The development of topological insulator (TI) materials has found rapid progress in the past few years [1]. Distinguished from ordinary insulators by the so-called $Z_2$ topological invariants associated with the bulk electronic band structure [2, 3], this class of materials is characterized by nonlocal topology of the electronic structure that gives rise to new electronic states with promise for realizing the next generation of technologies such as fault-tolerant quantum computation [4]. First predicted to be manifest in the Spin Quantum Hall effect [5, 6], a topological metallic edge state was first observed experimentally in two-dimensional HgTe quantum wells [7]. The same principle was then extended to the three-dimensional case [8, 9], and subsequently verified by observations of a two-dimensional surface state in Bi$_{1-x}$Sb$_x$ crystals [11], marking the beginning of a new field of research in 3D TI materials.

By far the most widely studied system, Bi$_2$Te$_3$ (T=Se,Te), was quickly identified as an ideal candidate material, owing to the realization of larger bulk band gaps (≈300 meV) and simplified electronic structures [12, 15], and continues to be the focus of current research [16, 17]. To date, the major experimental efforts on these non-interacting bismuth-based TI materials have focused on refining measurement techniques in order to detect signatures of surface states. However, a continuing problem with the stoichiometric materials lies in the fact that they are not bulk insulators as predicted, but rather doped semiconductors [18]. For instance, Bi$_2$Se$_3$ is a stable doped $n$-type material due to the presence of charged Se vacancies acting as electron donors [19–23]. Extensive work has been carried out to suppress bulk conductivity contributions by compensation doping [14, 15, 20, 21] or synthesis of defect-free epitaxial thin films [24, 25], but sensitivity to environmental conditions and crystalline quality [26] continues to pose severe problems. Both bulk and surface quality of TI materials are known to dramatically affect their properties, with the effects of site exchange (e.g. in Bi$_2$Te$_3$) or Se vacancy doping (e.g., in Bi$_2$Se$_3$) serving to severely reduce charge carrier mobilities and mix bulk and surface state conduction contributions. This requires non-trivial analysis of experimental data to identify and study the intrinsic nature of the topologically protected surface states. Electrostatic gating techniques can overcome this difficulty by utilizing ultra-thin crystals [27, 24], however increased attention is being devoted to other classes of materials [30, 31] in the absence of further progress.

The common method of crystal growth using excess selenium falls short of reaching even a non-metallic temperature dependence of resistivity [26], which has to date only been achieved by introducing excess impurity scattering via chemical substitution methods [35, 36] or Se-Te site substitution such as in Bi$_2$Te$_2$Se [37]. Here we employ a new growth technique to demonstrate the lowest attained bulk carrier concentrations in stoichiometric Bi$_2$Se$_3$, achieving a level where samples exhibit non-metallic transport behavior. A nonlinear Hall coefficient clearly identifies two carrier types and allows for the identification of separate bulk and surface state contributions to conductivity, with the coexistence of positive and negative carriers providing unequivocal proof of TI surface states from transport data alone.

The resistivity temperature dependence $\rho(T)$ shown in Fig. 1 illustrates the range of non-metallic behavior of three samples of as-grown Bi$_2$Se$_3$ crystals. Two additional samples, V and H, are included for comparison. Sample H shows metallic behavior typical of most samples of Bi$_2$Se$_3$ in the literature, while sample V shows semi-metallic behavior identical to the lowest carrier concentration samples reported to date [18, 20]. Unlike samples V and H, the non-metallic crystals (A, D, F)
using conventional methods, exhibit more metallic behavior decreasing temperature, while samples V and H, synthesized using conventional methods, exhibit more metallic behavior consistent with higher carrier densities.

exhibit an overall increase in resistivity with decreasing temperature. Furthermore, the most insulating-like samples exhibit a room temperature resistivity value far greater than the comparison samples or previous measurements of both pure and chemically substituted samples of Bi₂Se₃ [26, 35, 36], indicating that the insulating behavior is originating mainly from a clear decrease in overall carrier density (as opposed to a strong increase in scattering rate).

Low-temperature magnetoresistance measurements (see Supplemental Information) do not show any Shubnikov-de Haas (SdH) oscillations in the non-metallic samples at 2 K, indicating that the bulk carriers are at a low enough concentration to be in the quantum limit at moderate fields, but they were observed in samples V and H. The presence of a distinct minimum in resistivity near 30 K in all samples follows the concentration-independent trend reported previously [12, 20], and is consistent with a phonon-dependent scattering feature [38] that only changes with lattice density such as induced by external pressure, which readily pushes the minimum up in temperature [39].

Hall effect measurements are presented for two representative samples, V and A in Figs. 2(a) and 2(b). As shown, the Hall resistivities (ρₓᵧ) exhibit very unusual behavior with respect to magnetic field and temperature, especially in light of the well-characterized, simple single-band structure of Bi₂Se₃ [12]. Sample V, a low-carrier density sample that exhibits metallic behavior (c.f. Fig. 1) shows a small but pronounced curvature in ρₓᵧ(H) indicative of the presence of more than one type of charge carrier. Sample A, with pronounced non-metallic behavior in ρ(T), exhibits much more significant nonlinearity in ρₓᵧ(H) and even exhibits a hole-like response as temperature is raised.

A two-carrier Drude model was used to fit the data, assuming two carriers of the same sign (electron-like) for sample V and two with different sign (one electron- and one hole-like) carriers for sample A, respectively. Fits of ρₓᵧ(H) to this model (see Supplementary Information for details), shown as the solid lines in Figs. 2(a) and b), are in good agreement with the data especially at higher fields and temperatures. Together with self-consistent fits to low-field (≤ 1 T) longitudinal magnetoresistance (see SI), we reach a best match for the four physical parameters for the non-metallic samples.

The extracted mobility μ and carrier concentration n values for each carrier type are shown in Figs. 2c)-f) for comparison. The most striking result is the clear evidence of two carrier types, and moreover, evidence for two carriers with opposite signs in select samples. Samples of Bi₂Se₃ with p-type carriers have been previously reported [18], but the recent extensive set of measurements [12, 40–47] studying the electronic structure of Bi₂Se₃ have verified that its band structure is simplistic and includes only one bulk conduction and valence band together with Dirac surface states that cross the insulating gap. Therefore the most likely origin of the two carrier types is from bulk- and surface-derived bands. For two electron-like carriers (as for sample V), contributions from bulk and surface bands are understandable but one must also consider other causes, such as spin-split bulk bands [46, 47] and trapped quantum well states due to downward band bending at the surface of the crystal [15, 50]. However, the observation of hole-like carriers uniquely rules out such situations and allows for only one explanation: upward band bending.

While the direction of the band bending at the surface of Bi₂Se₃ is almost universally reported to be downward, such studies have been performed either on thin film samples or samples with significantly higher carrier concentrations than the nonmetallic samples being discussed here. However, one study of low carrier concentration samples did observe upward band bending [41]. A plausible explanation for this is that the presence of excess selenium in the growth process induces upward band bending at the surface, most likely due to interactions with elemental selenium at the surface. Assuming upward band bending, with chemical potential E_F located at the bottom of the bulk conduction band and crossing the Dirac cone at the surface, the band bend-
FIG. 2: Hall effect data and analysis of single-crystal Bi$_2$Se$_3$ obtained for two characteristic samples V and A, shown in panels a)-c) and d)-f), respectively. Transverse Hall resistance is presented in panels a) and d), with Drude model fits (see text) shown as solid lines. Panels b) and e) present the carrier densities extracted from the two-carrier analysis, and panels c) and f) present the resultant mobilities for each carrier type. The presence of two carrier contributions is easily discerned by the nonlinear behavior of $\rho_{xy}(H)$, in particular for sample A, which presents a crossover from electron- to hole-dominated conduction as a function of temperature. As described in the text, the two carrier types are ascribed to bulk and surface state carriers present in each sample, with hole-like conduction necessarily originating from surface states in sample A.

At low temperatures, $n_e$ in sample A is found to be higher than both concentrations found for sample V, which is unexpected. The extremely low electron mobility of sample A, shown in Fig. 2d), accounts for the lack of oscillations in its magnetoresistance, which should be observable in our field range given a carrier concentration $n = 4.3 \times 10^{17}$ cm$^{-3}$. The high mobilities of the minor bands in both samples are what account for their signatures in the Hall curves. The fact that the mobilities of the lower carrier bands are as large as 8,000 cm$^2$/Vs is in line with the theoretical assumption that topologically protected surface conduction suffers less from scattering, but yet is very surprising given the extensive efforts to increase mobilities of surface carriers observed in MBE-grown thin-films with atomically sharp epitaxial interfaces. