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## Experimental evidence of the nanoscaled topological metallic surface state of Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> films

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Abstract – There is a standing fundamental issue of topological insulators that their theoretically predicted nanoscaled metallic surface state (3-5 nm) has never been demonstrated substantially by experiments. We have designed an experiment to clarify this issue by measuring the surface-state and bulk-state resistances of topological insulators of Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> thin films. Interestingly, we found that the measured surface-state resistivity is lower than that of the bulk-state by 5 orders of magnitude, which indicated that the nanoscaled surface state (3-5 nm) is metallic. Further, the surface-state resistances decrease monotonically with the temperature decreasing from room temperature down to 5 K, which clearly showed that the metallic temperature dependence is consistent with the presence of the topologically protected Dirac surface state. Differently, the bulk-state resistances firstly decrease, and then reach a rock bottom near 125 K, and then increase with decreasing temperature and achieve the saturated state near 50 K. These results definitely showed that the bulk state exhibits a typical temperature dependence of insulators. Our experiments have, for the first time, provided the experimental evidence of the theoretically predicted nanoscaled metallic surface state of topological insulators.

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There is a standing fundamental issue of topological insulators that their theoretically predicted nanoscaled metallic surface state (3-5 nm) has never been demonstrated substantially by experiments [1-4]. In other words, there have not been any investigations which experimentally showed that the nanoscaled surface layer seems metallic and the bulk is insulating of a really topological insulator. Therefore, it is essential and urgent to experimentally demonstrate the landmark prediction above. Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> materials have been predicted to be the topological insulators with the robust and nontrivial surface metallic state by theory [5–7]. In situ angle-resolved photoemission spectroscopy (ARPES) experiments have confirmed that the surface electronic band structures of Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> consist of a single Dirac cone with a linear dispersion at the center of the Brillouin zone [8–12]. Recently, the quantum oscillations of the topological insulators have suggested that the surface conduction channels arise from their topological surface states [13-19]. Thus, we take  $Bi_2Te_3$  and  $Sb_2Te_3$ materials as our model system to study the metallic surface state of the topological insulators.

In this contribution, we design a unique experiment to explore the direct experimental evidence for distinguishing the surface-state conduction from the bulk-state conduction in the topological insulators of Bi<sub>2</sub>Te<sub>3</sub> and  $Sb_2Te_3$  polycrystalline thin films. Our results show that the electrical resistivity of the nanoscaled surface layer (3-5 nm) of these polycrystalline thin films is of the order of  $10^{-5}\Omega \cdot \text{cm}$ , and the bulk electrical resistivity is 5 orders of magnitude larger than that of the surface at room temperature. Thus, these results clearly reveal that the surface is metallic. Further, the temperature dependence of the surface resistivity displays the metallic behavior, while the temperature dependence of the bulk resistivity indicates an insulating behavior. Therefore, these results substantially demonstrate the theoretically predicted metallic surface state of topological insulators.

Firstly, the topological insulators of  $Bi_2Te_3$  and  $Sb_2Te_3$ thin films are prepared on Si and  $Pt/TiO_2/SiO_2/Si$  wafers by pulsed-laser deposition at 300 °C in Ar gas ambient. The surface topography, elemental composition and crystalline structure of the as-grown polycrystalline thin films are characterized by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray

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Fig. 1: SEM images of the as-grown  $Bi_2Te_3$  (a) and  $Sb_2Te_3$  (b) polycrystalline films, and the insets are the EDX analyses, respectively. Panels (c) and (d) are the corresponding XRD patterns, and (e) and (f) are the corresponding Raman spectra, respectively.

diffraction (XRD), respectively, as shown in fig. 1. From fig. 1, we can see that the prepared films are smooth and uniform. The recorded EDS data indicate that the compositions of  $Bi_2Te_3$  with a Bi/Te ratio and  $Sb_2Te_3$ with a Sb/Te ratio are very close to 2:3. From the typical XRD patterns as displayed in figs. 1(c) and (d), we can see that the highly *c*-axis-oriented  $Bi_2Te_3$  and  $Sb_2Te_3$ thin films are prepared, and the two films have the same rhombohedral structure, and the sharp peaks with high intensity reveal that the topological insulator samples

have good crystalline structure. To obtain more accurate data for the structure of the polycrystalline thin films, we carry out Raman scattering measurements. The typical Raman spectra for the Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> films ranging from 50 to 500 cm<sup>-1</sup> at 514 nm laser excitation are shown in figs. 1(e)-(f), respectively. Three pronounced optical phonon modes on Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> samples can be clearly observed at the low wave number region. As can be seen in fig. 1(e), three characteristic peaks of Bi<sub>2</sub>Te<sub>3</sub> appear in the positions of 62.5, 103 and 133.5 cm<sup>-1</sup>,



