Large bulk resistivity and surface quantum oscillations in the topological insulator Bi$_2$Te$_2$Se

Zhi Ren, A. A. Taskin, Satoshi Sasaki, Kouji Segawa, and Yoichi Ando

Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan

(Dated: November 15, 2010)

Topological insulators are predicted to present novel surface transport phenomena, but their experimental studies have been hindered by a metallic bulk conduction that overwhelms the surface transport. We show that a new topological insulator, Bi$_2$Te$_2$Se, presents a high resistivity exceeding 1 Ωcm and a variable-range hopping behavior, and yet presents Shubnikov-de Haas oscillations coming from the surface Dirac fermions. Furthermore, we have been able to clarify both the bulk and surface transport channels, establishing a comprehensive understanding of the transport in this material. Our results demonstrate that Bi$_2$Te$_2$Se is the best material to date for studying the surface quantum transport in a topological insulator.

PACS numbers: 73.25.+i, 71.18.+y, 73.20.At, 72.20.My, 71.55.Ht

The three-dimensional (3D) topological insulator (TI) is characterized by a non-trivial $Z_2$ topology of the bulk wave function, and it represents a new topological quantum state realized in a band insulator. In theory, 3D TIs are insulating in the bulk and unusual metallic surface states consisting of spin-filtered Dirac fermions give rise to interesting surface transport phenomena. In reality, however, TI samples available today are invariably conducting in the bulk, and charge transport is always dominated by the bulk current. Therefore, to exploit the novel surface transport properties of topological insulators, it is crucial to achieve a bulk-insulating state in a TI material.

Among the recently discovered TIs, Bi$_2$Se$_3$ has been the most attractive because of its simple surface-state structure. Unfortunately, near-stoichiometric Bi$_2$Se$_3$ is always n-type owing to a large amount of Se vacancies. An isostructural material Bi$_2$Te$_3$ can be grown as p-type but usually it is also highly metallic, most likely due to anti-site defects which are promoted by close electronegativities of Bi and Te. Significant efforts have been made to achieve bulk insulating behavior in Bi$_2$Se$_3$ and Bi$_2$Te$_3$; however, while an increase in resistivity with decreasing temperature has been observed, so far the bulk remains to be essentially a metal and a clearly insulating temperature dependence, such as the variable-range hopping (VRH) behavior has never been reported. For example, by growing a Bi$_2$Te$_3$ single crystal with a compositional gradient, it was possible to observe a resistivity upturn at low temperature and to measure the surface quantum transport but the resistivity remained low (< 12 mΩcm) in absolute terms and the surface contribution to the transport did not exceed ~0.3%. The situation is essentially the same in Bi$_2$Se$_3$.

Given this difficulty, searching for a new TI material better suited for achieving the bulk insulating state is obviously important. In this paper, we report that a new TI material, Bi$_2$Te$_2$Se, which has an ordered tetradymite structure [Fig. 1(a)] with the basic quintuple-layer unit of Te-Bi-Se-Bi-Te and was recently confirmed to have a topological surface state has desirable characteristics for surface transport studies. We found that high-quality single crystals of ordered Bi$_2$Te$_2$Se show a high resistivity exceeding 1 Ωcm, together with a variable-range hopping (VRH) behavior which is a hallmark of an insulator; yet, it presents Shubnikov-de Haas (SdH) oscillations which signify the 2D surface state consistent with the topological one observed by the angle-resolved photoemission spectroscopy (ARPES).

By examining the difference in the doping chemistry between Bi$_2$Se$_3$ and Bi$_2$Te$_3$, one may understand that the ordered Bi$_2$Te$_2$Se has reasons to be superior: i) The formation of Se vacancies is expected to be suppressed, because the Se trapped between two Bi atoms is less exposed to evaporation due to stronger chemical bonding with Bi in this position; ii) The formation of the anti-site defects between Te and Bi is also expected to be suppressed because of preferable bonding between Se and Bi in contrast to Se-Te bonding; iii) Ordered nature minimizes the additional disorder that could be caused by Se/Te randomness. In this work, single crystals of Bi$_2$Te$_2$Se were grown by melting high purity (6N) elements of Bi, Te and Se with a molar ratio of 2:1.95:1.05 at 850°C for two days in evacuated quartz tubes, followed by cooling to room temperature over three weeks. The ordering of the chalcogen layers in our Bi$_2$Te$_2$Se single crystals is confirmed by the X-ray powder diffraction patterns by comparing those from Bi$_2$Te$_2$Se and Bi$_2$Te$_3$ as shown in Fig. 1(b), where the characteristic peaks, which are intensified in the ordered Bi$_2$Te$_2$Se compound, are indicated by arrows. Note that the ordering does not cause a doubling nor a symmetry change of the unit cell.

