can be clearly seen on the top of nanowire. Scale bars in (a–e) are 200 nm. (f) HRTEM image and (g) corresponding SAED pattern clarify the Pb_{1−x}Sn_{x}Te nanowire are high symmetry cubic crystal structure. Scale bar in (f) is 2 nm. (h) TEM-EDX spectrum of the nanowire depicts the presence of Pb, Sn, Te, and catalyst Au. (i) Composition of Sn content (x) in Pb_{1−x}Sn_{x}Te nanowires versus Sn atomic ratio (x) in the source powder.

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In order to investigate the surface states transport of Pb_{1−x}Sn_{x}Te nanowires synthesized in our work, four-terminal devices of PbTe, Pb_{0.2}Sn_{0.8}Te, and Pb_{0.5}Sn_{0.5}Te nanowires are fabricated. Details of devices fabrication are supplied in the Supporting Information. Figure 3a presents the channel resistance R of PbTe nanowire which increases with the reduction of temperature, suggesting semiconductive feature of PbTe nanowire. As displayed in Figure 3b, thermal activation energy E_{a} of 8.2 meV at high temperature (260–133 K) is extracted from R = e^{E_{a}/kT}, where k_{B} is the Boltzmann constant. Experimental results confirmed that Pb_{1−x}Sn_{x}Te undergoes a topological phase transition from topological trivial insulator to topological nontrivial insulator when Sn content (x) exceeds 0.38 at 9 K. In our work, we find PbTe nanowire exhibits WL effect at low magnetic field. As shown in Figure 3c, the change of magnetoconductance at 2 K, \( \Delta G = G(B) - G(0) \), displays a sharp downward cusp near zero magnetic field, a signature of WL effect. Here, the magnetic field B is perpendicular to nanowire. The constructive quantum interference of two self-crossing loops explains the occurrence of WL effect. At higher temperature (5 and 10 K), the change of magnetoconductance is too small to be detected due to the limitation of the accuracy of our equipment. In stark contrast to PbTe nanowire, Pb_{0.8}Sn_{0.2}Te nanowire shows distinct WAL effect which is a positive quantum correction to the classical magnetoresistance. Figure 3d shows the channel resistance R of Pb_{0.8}Sn_{0.2}Te as the function of temperature. The resistance gradually decreases with the decrease of temperature, indicating a typical metallic transport behavior. The metallic feature of resistance is often observed in topological insulators due to the unintentional doping in the growth or device fabrication process. At low temperature, the resistance of Pb_{0.8}Sn_{0.2}Te nanowire slightly increases, which may be due to the weak carrier freeze-out effect (top inset of Figure 3d). Plot of \( \Delta G \) versus magnetic field B displays upward cusp near zero magnetic field, which suggests the WAL effect of topological surface states (Figure 3e). With the increase of temperature, the cusp in low magnetic field range disappears. This could be because the phase coherence length l_{p} dramatically decreases at high temperature due to the strong thermal scattering. The WAL effect of Pb_{0.8}Sn_{0.2}Te nanowire at 2 K is further fitted according to Hikami–Larkin–Nagaoka (HLN) model given by

\[
\Delta G = G(B) - G(0) = -\left(\frac{e\alpha^2}{2\pi}\right)[ln(B_0/B) - \Psi(1/2 + (B_0/B))]\tag{1}
\]

where B_{0} = h/(4e\alpha^2) with l_{p} as the phase coherence length, \( \Psi \) is the digamma function, describing the quantum correction to the conductivity in 2D systems, the l_{2d} is an estimation of the numbers of independent channels contributing to the interference. As shown in Figure 3f, fitting at low magnetic field gives \( \alpha = -0.32 \) and \( l_{p} = 41 \) nm, respectively. l_{2d} is estimated to be 0.64. Theoretically, a single surface channel should give l_{2d} of 1.5. Considering four Dirac valleys reside on (100) surface, the transport channels from top and bottom surfaces are expected to be 8. The deviation of our results from theoretical values likely originates from coupling between surface and bulk states. In addition, intervalley scattering among different Dirac valleys can also reduces the numbers of transport channels since each highly symmetry crystal plane of TCI s resides multiple topological surface states. The deviation of experimental results of l_{2d} from theoretical values are also observed in low dimensional topological insulators such as Bi_{2}Te_{3} thin film\(^{17}\) and Bi_{2}(Se_{0.5}Te_{0.5})_{3} nanoplates\(^{21}\) due to the intermixing of surface and bulk states and coupling between top and bottom surface states. Inset of Figure 3f shows the aperiodic conductance oscillation of Pb_{0.8}Sn_{0.2}Te nanowire, which can be ascribed to universal conductance fluctuations (UCF) effects. Here, the conductance changes are redrawn by subtracting the smooth background. UCF effects result from the change of interference of the time-reversal pair of electron waves in a disordered system of mesoscopic scale.