Fig. 2: (Color online) Schematic drawing of the measurement settings. (a) A standard four-probe configuration and (b) a two-terminal model.

respectively, and they are consistent with the previously measured Raman peaks of Bi<sub>2</sub>Te<sub>3</sub> crystals [20–22]. The mode located at  $62.5 \,\mathrm{cm}^{-1}$  corresponds to the characteristic  $A_{1g}^1$  vibration mode, the  $103 \,\mathrm{cm}^{-1}$  mode can be attributed to the  $E_g^2$  mode, and the peak observed at  $133.5 \,\mathrm{cm}^{-1}$  is identified as the  $A_{1g}^2$  vibration mode. Among these three modes, the  $A_{1g}^1$  and  $A_{1g}^2$  modes can be assigned to the out-of-plane vibration modes, and the mode with  $E_g^2$  symmetry can be attributed to the in-plane vibration mode. Meanwhile, the three characteristic  $A_{1g}^1, E_g^2$  and  $A_{1g}^2$  vibration modes of Sb<sub>2</sub>Te<sub>3</sub> at the peak positions of 71.2, 112 and  $167 \,\mathrm{cm}^{-1}$ , respectively, are detected as expected. Thus, our extensive Raman measurements indicate that the as-grown Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> polycrystalline thin films have the good crystallization nature.

To study the electrical transport properties of the prepared topological insulator of  $Bi_2Te_3$  and  $Sb_2Te_3$  films, we design a measurement model to identify the surface and bulk states of the samples. As shown in fig. 2, the samples are prepared on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si wafers with 150 nm thick Pt layer and Si substrates, respectively. Circular-shaped Pt top electrodes of  $300 \,\mu$ m diameter are deposited on the upper surfaces of  $Bi_2Te_3$  and  $Sb_2Te_3$  films by ion-plating technique at room temperature. The thickness of the Pt top electrodes is 150 nm, patterned using a shadow mask. In our case, the samples are regarded as bulk materials. In detail, in order to avoid the influence of Pt conducting layer (bottom electrode) on the measurement of the surface-state conductance and to isolate the role of surface states, the samples prepared on Si wafers are

used to investigate the surface-state transport as shown in fig. 2(a), and the samples deposited on  $Pt/TiO_2/SiO_2/Si$  wafers are used to study the bulk-state property as shown in fig. 2(b). The measurements are carried out by a Keithley 4200-SCS semiconductor characterization system.

The surface-state resistances are measured using a standard four-point collinear probe method, and the probe array is placed in the center of the samples. With a fourprobe, the two outer probes are used for sourcing current and the two inner probes are used for measuring the resulting voltage drop across the surface of the samples. The surface-state resistance  $R_{\rm s} = 4.532 \times (V/I)$ , with V the measured voltage and I the source current, and the surface electrical resistivity is calculated as follows:  $\rho_s =$  $R_{\rm s} \times t$ , where  $\rho_{\rm s}$  is the surface electrical resistivity and t is the surface thickness. By the ARPES measurement of the thickness-dependent band structure and first-principles calculations, the striking feature of the topological surface states forms at a thickness of 3-5 nm [7,10,11,23-25]. Therefore, we select 5 nm as the surface thickness of the two kinds of films to calculate the surface electrical resistivity in our experiments. The bulk-state resistances are obtained from the current-voltage characteristics of the as-fabricated stack cells such as Pt/Bi<sub>2</sub>Te<sub>3</sub>/Pt and  $Pt/Sb_2Te_3/Pt$ , as shown in fig. 2(b). The bulk electrical resistivity  $\rho_{\rm b}$  is determined by the formula of  $\rho_{\rm b} = \frac{R_{\rm b} \cdot S}{d}$ , where  $R_{\rm b} = V/I$  is the bulk resistance, S is the area of the Pt electrode and d is the sample thickness. The evolutions of the electrical transport properties of the two materials as a function of deposition time are shown in fig. 3. Compared with the observed resistances, Bi<sub>2</sub>Te<sub>3</sub> films are more resistive than  $Sb_2Te_3$  samples. Thus, the detailed measurements clearly show that the surface electrical resistivity  $\rho_s$  of the two kinds of films is of the same order of  $10^{-5}\Omega \cdot \mathrm{cm}$ , and the electrical resistivity of the bulk state is 5 orders of magnitude larger than that of the surface state. Therefore, the tremendous difference between the surface and bulk electrical resistivity is expected for the topological surface state as we mentioned, which implies that there are two different mechanisms, respectively, working in the electronic transports of the surface and bulk states of  $Bi_2Te_3$  and  $Sb_2Te_3$  films.

To extract more information on the surface and bulk states of the two kinds of films, we perform the temperature dependence of the surface and bulk resistances as shown in fig. 4. Clearly, we can see that the surface resistance of the samples monotonically decreases with the temperature decreasing down to 5 K, and exhibits a metallic resistance profile. However, the variation of the bulk resistances vs. the temperature is nonmonotonic, which implies that the bulk state has a nonmetallic resistance profile and the bulk transport channel clearly shows the temperature dependence of insulators. Thus, the profound discrepancy between the surface and bulk resistances confirms that the two-dimensional conduction channel is dominated by the surface electrons and transport, which



Fig. 3: (a) The surface-state resistance and resistivity evolutions of  $Bi_2Te_3$  films as a function of deposition time. (b) The evolutions of the bulk-state resistance and resistivity of  $Bi_2Te_3$  films changing with deposition time. The surface-state and bulk-state electrical properties of  $Sb_2Te_3$  films are shown in (c) and (d), respectively.

would originate from the topological surface states. On the other hand, the surface and bulk electrons are contributing in parallel under the standard four-probe model (fig. 2(a)), and the thermal activation carriers of these nonmetallic states will be frozen when the thin films are cooled down to low temperatures. Therefore, only the topological protected Dirac surface states could contribute to the unusual metallic behavior of the surface resistances. In the case of the two-terminal model (fig. 2(b)), the surface and bulk electrons are contributing in series, and the surface effect is presently masked by the electrical property of the bulk electrons, which is the dominant transport channel in our films.

In fact, the temperature dependence of the bulk transport of the samples (figs. 4(a), (b)) can be divided into three regions as shown in fig. 4(d). In the range from room temperature to 125 K (region I), the bulk resistance initially steeply and then gradually decreases with decreasing temperature, which shows a typical metallic behavior with a positive temperature coefficient. However, the bulk channel resistance shows a sharp upturn below 125 K as depicted in region II, which is an indication of a semiconducting behavior. Finally, the bulk resistance shows a relatively flat temperature dependence when the temperature falls below 50 K (region III), and it is nearly constant and approaches saturation. This electrical transport shows

the insulating transport behavior. Actually, the reason for which the bulk resistance of the near-stoichiometric  $Bi_2Te_3$  and  $Sb_2Te_3$  films initially exhibits conducting but not insulating behavior can be attributed to excess charge carriers. Well known, the unwanted bulk carriers will produce an intense bulk electron pocket at the Fermi level as shown schematically in fig. 4(c). The observed *n*type behavior with both the bulk conduction band and surface states crossing the Fermi level is suggested to be caused by a large amount of Te vacancies and Te antisite defects which are introduced during films growth [8, 26–29]. From the detailed measurement information, we have thus established a comprehensive understanding of the bulk transport mechanism in Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> films as follows. Initially, the decrease of the bulk channel resistance with decreasing temperature is primarily due to the weakening of the electron scattering by lattice vibration, while the bulk resistance increases with the temperature decreasing below 125 K, and such abnormal behavior of drastically different temperature dependence can be attributed to the freeze-out effect of the carrier, *i.e.*, the remarkable change observed can basically be correlated with the gradual decrease of the electron density. Although the bulk resistance of the *n*-type samples shows a significant increase under the temperature below  $125\,\mathrm{K},$  and the measurement results of the bulk conduction channels



