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Sn-doped $Bi_{1.1}Sb_{0.9}Te_2S$, a bulk crystal topological insulator with excellent properties

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Abstract

A long-standing issue in topological insulator research has been to find a bulk single crystal material that provides a high quality platform for characterizing topological surface states without interference from bulk electronic states. This material would ideally be a bulk insulator, have a surface state Dirac point energy well isolated from the bulk valence and conduction bands, display quantum oscillations from the surface state electrons, and be growable as large, high quality bulk single crystals. Here we show that this materials obstacle is overcome by bulk crystals of lightly Sn-doped $Bi_{1.1}Sb_{0.9}Te_2S$ grown by the Vertical Bridgeman method. We characterize Sn-BSTS via angle-resolved photoemission spectroscopy, scanning tunneling microscopy, transport studies, X-ray diffraction, and Raman scattering. We present this material as a high quality topological insulator that can be reliably grown as bulk single crystals and thus studied by many researchers interested in topological surface states.

Introduction

Topological insulators (TIs) display a new state of quantum matter[1-5]. In these three-dimensional (3D), small band gap bulk insulators, metallic two-dimensional (2D) spin-momentum locked Dirac fermions exist on the surfaces. These fermions, exhibiting a quasi-linear energy vs. wavevector dispersion relation near their Dirac point, owe their existence and protection to the time-reversal-symmetry[6]. 3D TIs have sparked wide interest in the research community due to both their fundamental scientific interest and the opportunities they offer for observing new electronic phenomena and properties that may be exploited for spintronics or other advanced electronic applications[7-13]. Unfortunately, however, the transport properties of the actual materials involved are typically dominated by the bulk-electrons[5,14-16], making the true electronic properties of the surface states difficult to observe and exploit.

Bi_2Se_3 and Bi_2Te_3, with bulk band gaps of ~300 meV and ~150 meV respectively, are members of the larger M_2X_3 (M = Sb, Bi; X = S, Se, Te) tetradymite family and are widely considered to be fundamental materials platforms for the investigation of topological surface states (TSS). The best bulk Bi_2Se_3 crystals are heavily doped[16], with their Fermi level in the bulk conduction band (BCB), and so the SS cannot be characterized independently of interference from the bulk states, and in Bi_2Te_3 the surface state Dirac point (DP) energy is below that of the top of the Bulk Valence Band (BVB) and the crystals have large bulk carrier concentrations due to antisite defects[17,18]. Thus neither of the simple materials is suitable for experimentally probing the intrinsic character of the TSS.

Thus, efforts have been underway since the inception of the field to find a material that is the best bulk single crystal TI for studying the intrinsic properties of the surface Dirac electrons[19-30].

So far, the primary desirable characteristics for the ideal bulk crystal material– to have a surface state DP well isolated in energy from the bulk states and a very low bulk carrier concentration, both of which would allow for the study of the Dirac electrons at very low energies without interference from the bulk states, quantum oscillations from the TSS electrons, and reliable growability as high quality single crystals - have proven to be difficult to satisfy in a single real bulk material. Until the current work, Bi_2Te_2Se, with well-controlled stoichiometry and defect chemistry, has been considered as the best bulk crystal material from this perspective, but its DP energy is below the maximum energy of the BVB by ~60 meV, making it impossible to study the SS electrons close to the DP without interference from bulk states[20,24-27]. An alternative material is the quaternary solid solution $(Bi_{1-x}Sb_x)_2(Se_{1-y}Te_y)_3$ [28-30], but the stoichiometry of that material is not fixed by any intrinsic thermodynamic materials characteristic such as chemistry or structure, making it unsuitable as a general materials platform for the study of TSS. Thus, although very important measurements have been performed on carefully prepared thin films of materials in the $(Bi_{1-x}Sb_x)_2(Se_{1-y}Te_y)_3$ family, the lack of a bulk material with excellent properties that can be reproducibly grown as large bulk single crystals has significantly limited the number of experimental research groups that can contribute to the development of the field.