Another Pb_{1−x}Sn_{x}Te nanowire with Sn content (x) of 0.8 also exposes dominant topological surface transport. Figure 4a shows channel resistance R of Pb_{0.2}Sn_{0.8}Te nanowire with the decrease of temperature, indicating the metallic transport...
behavior. Figure 4b presents the change of magnetoconductance measured at various angle ($\theta$) that denotes the angle between the direction of magnetic field and current flow along the nanowire. Prominent upward cusp can be observed at all angles, indicating the WAL effects of topological surface states. Theoretically, WAL effect induced by 2D surface states depends on perpendicular component of magnetic field. Therefore, the cusp should become sharper with the increase of perpendicular component of magnetic field. In the study of surface transport of 2D TIs such as Bi$_2$Te$_3$ thin film and Bi$_x$(Se$_x$Te$_{1-x}$) nanoribbons, 2D WAL effect mainly results from Dirac Fermions of top and bottom surface which dominates the surface area. And their WAL effect gradually enhances with increasing perpendicular component of magnetic field. However, our results seem to deviate from this feature. It should be noted that direction of magnetic field cannot be kept strictly perpendicular to the top and bottom surfaces of rectangular Pb$_{0.2}$Sn$_{0.8}$Te nanowire initially. Also, the width and thickness of the nanowires are similar, as displayed in Figure 1d−f. Therefore, as shown in Figure S4a in Supporting Information, the lateral surfaces also contribute to the transport because they will obtain perpendicular component of magnetic field with the decrease of angle from 90° to 50°. In this case, the angle-dependent measurement can add extra complexity. However, WAL effect of Pb$_{1-x}$Sn$_x$Te nanowire can still be identified as 2D because 3D WAL effect of bulk states is independent of the tilt angle. Supporting Information Figure S4b plots the change of magnetoconductance measured at various angle, indicating pronounced WAL effect. (c) Fitting of $\Delta G$ at tilt angle 90° based on 2D localization theory.
bottom surface states by fitting the plots of $\Delta G$ vs magnetic field at 90° as shown in Figure 4c. According to eq 1, we get an $\alpha$ of 0.40 and $q_x$ of 15 nm. Thus, numbers of transport channels $l_2$ is estimated to be 0.80.

Controllable synthesis of Pb$_{1−x}$Sn$_x$Te nanowires with tunable composition and distinct high-symmetry facets enables the study of topological surface states of TCIs due to the large surface-to-volume ratio of Pb$_{1−x}$Sn$_x$Te nanowires. As demonstrated in this work, PbTe nanowire exhibits WL effect, whereas Pb$_{0.2}$Sn$_{0.8}$Te and Pb$_{0.3}$Sn$_{0.7}$Te nanowires shows obvious WL effect which would be because of the phase transform from topological trivial insulator to topological nontrivial insulator when Sn content (x) goes beyond 0.38. The controllable topological nature of Pb$_{1−x}$Sn$_x$Te nanowire by modulating composition could lead to the application of tunable spintronics. As mentioned in the introductory part of this paper, Pb$_{1−x}$Sn$_x$Te is an intriguing TCIs. In addition to the composition, temperature and strain can also adjust its surface states. In the future, modulation of topological surface states may be realized by strain engineering, which will bring us novel applications such as pressure sensor. One thing should be noted that the materials exhibit WL effect when they have strong spin−orbital interaction which reverses the sign of the resistance correction of WL effect.$^{38}$ Pb$_{0.2}$Sn$_{0.8}$Te and Pb$_{0.3}$Sn$_{0.7}$Te nanowires have strong spin−orbital interaction in the bulk. It is possible that WL in these nanowires is partially contributed by 3D bulk states.

In summary, rectangular prismatic Pb$_{1−x}$Sn$_x$Te nanowires have been synthesized by Au-catalyst vapor phase deposition. Importantly, the rectangular prismatic Pb$_{1−x}$Sn$_x$Te nanowire exhibits distinct high-symmetry (100) surfaces that belong to topological surfaces. The Sn (x) content in Pb$_{1−x}$Sn$_x$Te nanowires can be modulated from 0 to 1 by controlling the mole ratio of SnTe to PbTe in source. Furthermore, PbTe nanowire shows WL effect, whereas Pb$_{0.2}$Sn$_{0.8}$Te and Pb$_{0.3}$Sn$_{0.7}$Te exhibits WL effect. This transition can be explained by the topological phase transition that Pb$_{1−x}$Sn$_x$Te changes from trivial insulator to nontrivial insulator when Sn content (x) exceeds 0.38. Phase coherence length and the numbers of transport channels of Pb$_{0.2}$Sn$_{0.8}$Te nanowire are estimated to be 41 nm and 0.64, respectively. Our work paves the way for the study of topological surface transport in TCIs and for the implementation of Pb$_{1−x}$Sn$_x$Te nanowires in tunable electronics and spintronics.

ASSOCIATED CONTENT

Supporting Information

Experimental section, SEM images, EDX spectra, electronic transport, and magnetotransport. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

This work was supported by 973 Program of the Ministry of Science and Technology of China (No. 2012CB934103), the 100-Talents Program of the Chinese Academy of Sciences (No. Y1172911ZX), the National Natural Science Foundation of China (No. 21373065) and Beijing Natural Science Foundation (No. 2144059). We thank Prof. Kaisheng Li and Kaiming Cai in Institute of Semiconductors, Chinese Academy of Sciences for magnetotransport measurements.

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