For transport measurements, cleaved crystals were aligned using the X-ray Laue analysis and cut along the principal axes, and the (111) surface was protected by depositing an alumina thin film after cleaning the surface by bias sputtering with Ar ions. Ohmic contacts were prepared by using room-temperature cured silver paste. The sample reported here was 0.51-mm wide and 0.26-mm thick, with the voltage contact distance of 0.86 mm. The resistivity $\rho_{xx}$ and the Hall resistivity $\rho_{yz}$ were mea-
most two orders of magnitude increase in $\rho$ sweeping the magnetic field between parallel metallic conduction. The saturation of the resistivity at low temperature implies a finite metallic conductivity at $T = 0$ K. To clarify the nature of this metallic state, we employed the SdH oscillations, whose angular dependence in tilted magnetic fields can provide the information about the size and the shape of the Fermi surface (FS) and, more importantly, about the dimensionality of the FS. In our Bi$_2$Te$_2$Se crystals, we observed SdH oscillations in both $\rho_{xx}$ and $\rho_{yx}$ (the latter presenting more pronounced oscillations), and the two show essentially the same frequency with a phase shift of approximately $\pi/2$. Figure 2(a) shows the derivative of $\rho_{yx}$ with respect to the magnetic field $B$ plotted in $1/B_{\perp} = 1/(B \cos \theta)$ coordinates, where $\theta$ is the angle between $B$ and the $C_3$ axis as shown schematically in the bottom inset. Two important features can be readily recognized: First, $d\rho_{yx}/dB$ is periodic in the inverse magnetic field, indicating the existence of a well-defined FS. Second, oscillations depend solely on $B_{\perp}$, implying a 2D character. Note that the oscillations quickly disappear with increasing $\theta$ (above $\sim 40^\circ$ they are hardly distinguishable) because the amplitude of the oscillations strongly depends on the magnetic-field strength. The signature of a 2D FS can be also seen in the plot of the oscillation frequency vs. $\theta$, which shows the characteristic $1/\cos \theta$ dependence [upper inset of Fig. 2(a)].

The obtained frequency for $\theta \approx 0^\circ$ of 64 T, which is directly related to the Fermi-surface cross section $A$ via the Onsager relation $F = (\hbar e/2\pi c)A$, gives $k_F = 4.4 \times 10^6$ cm$^{-1}$, which means the surface charge-carrier concentration $N_s = k_F^2/4\pi = 1.5 \times 10^{12}$ cm$^{-2}$ for a spin-filtered surface state. It is important to notice that our measured $k_F$ is too large if the oscillations come from the bulk; for example, the carrier concentration for a 3D ellipsoidal FS that might be consistent with our SdH data would be $\approx 1 \times 10^{19}$ cm$^{-3}$, which is orders of magnitude larger than what we obtain from the Hall data described later.

Fitting the standard Lifshitz-Kosevich theory to the temperature dependence of the SdH amplitudes [inset of Fig. 2(b)] gives the cyclotron mass $m_c = 0.11m_e$, where $m_e$ is the free electron mass. Assuming that the electrons are Dirac-like, one obtains the Fermi velocity $v_F = \hbar k_F/m_c = 4.6 \times 10^6$ cm/s. This $v_F$ is consistent with the ARPES data affirming the Dirac-fermion assumption. The position of the surface Fermi level $E_F^s$ measured from the Dirac point can be estimated from $v_F$ and $k_F$ to be 130 meV, suggesting that the observed surface carriers are electrons.

Once $m_c$ is known, the Dingle analysis [shown in Fig. 2(b)] uncovers the scattering time $\tau$ through the Dingle temperature $T_D = \hbar/(2\pi e k_B)$; the slope of the linear fit to the data yields $T_D$ of 25.5 K, which gives $\tau = 4.8 \times 10^{-14}$ s. Hence, one obtains the mean free path on the surface $\ell_{\text{SdH}} = v_F \tau \approx 22$ nm and the surface mobility $\mu_s = (e\ell_{\text{SdH}})/(h k_F) \approx 760$ cm/Vs. Note that both quantities are underestimated, because $\tau$ obtained from the SdH effect reflects scattering events in all directions, whereas in the transport properties the backward scattering, which is prohibited in topological insulators, plays the most important role.