Here we describe the design, growth and characterization of a material that we argue satisfies all the synthesis and electronic structure criteria to be an ideal bulk topological insulator. This material is derived by combining concepts in crystal chemistry, defect chemistry, strain-mediated chemical stability, the effect of atomic electronegativites on the absolute energies of bulk electronic states, and resonant level doping. The resultant is the stable, bulk insulating, high crystallinity single crystal material $Bi_{1.1}Sb_{0.9}Te_2S$, grown by the vertical-Bridgeman-technique (VBT), doped with a very small percentage of Sn. Large crystals with excellent properties can be

reproducibly grown. This material displays a surface state DP energy fully isolated from the BVB and BCB, very-low bulk carrier concentrations, strong domination of the conductance by surface currents below 100 K, and reproducibly observed quantum oscillations from the topological surface states. Its growth, described here, will make the characterization of topological surface states available to a wide community of researchers.

Results

Material Design. Figure 1**a** shows a schematic view of the materials design process that leads us to $Bi_{1.08}Sn_{0.02}Sb_{0.9}Te_2S$ (Sn-BSTS). We start with Bi_2Se_3 and Bi_2Te_3, which are the simplest, though far from ideal, tetradymite-type TI materials. To obtain bulk insulating TI crystals based on these tetradymites, two main approaches and their combination have been employed. In Approach-**1,** starting from Bi_2Se_3, Te has been partially substituted for Se to form Bi_2Te_2Se (BTS), where the electron-donating Se vacancies in Bi_2Se_3 are controlled by confining the Se to the middle layer in the quintuple layer (QL) structure, or, alternatively, by the much less well controlled random $Bi_2(Se_{1-x}Te_x)_3$ solid solution. In Approach-**2**, the composition of Bi-site is adjusted by Sb-Bi partial substitution. This method has the advantage of yielding materials, whose DP is isolated from the bulk states, but the defect chemistry is again difficult to control. By using both approaches simultaneously, yielding tetradymites of the type $(Bi_{1-x}Sb_x)_2(Se_{1-y}Te_y)_3$, the energy of the SS DP can be placed in the bulk band gap and films and crystals can be grown with low bulk carrier concentrations at low temperature[28-30]. The disadvantage of this material is the difficulty in controlling its composition, and therefore its defect chemistry, to grow large high quality bulk single crystals.

Here we develop an alternative material system based on incorporating S rather than Se in the middle layer of Bi_2Te_2Se. The incorporation of S in place of Se in the middle layer of the tetradymite QL sandwich decreases the absolute energy of the valence band due to the higher electronegativity[31] of the S and makes the surface DP isolated in energy from the bulk states. This is a parallel materials development path to Approach-**1**. The formation of a thermodynamically stable compound of composition Bi_2Te_2S is not possible, however, due to crystallographic strain from layer size mismatch, as was early described by Linus Pauling[32], and so a decrease of the size of the Bi layers must be made through Approach-**2** to obtain a stable material. Through experimentation we have found that the composition of that stable material is $Bi_{1.1}Sb_{0.9}Te_2S$. This composition is a result of chemical synergism: the incorporation of S in the middle of the QL requires a contraction of the metal layers (the ones containing Bi and Sb, Sb is smaller than Bi) for size matching and selects a Bi/Sb ratio near 1:1 for stability (Figure 1**b**). This is a very strong crystal-chemical driving force for stability, and results in the optimal growth of this composition as large single crystals directly from a melt of the same composition. This material already has a low carrier concentration, but as a final step we employ the concept of resonant level doping, developed in previous work to optimize the properties of tetradymite thermoelectrics, where small amounts of Sn are known to act in that capacity[24,25,33], to compensate for the last of the native defects present. We thus obtain a bulk-insulating ideal topological insulator through 1% Sn substitution for (Bi, Sb), and develop the material $Bi_{1.08}Sn_{0.02}Sb_{0.9}Te_2S$ (Sn-BSTS).

Crystals. Our high quality bulk single crystals of Sn-BSTS were grown by the VBT[24] (Figure 2**a**). The perfection of the grown crystals was established by X-ray diffraction and Raman spectroscopy[34-36] (Supplementary Note 1, Supplementary Figure 1 and Supplementary Note 2,

Supplementary Figure 2). We observed no indication of Sn precipitates in these crystals, even at the nanoscale in our STM studies (described below), consistent with expectations from the very small Sn content used, and the successful use of Sn as a resonant level dopant in small percentages in previous studies on tetradymites (see, e.g. refs 24, 25 and 33). The excellent cleavage characteristics of our single crystals are further indication of the absence of Sn precipitates.

