Surface conduction of topological Dirac electrons in bulk insulating Bi$_2$Se$_3$

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The newly discovered three-dimensional strong topological insulators (STIs) exhibit topologically protected Dirac surface states$^{12}$. Although the STI surface state has been studied spectroscopically, for example, by photoemission$^{3-5}$ and scanned probes$^{6-10}$, transport experiments$^{11-17}$ have failed to demonstrate the most fundamental signature of the STI: ambipolar metallic electronic transport in the topological surface of an insulating bulk. Here we show that the surfaces of thin (≈10 nm), low-doped Bi$_2$Se$_3$ (≈10$^{17}$ cm$^{-3}$) crystals are strongly electrostatically coupled, and a gate electrode can completely remove bulk charge carriers and bring both surfaces through the Dirac point simultaneously. We observe clear surface band conduction with a linear Hall resistivity and a well-defined ambipolar field effect, as well as a charge-inhomogeneous minimum conductivity region$^{16-20}$. A theory of charge disorder in a Dirac band$^{20-21}$ explains well both the magnitude and the variation with disorder strength of the minimum conductivity (2 to 5 $\Omega$/h per surface) and the residual (puddle) carrier density (0.4 x 10$^{12}$ to 4 x 10$^{12}$ cm$^{-2}$). From the measured carrier mobilities 320-1,500 cm$^2$V$^{-1}$s$^{-1}$, the charged impurity densities 0.5 x 10$^{12}$ to 2.3 x 10$^{12}$ cm$^{-2}$ are inferred. They are of a similar magnitude to the measured doping levels at zero gate voltage (1 x 10$^{12}$ to 3 x 10$^{12}$ cm$^{-2}$), identifying dopants as the charged impurities.

Bi$_2$Se$_3$, as prepared, is observed to be n-type owing to Se vacancies. We find that mechanically exfoliated thin (thickness t ≈ 10 nm) Bi$_2$Se$_3$ on SiO$_2$/Si is invariably highly n-doped with sheet charge densities $\gtrsim$10$^{15}$ cm$^{-2}$, much greater than expected considering the bulk charge density ($\sim$10$^{17}$ cm$^{-3}$) in our low-doped starting material$^{26}$, suggesting additional doping is induced by mechanical cleavage, reaction with ambient species$^{16}$, or substrate interaction. To remove this doping, we employed two types of p-type doping schemes on mechanically exfoliated thin Bi$_2$Se$_3$ field-effect transistors on 300 nm SiO$_2$/Si back-gate substrates$^{18-22}$: (1) chemical doping with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) or (2) electrochemical doping with a polymer electrolyte top gate.

Figure 1a,b shows the schematics of the device structures and gating schemes. We exploit either the strong electron affinity (≈5.4 eV) of F4TCNQ molecules$^{27}$ or the large capacitance ($\sim$1 $\mu$F/cm$^2$) of the electrochemical double layer at the interface between accumulated ions and the sample surface$^{24-26}$ to induce negatively charged ions near the surface and p-type doping of Bi$_2$Se$_3$. In both cases the dopant density was fixed after cooling to cryogenic temperature, but further tuning of the carrier density was possible using the back gate (see Methods).

Figure 1c,d shows the longitudinal resistivity $\rho_{xx}$ and Hall carrier density $n_1 = 1/(eR_H)$ (where $R_H$ is the Hall coefficient and $e$ is the elementary charge) of a representative device (F4TCNQ-doped device 4) at various temperatures $T$ from 2 to 50 K as a function of the back-gate voltage $V_g$. The plot of $\rho_{xx}(V_g)$ shows a peak at $V_{g,0} \approx -45$ V, and $n_1$ changes sign at a similar $V_g$, diverging positively (negatively) when approaching $V_{g,0} = -45$ V from above (below). There is no evidence of an energy gap: $\rho_{xx}(T)$ is metallic ($\partial \rho_{xx}/dT > 0$) and saturates at low $T$, and $n_1(T)$ shows little temperature dependence. The behaviour is strongly reminiscent of that seen for the two-dimensional Dirac electronic system in graphene$^{18}$. Likewise, we identify the linear regions of $n_1$ versus $V_g$ for $V_g > -35$ V and $V_g < -60$ V as unipolar n- and p-doped regimes respectively, and the region $-35 < V_g < -60$ V as an inhomogeneous regime where electron and hole transport are both present.