In the SdH oscillations, the resistivity oscillates as $\Delta\rho_{xx} \sim \cos[2\pi(\ell_{\text{SdH}} + \frac{1}{2} + \beta)]$, where $2\pi\beta$ is the Berry phase. It is known that the cyclotron orbit of an electron in a magnetic field acquires a Berry phase $\pi$ if its energy dispersion is linear near the degenerate point.
of the Landau level number \( \frac{1}{B} \) shown in Fig. 2(c) for the oscillations obtained from the Landau-level fan diagram, which signifies the activation of holes with an effective activation energy \( \Delta^* \approx 33 \text{ meV} \). This \( \Delta^* \) is of the same order as we found for the resistivity [inset of Fig. 1(c)], and the small difference is attributed to the temperature dependence of the mobility. The prefactor of the activated behavior gives an estimate of the acceptor concentration \( N_a \approx 9 \times 10^{18} \text{ cm}^{-3} \).

When we look at the magnetic-field dependence of \( \rho_{yx} \) at 1.6 K, the low-field and high-field slopes are essentially different [inset of Fig. 2(d)]. The low-field \( R_H \) is \(-200 \text{ cm}^3/\text{C} \), giving the effective carrier concentration of \( 3.1 \times 10^{16} \text{ cm}^{-3} \). As we know from SdH oscillations, the surface-electron concentration is \( 1.5 \times 10^{12} \text{ cm}^{-2} \), corresponding to an effective 3D Hall coefficient of \(-5.4 \times 10^4 \text{ cm}^3/\text{C} \), which is much larger than the observed value. Therefore, surface electrons alone cannot account for the low-temperature \( R_H \) and there should be other charge carriers in the system. Their concentration and type can be inferred from the high-field slope of \( \rho_{yx}(B) \), since the high-field limit of \( R_H \) is determined only by the number (and type) of carriers irrespective of their mobilities; in our data, the high-field slope is \(-26 \text{ cm}^3/\text{C} \), which points to the existence of bulk electrons with the concentration \( n = 2.4 \times 10^{17} \text{ cm}^{-3} \) in addition to the surface electrons. This example demonstrates that estimations of the bulk carrier density based on the low-field \( R_H \), though often done in Tis, can be too optimistic.

The above analysis indicates that at low temperature the surface electrons and bulk electrons are contributing in parallel. It turns out that the standard two-band model fits the whole \( \rho_{yx}(B) \) curve very well [solid line in the inset of Fig. 2(d)]; here, \( R_n \) and \( \rho_n \) are the Hall coefficient and resistivity of the bulk electrons, \( R_s = t/(eN_s) \) and \( \rho_s = \rho_\perp t \), with \( \rho_\perp \) the surface sheet resistance and \( t \) the sample thickness. This fitting yields the surface mobility \( \mu_s = 1450 \text{ cm}^2/\text{Vs} \) and the bulk mobility \( \mu_n = 11 \text{ cm}^2/\text{Vs} \), along with \( N_s = 1.5 \times 10^{12} \text{ cm}^{-2} \) and \( n = 2.4 \times 10^{17} \text{ cm}^{-3} \). The obtained \( \mu_s \) is about two times larger than the \( \mu_{\text{SdH}} \) estimated from the SdH analysis [Fig. 2(b)]. This is expected for the topological surface state as we mentioned before. On the other hand, the bulk mobility \( \mu_n \) of 11 cm²/Vs is near the boundary between the band and hopping transport regimes suggesting that the bulk electrons move in a very disordered potential. The fraction of the surface contribution in the total conductance at 1.6 K is calculated to be \(-6\% \), which is about 20 times larger than that achieved in Bi₂Te₃.

To elucidate the bulk contribution to the transport properties, the Hall data is useful. As shown in Fig. 2(d), the low-field Hall coefficient \( R_H (= \rho_{yx}/B \) near \( B = 0 \text{ T} \) changes sign from positive to negative upon cooling, signifying the change of dominant charge carriers from holes to electrons. At high temperature (\( \gtrsim 150 \text{ K} \)), the behavior of \( R_H(T) \) is thermally activated; the dotted line is an Arrhenius-law fitting, which signifies the activation of holes with an effective activation energy \( \Delta^* \approx 33 \text{ meV} \). This \( \Delta^* \) is of the same order as we found for the resistivity [inset of Fig. 1(c)], and the small difference is attributed to the temperature dependence of the mobility. The prefactor of the activated behavior gives an estimate of the acceptor concentration \( N_a \approx 9 \times 10^{18} \text{ cm}^{-3} \).