Bulk transport characterization. The temperature-dependent bulk resistivity (ρ) plots (Figure 2**b**) of three samples of Sn-BSTS from a 15 cm long single crystal boule, separated by a total of 8 cm along the boule, show that bulk Sn-BSTS is highly insulating. ρ increases exponentially with decreasing T, attains maximum values (~125 Ωcm was the largest observed) at ~100-150 K, and starts decreasing with decreasing T. This decrease, which has been observed numerous times in previous studies on tetradymite-based materials with low carrier concentrations, is widely taken as an indication that the resistivity of the insulating bulk material has been short-circuited at low temperatures by the metallic TSS[20,30,37,38]. The temperature at which the surface states finally dominate the bulk resistivity depends on intrinsic factors such as the exact defect concentration in the bulk crystal, and the surface and bulk carrier mobilities, and extrinsic factors such as the sample shape. These are the origin of the relatively small differences in behavior observed here for crystals extracted from different locations in the large single crystal boule. The point is that the same basic behavior is seen for crystals extracted from widely varying positions, an indication of the uniformity of the defect chemistry in the large bulk single crystal. The high resistivities observed are excellent for a tetradymite; at $T < 100$ K the bulk resistivity must be substantially higher but it cannot be measured directly due to the dominance of the surface state conductance. The Log ρ vs. T^{-1} plots (Figure 2**c**) exhibit an activated behavior with the activation

energy for transport, Δ, ≈ 165 meV. This Δ is very high and is consistent with half of the bulk band gap measured by ARPES (see below) ($\Delta = E_{g\,(transport)}/2$, so E_g = 330 meV, $E_{g(ARPES)}$ = 350 meV), an indication of the intrinsic nature of the semiconducting Sn-BSTS crystals. The Hall coefficient (R_H) (Figure 2**d**) increases with decreasing T and attains very high values (~ -5×10^4 cm^3/C) at low T. At high T, activated behavior can be seen. Some samples show a change in sign of R_H from positive to negative on cooling, which is typical behavior for highly compensated bulk tetradymites (see, e.g. ref. 39), and, for T <150 K, all samples have negative R_H, indicating *n*-type carrier conduction. At the low T transport is dominated by surface states, the bulk carrier concentrations must actually be substantially lower than the ~3×10^{14} cm^{-3} that results when one assumes that the conduction is from bulk states only. The feature in ρ near T ~ 50 K, where surface state transport dominates the conductance, is reproduced in all of the crystals studied, and is discussed further below.

Angle resolved photoemission spectroscopy (ARPES). The low-energy band structure of Sn-BSTS was investigated by ARPES and is shown in Figure 3.The observations are consistent with what is seen in other tetradymite-based materials, and no indication of the energy levels of the 1% Sn-dopant states is seen. The pristine crystal surface shows conical states in the center of the surface Brillouin zone that are linearly dispersing (Supplementary Figure 3) at 4 eVÅ from a DP that is about 120 meV below the Fermi level (Figure 3**a**). The bands probed by ARPES were then electron doped through the deposition of K atoms on the surface, pushing the chemical potential into states that are not occupied in the pristine crystals. Consistent with previous studies on tetradymites, the conical bands display no photon-energy dependence, a test of the k_z dependence of their energy dispersion, and therefore represent surface states. The photon and k dependent ARPES spectra of the K-deposited crystals enabled the determination of the extrema

of the bulk valence and conduction bands that form the energy gap in which the surface states reside, Figure 3**b**. The DP was thus found to be isolated from the bulk bands, as the highest BVB states only reach energies of 120 meV below, and the lowest energy BCB states appear 230 meV above the DP (these could also be BCB-derived quantum well states of electrons trapped near the surface by band bending; however, since no Rashba splitting is observed, it is likely that the band bending is small and that these states only trace the bottom of the BCB[40,41]) and the highest bulk valence bands only reach energies of 120 meV below it. These findings are shown schematically in Figure 3c. The bulk gap is found to be ~350 meV, consistent with the transport activation energy. E_F falls in the surface states only, and the Fermi surface, shown in Figure 3**g**, consists only of a small ring centered at the Γ point of the Brillouin zone (**f**), with the Fermi wave vector $k_F = 0.03$ Å^{-1}, for the surface state electrons. Constant energy cuts through the band structure, Figure 3**g-i** show that the surface states, as one moves away from the DP, acquire some hexagonal warping, and are joined by the six petals of the bulk valence bands some 240 meV below the Fermi level in the pristine sample, or the circular bottom of the bulk conduction band when the chemical potential is raised by 110 meV through K deposition (Figure 3**d-e**). This is confirmed in our tunneling microscopy experiments.