Figure 2a shows the Hall resistivity of device 4 as a function of magnetic field $\rho_{xy}(B)$ at various gate voltages in the unipolar n- and p-doped regimes. The Hall resistivity in the unipolar regime is always linear over the entire range of magnetic field ($\pm$9 T), indicating all bands contributing to the transport have similar mobility and the same carrier sign. Specifically, we can rule out the possibility of both bulk and surface channels participating in conduction (previously observed to give a nonlinear $\rho_{xy}(B)$; refs 11,12,28) or significant contribution to conduction by impurity bands, which should have much lower carrier mobilities (1–10 cm$^2$V$^{-1}$s$^{-1}$; ref. 17). The measured linear ambipolar Hall effect, with carrier mobility of $>10^4$ cm$^2$V$^{-1}$s$^{-1}$, is therefore a strong indication that conduction in our samples is dominated by the surface states.

We note that a previous work on single-gated Bi$_2$Se$_3$ of similar thickness, but heavily (0.5%) Ca-doped$^{27}$, also showed a superficially similar resistivity peak, interpreted there as the transition from bulk to surface conduction. No region of unipolar p-type Hall effect was observed. The authors concluded that significant band bending in these highly doped crystals led to very different carrier densities on either side of the device as well as an effective reduction of the bulk gap$^{11,15,17}$. To determine whether band bending is important in our devices, we fabricated a further top gate on an F4TCNQ-doped device (device 5), using hydrogen silsesquioxane (HSQ) as a top-gate dielectric.

Figure 2b shows the resistivity $\rho_{xy}$ of dual-gated device 5 as a function of applied displacement field to the top ($D_{xy}$) and bottom
(D_{tg}) surfaces (see Methods). The data are presented as a polar plot of the normalized resistivity ($\rho_{nx}/\rho_{max}$) of the device as a function of total magnitude of displacement field $D_{total} = |D_{tg} + D_{bg}|$, and asymmetry factor, defined by $\alpha = (4/\pi) \tan^{-1}(D_{tg} - D_{bg})/D_{total}$. We find that the measured resistivity depends only on the total displacement field, proportional to the total charge density in the Bi$_2$Se$_3$ slab. We conclude from the observed azimuthal symmetry that both surfaces are gated simultaneously with either gate and their chemical potential lies at the same level. If the gates acted independently on top and bottom surfaces, then the maximum asymmetry factor, defined by $\alpha = (4/\pi) \tan^{-1}(D_{tg} - D_{bg})/D_{total}$, would exceed the quantum capacitance of each surface, in which case the two surface potentials become locked together (see Supplementary Information for a further discussion).

Having eliminated the possibilities of band bending or significant contribution to the conductivity by bulk or impurity states, we conclude that our measurement probes the conductance of the topological surface state in Bi$_2$Se$_3$ in the absence of bulk carriers; the defining quality of a topological insulator.

Below, we analyse in more detail the transport properties of the topological surface state as a function of carrier density per surface $n$ estimated from $n = (C_g/2e)(V_g - V_{bg})$, where $V_{bg}$ is the gate voltage at which $R_{H} = 0$, which corresponds closely to the gate voltage of minimum conductivity. Figure 3a–c shows the conductivity per layer ($\sigma$), the Hall carrier density per layer ($n_{H,layer}$ = $1/2R_{H,e}$), and field effect mobility $\mu = \sigma/ne$ versus carrier density per layer $n$. Data are shown for devices 1–5, with electrolyte gating, and devices 4 and 5, charge-transfer-doped with F4TCNQ. Several features are notable immediately in Fig. 3 and comprise the main experimental observations in this work. On tuning the carrier density: (1) $\sigma$ and $n_{H,layer}$ show clear ambipolar conduction with well-defined p- and n-regions, (2) $n_{H,layer}$ shows a minimum value ($n_{H}^{*}$) for p- and n-conduction, (3) $\sigma$ shows a roughly linear carrier density dependence for $n^{*} < n < n_{H,alk}$, where $n_{H,alk} \approx 5 \times 10^{12} \text{cm}^{-2}$ is the carrier density above which the bulk conduction band is expected to be populated, and (4) a minimum conductivity ($\sigma_{min} = 2e^2/h$ to $5e^2/h$) is observed.