![FIG. 2: (Color online) (a) \( d\rho_{yx}/dB \) vs. \( 1/B \) \([= 1/(B \cos \theta)]\) in magnetic fields tilted from the C\(_3\) axis at different angles \( \theta \), where all curves are shifted for clarity; lower inset shows the schematics of the experiment and the definition of \( \theta \). Equidistant dashed lines in the main panel emphasize the positions of maxima for any \( \theta \) depends only on \( B \); upper inset shows the \( 1/\cos \theta \) dependence of the oscillation frequency. Both point to the 2D FS. (b) Dingle plot for the oscillations in \( \Delta \rho_{yx} \), which is obtained after subtracting a smooth background from \( \rho_{yx} \), giving \( T_D = 25.5 \text{ K} \); inset shows the \( T \) dependence of the SdH amplitude for \( \theta \approx 0^\circ \), yielding \( m_c = 0.11m_e \). (c) Landau-level fan diagram for oscillations in \( d\rho_{xx}/dB \) measured at \( T = 1.6 \text{ K} \) and \( \theta \approx 0^\circ \). Inset shows \( d\rho_{xx}/dB \) vs. \( 1/B \) after subtracting a smooth background. Minima and maxima in \( d\rho_{xx}/dB \) correspond to \( n + 1/2 \) and \( n + 3/2 \), respectively. The linear fit intersects the axis at \( n = 0.22 \). (d) Temperature dependence of the low-field \( R_H \); dotted line represents the activated behavior. Inset shows the \( \rho_{yx}(B) \) curve at 1.6 K and its fittings with the two-band model.](image-url)
The observed phase shift of \( \sim \pi \) is at odds with the expected \( \frac{\pi}{2} \) shift. The reason for this unexpected observation is not clear at the moment.

D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge University Press, Cambridge, 1984).

Y. Zhang et al., Nature (London) **438**, 201 (2005).

G.P. Mikitik and Yu.V. Sharlai, Phys. Rev. Lett. **82**, 2147 (1999).

D. Xiao, M.C. Chang, and Q. Niu, Rev. Mod. Phys. **82**, 1957 (2010).

T. Ando, T. Nakanishi, and Q. Niu, J. Phys. Soc. Jpn. **67**, 2857 (1998).

Since the oscillations in \( \rho_{yx} \) present the unusual \( \pi \) phase shift compared to those in \( \rho_{xx} \), the phase analysis of \( \rho_{yx} \) is not very meaningful and we concentrate on \( \rho_{xx} \) here.

Since \( d \Delta \rho_{xx}/dB \sim 2\pi \frac{\Delta}{h} \sin[2\pi(\frac{n}{2} + \frac{1}{2} + \beta)] \), we assign \( n + \frac{1}{2} \) to the minima (and \( n + \frac{1}{2} \) to the maxima) in \( d\rho_{xx}/dB \).

In the extrinsic range, \( R_H(T) \) is determined by \( \Delta^* \) and \( N_a \) as \( R_H \approx cN_aN_V \exp(-\Delta^*/k_BT) \), where \( N_V = 2(2\pi m^*_e k_B T/h^2)^{3/2} \) is the effective density of states of the valence band with \( m^*_e \) the effective density-of-state mass. \( m^*_e \) is not known for Bi\(_2\)Te\(_3\)Se, but if we take \( m^*_e = 0.166m_e \) measured for Bi\(_2\)Te\(_3\), \( N_V = 5.2 \times 10^{18} \) cm\(^{-3}\) at 300 K and \( N_a \) is estimated to be about \( 9 \times 10^{18} \) cm\(^{-3}\).

We thank L. Fu, M.Z. Hasan, N.P. Ong, and D. Vanderbilt for helpful discussions. This work was supported by JSPS (KAKENHI 19674002), MEXT (KAKENHI 22103004), and AFOSR (AOARD 10-4103).

**Acknowledgments**

FIG. 3: (Color online) Schematic picture of the bulk and surface band structures (left), together with the energy diagram of the density of states of the bulk and impurity bands (right). In the impurity band which is due to the acceptor levels and is located within the band gap, only the central part forms the extended states and the tails consist of localized states.