Scanning tunneling microscopy (STM). The topographic image of the Te-terminated (001) surface of an Sn-BSTS crystal at 30 K displays large atomically flat regions with atomic modulations corresponding to the rhombohedral crystal structure (Figure 4**a**); the Fourier transform of this image reflects the hexagonal symmetry of the crystal surface (Figure 4**b**). In addition to the Te atoms, several defects are observed[26]. We probed the electronic structure on the surface of Sn-BSTS by using scanning tunneling spectroscopy (STS) [42-45]. First, we measured the differential conductance, which is proportional to the local density of states, across the

surface along a line of length of 90 nm (Figure 4**c**). The spectra show a 'U' shape curve with a minimum at -120 meV and multiple inflection points. Since STS is sensitive to both TSS and bulk bands, to correctly identify the features in the spectra, the STS results are compared with the *E-k* structure established by ARPES. We identify the observed changes in the STS spectra at around -200 meV and +120meV to be the indication of the edges of the bulk bands. The tunneling between these energies is dominated by the surface states. The minimum of the conductance corresponds approximately to the DP energy. The Dirac point energy (120 meV below the Fermi energy) is in agreement with the ARPES data measured in different crystals from the same boule, showing the long-range homogeneity of the material. The variation in the position of the minimum energy along the scan line is small (with 2.4 meV standard deviation), which suggests that the chemical potential is homogeneous at the nanometer length scale and the Dirac point energy is not affected significantly by the defects on the surface. However, as the energy is tuned away from the Dirac energy, the density of states develops significant modulations. These inhomogeneities in the spectra are mainly the result of the disordered Sb-Bi distribution in the layers, which leads to enhanced quasi-particle interference on the surface. Scattering of the surface electronic states was examined by recording differential conductance maps at various energies (Figure 4**d-e**). Although the conductance maps are strongly influenced by the Sb-Bi disorder, the Fourier transforms of the maps capture the signal corresponding to the scattering of TSS and reveal a linearly dispersing scattering cone between the BCB and BVB (Figure 4**f**). To compare the STM and ARPES data, we note that scattering between the opposite sides of the Dirac cone is prohibited by time-reversal symmetry. In the case of a single Dirac cone, the prohibition suppresses the amplitude of the largest scattering wave vectors, resulting in a scattering cone with a smaller diameter. However, unambiguously resolving the diameter

change is beyond our measurement resolution. Thus, we simply approximate the observed scattering cone as a manifold of vectors connecting regions of large density of states measured by ARPES. In this picture the boundary of the observed energy-momentum structure for a single linear dispersing band has half of the slope as measured by ARPES. The expected energy-momentum relation is indicated as a red line (Figure 4**f**), in good agreement with our ARPES measurement.

Magnetoresistance and 2D surface states. To study the availability of the TSS for charge transport experiments and potential applications of Sn-BSTS in advanced devices, we performed transport measurements on crystals at 20 mK, under magnetic fields up to 18 T. Figure 5**a** and **b** are the magnetoresistance (MR, ρ_{xx} vs. H) and Hall (ρ_{yx} vs. H) plots, respectively, measured by tilting H in the x-z plane (z is the direction of the surface normal and x is the direction of current flow in the basal plane). The ρ_{yx} vs. H plots show that the charge transport is mainly due to electrons. Both ρ_{xx} and ρ_{yx} exhibit strong quantum oscillations at $\theta = 90°$, which gradually die out as θ approaches 0°. To visualize the oscillations and study their origin, the angular dependence of ρ_{xx} and ρ_{yx} are plotted as a function of H^{-1} (Figure 5**c, d**). The Shubnikov-de Haas (SdH) oscillations are extracted from ρ_{xx} and ρ_{yx}, and the resulting difference resistivity ($\Delta\rho$) plots are shown in Figure 6**a** and **b**; the oscillations are as large as ~ 6%, with a low frequency. For a particular oscillation peak (n = 5) the field value corresponding to the peak position ($(\mu_0 H)^{-1}_{n=5}$) is plotted with tilt angle (Figure 6**c**). It is clear that the peak shift is proportional to sinθ, which has been widely taken as a reflection of the 2D TSS origin of the oscillations (see, e.g. Refs. 16 and18). The Fermi surface cross-section area (S_F) is calculated as 37 T. The 2D SS carrier density (n_s) is 8.93×10^{11} cm^{-2} and the SS carriers are n-type. Using the ARPES Fermi velocity (v_F = 4eVÅ), the Fermi surface in this crystal is found to be 134 meV above the DP,