Fig. 4: (Color online) The temperature dependence of the surface-state and bulk-state resistances for  $Bi_2Te_3$  (a) and  $Sb_2Te_3$ (b) films, respectively. (c) A sketch of the band structure of topological insulator films, with the BCB, BVB, and SS indicated along the  $\Gamma$ -M direction near the  $\Gamma$ -point, respectively, and the bulk-state conduction band, bulk valence band and surface state are denoted BCB, BVB, and SS, respectively. (d) The schematic drawing for the bulk-state resistance evolution of the samples varying with the temperature.

have also demonstrated the insulating behavior. The residual conductance at low temperature (50-5 K) appears to be relatively larger. Considering the relatively large defects concentration, it is reasonable to speculate that these defects may form an impurity band within the bulk energy gap of the thin films. At higher temperature, the thermal activation of electrons from the defect energy level to the bulk conduction band creates free electrons in the conduction band, which leads to the *n*-type bulk conduction. When the temperature goes to zero, both localized and extended electrons still coexist in the impurity band near the conduction band edge, and they are responsible for the finite bulk residual conduction.

In summary, we have, for the first time, experimentally demonstrated the theoretically predicted nanoscaled metallic surface state of topological insulators in the system of the polycrystalline  $Bi_2Te_3$  and  $Sb_2Te_3$  films prepared by pulsed-laser deposition. By constructing an effective measurement, we could accurately distinguish the surface and bulk states of  $Bi_2Te_3$  and  $Sb_2Te_3$  films, and provided a definite evidence for the presence of the topologically protected Dirac surface state. In fact, the polycrystalline films of topological insulators are more realistic for applications, and create new opportunities for fundamental and application research.

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## REFERENCES

- YU R., ZHANG W., ZHANG H.-J., ZHANG S.-C., DAI X. and FANG Z., *Science*, **329** (2010) 61.
- [2] WRAY L. A., XU S.-Y., XIA Y. Q., HOR Y. S., QIAN D., FEDOROV A. V., LIN H., BANSIL A., CAVA R. J. and HASAN M. Z., *Nat. Phys.*, 6 (2010) 855.
- [3] WRAY L. A., XU S.-Y., XIA Y. Q., HSIEH D., FEDOROV A. V., HOR Y. S., CAVA R. J., BANSIL A., LIN H. and HASAN M. Z., *Nat. Phys.*, 7 (2011) 32.
- [4] XIU F., HE L., WANG Y., CHENG L., CHANG L.-T., LANG M., HUANG G., KOU X., ZHOU Y., JIANG X. W., CHEN Z. G., ZOU J., SHAILOS A. and WANG K. L., to be published in *Nat. Nanotechnol.*, www.nature.com/ naturenanotechnology.

- [5] ZHANG H. J., LIU C.-X., QI X.-L., DAI X., FANG Z. and ZHANG S.-C., *Nat. Phys.*, 5 (2009) 438.
- [6] HSIEH D., XIA Y., QIAN D., WRAY L., MEIER F., DIL J. H., OSTERWALDER J., PATTHEY L., FEDOROV A. V., LIN H., BANSIL A., GRAUER D., HOR Y. S., CAVA R. J. and HASAN M. Z., *Phys. Rev. Lett.*, **103** (2009) 146401.
- [7] PARK K., HEREMANS J. J., SCAROLA V. W. and MINIC D., Phys. Rev. Lett., **105** (2010) 186801.
- [8] CHEN Y. L., ANALYTIS J. G., CHU J.-H., LIU Z. K., MO S.-K., QI X. L., ZHANG H. J., LU D. H., DAI X., FANG Z., ZHANG S. C., FISHER I. R., HUSSAIN Z. and SHEN Z.-X., *Science*, **325** (2009) 178.
- [9] XIA Y., QIAN D., HSIEH D., WRAY L., PAL A., LIN H., BANSIL A., GRAUER D., HOR Y. S., CAVA R. J. and HASAN M. Z., *Nat. Phys.*, 5 (2009) 398.
- [10] LI Y.-Y., WANG G., ZHU X.-G., LIU M.-H., YE C., CHEN X., WANG Y.-Y., HE K., WANG L.-L., MA X.-C., ZHANG H.-J., DAI X., FANG Z., XIE X.-C., LIU Y., QI X.-L., JIA J.-F., ZHANG S.-C. and XUE Q.-K., Adv. Mater., 22 (2010) 4002.
- [11] WANG G., ZHU X. G., WEN J., CHEN X., HE K., WANG L. L., MA X. C., LIU Y., DAI X., FANG Z., JIA J. F. and XUE Q. K., *Nano Res.*, **3** (2010) 874.
- [12] ZHANG Y., HE K., CHANG C.-Z., SONG C.-L., WANG L.-L., CHEN X., JIA J.-F., FANG Z., DAI X., SHAN W.-Y., SHEN S.-Q., NIU Q., QI X.-L., ZHANG S.-C., MA X.-C. and XUE Q.-K., *Nat. Phys.*, 6 (2010) 584.
- [13] QU D.-X., HOR Y. S., XIONG J., CAVA R. J. and ONG N. P., Science, **329** (2010) 821.
- [14] ANALYTIS J. G., MCDONALD R. D., RIGGS S. C., CHU J.-H., BOEBINGER G. S. and FISHER I. R., *Nat. Phys.*, 6 (2010) 960.
- [15] PENG H. L., LAI K. J., KONG D. S., MEISTER S., CHEN Y. L., QI X.-L., ZHANG S.-C., SHEN Z.-X and CUI Y., *Nat. Mater.*, 9 (2010) 225.