Extending the theory of charge disorder in graphenes, a recent theoretical study predicts the conductivity as being limited by charged-impurity scattering in STI of the form (assuming a linear Dirac band):\

$$\sigma(n) \sim C \left(\frac{n}{n_{imp}}\right) [e^2/h] \text{ for } n > n^*$$  (1a)\

$$\sigma(n) \sim C \left(\frac{n^*}{n_{imp}}\right) [e^2/h] \text{ for } n < n^*$$  (1b)

where $n_{imp}$ is the charged impurity density, $C$ is a constant that depends on the Wigner–Seitz radius $r_s$ and $n^*$ is identified as the residual carrier density in electron and hole puddles. For Bi$_2$Se$_3$ on SiO$_2$ (ref. 21) we expect $0.05 < r_s < 0.2$ and $30 < C < 300$. See Supplementary Information for a more detailed description of the theory. For $n^* < n < 5 \times 10^{12} \text{cm}^{-2}$, we fit $\sigma(n)$ to equation (1a) (Fig. 3a, dashed lines), to obtain the field-effect mobility $\mu_{FE} = Ce/n_{H,alk}^2$ for each device. $\mu_{FE}$ ranges from 320–1,500 cm$^2$/V·s$^{-1}$, reflecting different amounts of disorder in the samples. We identify the initial n-type dopants and defects induced by mechanical exfoliation as likely sources of the disorder. The decrease in $\mu_{FE}$ with further electrolytic
gating (device 1 run 2) indicates electrochemical damage, probably solvation of Se ions. The observation of sublinear $\sigma(n)$ at $n < n_{\text{bulk}}$ in devices 3–5 may indicate that there are further types of disorder, for example neutral point defects, that should be considered.

The observed minimum conductivity of the Dirac electronic band can be understood well through equation (1b) as being due to the residual carrier density $n^*$ in electron and hole puddles induced by the charged impurity potential at nominally zero carrier density; $\sigma_{\text{min}} = n^* e \mu$, where $n^*$ is calculated self-consistently as a function of $n_{\text{imp}}, r_c$ and $d$, the distance of the impurities to the Dirac surface. The self-consistent theory predicts that $n^*$ increases with increasing disorder and $\sigma_{\text{min}}$ depends only weakly on disorder. Figure 4 shows the experimentally observed residual carrier density $n^*$ per surface for each device (Fig. 4a) as well as $\sigma_{\text{min}}$ per surface (Fig. 4b) as a function of the experimentally measured inverse mobility $1/\mu_{\text{FE}}$, which reflects the disorder strength. (For devices in which $n^*$ could be measured for $p$- and $n$-type conduction, both values are shown.) The shaded regions reflect the expectations of the self-consistent theory using parameter ranges $0.05 < r_c < 0.2$ and $d = 0.1\text{Å}–15\text{Å}$. We see a good agreement between experiment and theory in that (1) $\sigma_{\text{min}}$ is weakly dependent on disorder strength ($1/\mu_{\text{FE}}$) and (2) $n^*$ increases with disorder strength ($1/\mu_{\text{FE}}$). Particularly for increasing disorder in the same device (Device 1 run 1 versus run 2), $n^*$ increases but $\sigma_{\text{min}}$ is almost unchanged (arrows in Fig. 4a,b). The experimental data agree best with the upper range of the theoretical estimates, corresponding to small $d = 0.1\text{Å}$ and large $r_c = 0.2$. Assuming $r_c = 0.2$, we infer an impurity density $n_{\text{imp}}$ ranging from $0.5 \times 10^{13}$ to $2.3 \times 10^{13}\text{ cm}^{-2}$, much larger than for graphene exfoliated on similar SiO$_2$ substrates but comparable to the observed initial doping level of $1 \times 10^{13}$ to $3 \times 10^{13}\text{ cm}^{-2}$, suggesting that the dopants are the charged impurities responsible for limiting the mobility (see Supplementary Information).

The simple theory somewhat underestimates $n^*$ and $\sigma_{\text{min}}$ but we expect that the theory can be refined to take into account the...
nonlinearity and asymmetry of the Bi$_2$Se$_3$ surface state bands. Notably, the larger Fermi velocity for the electron band would increase the conductivity above the estimate in equation (1) for n-type conduction, indicating that the disorder strength is probably somewhat underestimated from the n-type mobility. Shifting the points to the right (to larger disorder strength) in Fig. 4 would indeed improve the agreement between experiment and theory.

Reducing the n-type doping of TI thin films by external agents provides an effective and simple way to probe topological surface transport properties in the absence of bulk conduction. For the present devices the level of charged impurity disorder is on the order of $\sim 10^{13}$ cm$^{-2}$, limiting the mobility to 320–1,500 cm$^2$ V$^{-1}$ s$^{-1}$. However, owing to the large dielectric constants in existing topological insulators, reduction of impurity concentrations to levels seen in the best bulk crystals ($<10^{17}$ cm$^{-3}$ corresponding to $<10^{11}$ cm$^{-2}$ in a 10 nm thick crystal) would allow mobilities exceeding $10^2$ cm$^2$ V$^{-1}$ s$^{-1}$. Hence understanding and eliminating the doping presently observed in all thin crystals and films is of central importance to increasing the mobility of the topological surface state.