consistent with ARPES and STM measurements, again an indication of the homogeneity of the material over macroscopic distances in the single crystal. (For more clarity concerning the 2D nature of the states, ρ_{xx} and ρ_{yx} are plotted as a function of $(\mu_0 H \sin\theta)^{-1}$ in Supplementary Figure 4; the consistent shift of the peak positions of oscillations confirms that these oscillations are owing to 2D conduction.) We note that quantum oscillations due to the surface states are seen for the vast majority of samples that we have cut from the crystal boules of Sn-BSTS. Although to the authors' knowledge there has been no systematic study of when such oscillations are present in tetradymites and when they are absent, their presence must be related to the crystal surface quality, otherwise they would be observed more frequently.

The TI crystals can be considered as having parallel conductance paths, with the measured electrical conductance being a linear combination of bulk (G_{bulk}) and surface (G_s) conductances, $G = G_{bulk} + G_s$[39]. With this in mind, the Sn-BSTS crystals allow for the surface state conductance to be characterized over a wide temperature range. Taking the data for a very high bulk resistivity crystal, G is plotted vs. T^{-1} in Figure 6**d**. At high T, G_{bulk} is dominant; it decreases exponentially as T decreases and for a wide range of temperatures, in the range of 150 to 100 K, both surface and bulk carriers are contributing significantly to the observed transport. For temperature below 100 K surface carriers likely dominate the transport. G_s can then be estimated at low temperature, where the influence of the bulk is less significant. The estimated T dependence of G_s in the range 4 – 100 K is plotted in the inset of Figure 6**e**. G_s shows an unusual step at ~50 K. This feature may either be an experimental artifact, or purely due to TSS behavior, or due to a structural phase transition in the underlying bulk crystal. Synchrotron diffraction analysis at low T (Supplementary Note 5 and Supplementary Figure 5) rules out the possibility of a bulk structural phase transition, and the STM images taken at low T do not show any sign of a

surface reconstruction. Therefore this anomaly cannot reflect the presence of structural transitions either on the surface of the or in the bulk material. We speculate that it may reflect the sensitivity of the conductance of the TSS on Sn-BSTS to the adsorption of a residual active gas (e.g. H_2 or O_2) in the experimental chamber.

Discussion

In summary, we have shown that highly bulk insulating TI crystals of $Bi_{1.08}Sn_{0.02}Sb_{0.9}Te_2S$, with intrinsic semiconductor characteristics (Δ~165 meV, and bulk carrier density $n < 3\times10^{-14}$ cm^{-3} at low temperatures), can be successfully grown by the vertical Bridgeman technique, with nearly uniform properties over 8 cm or more of a large single crystal boule. The bulk band gap is consistently estimated to be ~350 meV by spectroscopy and transport methods, and the DP is found to be completely exposed in the gap, ~120 meV above the valence band maximum and ~230 meV below the conduction band minimum. The chemical potential for these crystals consistently falls in the surface states only, at an energy of ~120 meV above the DP. Quantum oscillations from the TSS electrons are reproducibly observed. The SS carriers in Sn-BSTS are *n*-type, which are preferable for charge transport experiments and potential spintronics applications. Our results lead us to conclude that Sn-BSTS is an excellent tetradymite-type bulk single crystal TI, and that it will be highly advantageous for use in future experimental studies of topological surface states, especially for the characterization of surface state quantum transport very close to the Dirac point.

Methods

Crystal Growth. The bulk single crystals were grown by the vertical Bridgman technique (VBT). The required amounts (according to the formula: $Bi_{1.08}Sn_{0.02}Sb_{0.9}Te_2S$) of elements with high purities (5N) were placed in C-coated bottom-pointed quartz ampoules of inner diameter 4 mm. The as-received high purity starting materials (Bi, Sb and Te) were further purified by heating under vacuum of ~ 10^{-5} mbar, at 950 °C in the presence of C, in sealed quartz tubes. The crystal growth ampoules were sealed under a vacuum of ~ 10^{-5} mbar. The crystal growth was performed at ~700 °C with a translation rate of ampoule of 1 mm/hr through the crystallization zone[24], and ~15 cm long crystal boules were obtained.

Crystalline quality. The crystals extracted from the single crystal boule were studied for phase identification on a laboratory X-ray diffractometer (Bruker Eco D8 Advance) equipped with Cu$K\alpha$ source and LYNXEYE XE detector. To check the homogeneity of the crystal structure we also performed Raman microscopy at ambient temperature using 10 μW from a 532 nm excitation laser, focused to 1 μm spot. Temperature-dependent Synchrotron powder X-ray diffraction measurements were performed on beamline 11-BM at the Advanced Photon Source to probe the bulk crystal structure at low temperature.

Bulk resistivity and carrier density. The bulk resistivity and carrier density were measured respectively in four-probe and Hall configurations on a Quantum Design Physical Properties Measurement System (PPMS). Samples were in the rectangular shape with thickness of ~0.5 mm. The electrical contacts were made on the (001) surface through Pt-wires with silver paint. The Hall data were recorded by applying magnetic field of 1 T normal to the (001) sample surface, and the current flow was in the basal plane.

ARPES and STM band structure analysis. The electronic band structure was established by ARPES using a Scienta SES-3000 electron spectrometer set to the resolution of 12 meV and 0.1° at beamline 12.0.1 of the Advanced Light Source (ALS). Photon energies were in the range of 30 to 100 eV. Samples were cleaved at 15 K in ultrahigh vacuum of 5×10^{-9} Pa and all the data were collected at 15 K. The STM measurements were performed on the (001) crystal surface in the temperature range of 30 K to 90 K, on a home-built variable temperature STM.

Magnetoresistance and Hall effect. Angular dependent MR and Hall data were obtained in a dilution refrigerator at T = 20 mK at applied fields up to $\mu_0 H$ = 18 T, using standard six contact measurements. The SdH quantum oscillations were obtained by subtracting the background from the data. The thickness of samples used for measurements was ~50 μm.

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Author Contributions

S.K.K., H.J. and R.J.C designed the research. S.K.K. synthesized the compound, performed optimized crystal growth, X-ray and bulk electronic measurements. I.P. and T.V. performed ARPES studies, T.L., J.L. W.W. and N.P.O. carried out and interpreted the magnetoresistance transport measurements, A.G. and A.Y. performed the low temperature STM measurements, Y.T., H.Z. and K.S.B. performed the Raman experiments, and S.L. performed the low temperature X-ray diffraction measurements. S.K.K. & R.J.C. wrote the manuscript with input from all the coauthors.

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Figure Legends:

Figure 1 | Evolution of tetradymite type TIs. (**a**) Schematic representation of the evolution of Bi_2Se_3, (M_2X_3) type TIs, through the two approaches, (Approach-**1** and Approach-**2**). The arrows represent approaches and progresses made in achieving better materials. The solid lines represent the single atomic layers and zebra lines represent multi-element layers. The purple, green, red, dark orange and yellow colors are taken respectively for Bi, Sb, Se, Te, and S atoms. (**b**) The schematic of a quintuple layer (QL) for Sn:$Bi_{1.1}Sb_{0.9}Te_2S$ and a QL obtained by structure refinement of a powdered specimen. The color fraction of Bi/Sb atoms is according to the composition obtained by unit cell refinement.