- [16] ETO K., REN Z., TASKIN A. A., SEGAWA K. and ANDO Y., Phys. Rev. B, 81 (2010) 195309.
- [17] ANALYTIS J. G., CHU J.-H., CHEN Y. L., CORREDOR F., MCDONALD R. D., SHEN Z. X. and FISHER I. R., *Phys. Rev. B*, **81** (2010) 205407.
- [18] CHECKELSKY J. G., HOR Y. S., LIU M.-H., QU D., CAVA R. J. and ONG N. P., *Phys. Rev. Lett.*, **103** (2009) 246601.
- [19] TASKIN A. A., SEGAWA K. and ANDO Y., *Phys. Rev. B*, 82 (2010) 121302 (R).
- [20] TEWELDEBRHAN D., GOYAL V. and BALANDIN A. A., *Nano Lett.*, **10** (2010) 1209.
- [21] DANG W. H., PENG H. L., LI H., WANG P. and LIU Z. F., Nano Lett., 10 (2010) 2870.
- [22] LIU H. W., YUAN H. T., FUKUI N., ZHANG L., JIA J. F., IWASA Y., CHEN M. W., HASHIZUME T., SAKURAI T. and XUE Q. K., Cryst. Growth Des., 10 (2010) 4491.
- [23] LU H.-Z., SHAN W.-Y., YAO W., NIU Q. and SHEN S.-Q., Phys. Rev. B, 81 (2010) 115407.
- [24] YAZYEV O. V., MOORE J. E. and LOUIE S. G., Phys. Rev. Lett., 105 (2010) 266806.
- [25] SAKAMOTO Y., HIRAHARA T., MIYAZAKI H., KIMURA S.-I. and HASEGAWA S., *Phys. Rev. B*, 81 (2010) 165432.
- [26] HSIEH D., XIA Y., QIAN D., WRAY L., DIL J. H., MEIER F., OSTERWALDER J., PATTHEY L., CHECKELSKY J. G., ONG N. P., FEDOROV A. V., LIN H., BANSIL A., GRAUER D., HOR Y. S., CAVA R. J. and HASAN M. Z., *Nature*, 460 (2009) 1101.
- [27] REN Z., TASKIN A. A., SASAKI S., SEGAWA K. and ANDO Y., Phys. Rev. B, 82 (2010) 241306(R).
- [28] HIRAHARA T., SAKAMOTO Y., TAKEICHI Y., MIYAZAKI H., KIMURA S.-I., MATSUDA I., KAKIZAKI A. and HASEGAWA S., *Phys. Rev. B*, 82 (2010) 155309.
- [29] KONG D. S., RANDEL J. C., PENG H. L., CHA J. J., MEISTER S., LAI K., CHEN Y. L., SHEN Z., MANOHARAN H. C. and CUI Y., Nano Lett., 10 (2010) 329.