**Note added in proof:** After submission of this work we became aware of a scanning tunnelling microscopy study that directly observed the screened potential fluctuations caused by charged impurity disorder in Bi$_2$Se$_3$ and Bi$_2$Te$_3$, consistent with our interpretation of the minimum conductivity arising from charge inhomogeneity.

**Methods**

Bi$_2$Se$_3$ thin crystals were produced by micro-mechanical cleavage of bulk Bi$_2$Se$_3$ single crystals and deposited on doped Si covered with 300 nm SiO$_2$. Thin crystals (thickness about 10 nm) were identified using atomic force microscopy (AFM). The thin film was patterned in a Hall bar geometry using an Ar plasma at a pressure of $\sim 6.7$ Pa (5 $\times$ 10$^{-2}$ torr). Au/Cr electrodes were defined by electron-beam lithography (see inset of Fig. 1d). A brief (10 s) selective surface treatment of the contact area with a N$_2$ or Ar plasma before the deposition of metals was used to enhance the ohmic conduction of the contacts.

The p-type doping for devices 1–3 was achieved by applying a negative voltage to a polymer electrolyte consisting of LiClO$_4$ and polyethylene oxide (PEO) in the weight ratio 0.12:1, as previously used for carbon nanotubes and graphene devices$^{4,9}$. Molecular charge transfer doping for device 4 and 5 was done by thermal evaporation of $\sim 15$ nm of F4TCNQ molecules (Aldrich) on top of the samples$^{27}$. The devices were subsequently cooled down and further tuning of carrier density was done by sweeping the back-gate voltage at cryogenic temperature. For electrolyte-gated measurements, the samples were cooled down to 250 K in less than 1 min after applying the top-gate voltage to minimize electrochemical reactions$^{27}$.

As well as single-gated samples, we fabricated dual-gated samples based on F4TCNQ-doped samples (Fig. 2b). 60 nm of hydrogen silylquinoxaline (HSQ, XR-1541, Dow Corning) was spin-coated on an F4TCNQ-coated Bi$_2$Se$_3$ device and a top-gate electrode was defined by electron-beam lithography. We found that further fabrication on pre-doped devices increased the n-type doping level (for example, $\sim 1.2 \times 10^{13}$ cm$^{-2}$ at zero gate field in Fig. 2b compared with $\sim 0.3 \times 10^{13}$ cm$^{-2}$ in Fig. 1d). From the Hall carrier density versus gate voltage, the bottom-gate and top-gate capacitances were determined to be $\sim 11$ nF cm$^{-2}$ and $\sim 33$ nF cm$^{-2}$, respectively; reasonable values considering the dielectric constants of SiO$_2$ ($\kappa \approx 3.9$) and HSQ ($\kappa \approx 3$).

Four-probe measurements of longitudinal and transverse electrical resistances were conducted using Stanford Research Systems SR830 Lock-in amplifiers and a commercial cryostat equipped with a 9 T superconducting magnet. The Hall voltage was recorded in both polarities of the magnetic field ($\pm 1$ T) and anti-symmetrized to remove longitudinal voltage components. In the transport experiments a small and reproducible hysteresis in $V_{g,p} (\approx 2 V)$ was observed during forward and backward gate voltage scans. As a consequence, resistivity and Hall data with the same scan directions were compared in this work. Best fits to equation (1a) were determined using a least squares linear fit to $\sigma(n)$ in the linear regime, determined by identifying the region of roughly constant slope $d \sigma / dn$. Thermal runs as described here were performed for more than ten different Bi$_2$Se$_3$ samples of similar thickness, with qualitatively consistent results.

Note: certain commercial equipment, instruments or materials are identified in this paper to specify the experimental procedure adequately. Such an identification is not intended to imply any recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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Author contributions
D.K. conceived the p-type doping schemes. D.K. and S.C. fabricated devices, performed the electrical measurements with K.K. and analysed the data. N.P.B., P.S. and J.P. prepared single crystal Bi$_2$Se$_3$ starting material. S.A. assisted with the theoretical analysis. D.K., S.C. and M.S.F. wrote the manuscript.

Additional information
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