Figure 2 | Crystal growth and bulk electronic (ρ and n) properties of Sn-BSTS. (**a**) The photograph of a crystal boule grown by vertical Bridgman technique (VBT), an orange line bar represents 1 cm scale. (**b**) The ρ vs. T plots for three freshly cleaved representative samples, A, E and G, respectively taken from the segments at 1, 6 and 10 cm from crystal boule. (**c**) The log ρ vs. $1/T$ plots for three samples A, E and G, to evaluate thermal activation energy, Δ. The straight lines are exponential fits to the high T data points. (**d**) The Hall coefficient (R_H) vs. T plots for the same crystals. The black dotted line is guide to the eye. For samples E and G, R_H values show the change of sign from +ve to -ve.

Figure 3 | Probing the electronic band structure by ARPES measurements. (**a**) The ARPES-determined band dispersion for k_y along M–Γ–M measured at 30 eV photon energy, at 15 K. The bands were electron doped through deposition of potassium (K) to allow for the determination of the energy of the conduction band minimum. (**b**) Excerpts from the excitation energy dependence ($h\nu$ = 82, 74 and 66 eV) study of the photoemission from the electron-doped bands

reflect the perpendicular momentum k_z positions of the bulk valence band (BVB) and conduction band (BCB) extrema. The surface states are unaffected by the change of k_z. (**c**) A schematic for the electronic structure of Sn-BSTS in the vicinity of the Fermi energy derived from the ARPES data. Gray dashed lines mark the bulk band gap region, two crossed red lines correspond to the surface states, and the turquoise line shows the position of the Dirac point, DP. The constant-energy ARPES maps, referenced relative to the Fermi level E_F for the pristine sample (**g-i**) or the Dirac point E_{DP} for the K-deposition-generated electron doped sample (**d**, **e**), showing a few critical points in the low energy band structure of Sn-BSTS. (**f**) is a schematic for Brillouin zone with high symmetry points.

Figure 4 | Mapping of electronic conductance and 2D surface states by STM. (**a**) Real space topographic image of the (00l) surface of an Sn-BSTS crystal at V_{bias} = - 600 mV set-point bias voltage and I = 60 pA tunneling current. (**b**) Fourier transform of the topographic image revealing the Bragg peaks corresponding to the hexagonal surface structure. **c**, The differential conductance (dI/dV) along a line shows only small fluctuations in the electronic surface structure (V_{bias} = - 600 mV and I = 60 pA). The red line indicates the minima of the spectra, while the brown line displays the average spectrum along the line. Arrows point to the approximate positions of the edges of the bulk valence and conduction bands (BVB and BCB) and the position of the Dirac point (DP). (**d-e**) Real space differential conductance (dI/dV) maps recorded at -300 and 60 meV with respect to the Fermi level. (**f**) Fourier-transform scanning tunneling spectroscopy (STS) maps at different energies, reveal the structure of the quasiparticle scattering on the surface of the crystal. The images were obtained from symmetrized (considering the mirror and rotational symmetry of the underlying crystal). Fourier transforms of dI/dV conductance maps of size of 1320 Å x 1320 Å (V_{bias} = - 500 mV and I = 80 pA). The red lines

with a slope of 2 eV/Å^{-1} correspond to the expected dispersion relation that should be seen by STM, based on the ARPES measurements (Figure 3, v_{ARPES} = 4 eV/Å^{-1}). All measurements were performed at 30 K.

Figure 5 | Magnetoresistance and Hall transport characterization of Sn-BSTS. (**a**), the magnetoresistance and (**b**) Hall plots and their dependence on the angle (θ) between H and the current in the sample, all the measurements were performed at 20 mK. An Schematic in (**a**) shows the direction of H in x-z plane with respect to current in sample plane along -x. (**c-d**), $\rho_{\mathrm{xx}}(H, \theta)$ and $\rho_{\mathrm{yx}}(H, \theta)$ vs. $(\mu_0 H)^{-1}$ plots as a function of θ.

Figure 6 | The Shubnikov-de Hass (SdH) oscillations and 2D surface states . (**a**) and (**b**) the SdH oscillations extracted from ρ_{xx} and ρ_{yx} for θ = 90°, respectively. (**c**) The θ dependence of $(\mu_0 H)^{-1}{}_{\mathrm{n=5}}$ peak of SdH oscillations for ρ_{xx}. (**d**) Temperature dependence of the conductivity, for the most insulating crystal of Sn-BSTS studied, plotted as a function of inverse temperature. (**e**) The G_{s} vs. T plot for T < 100 K, extracted from G.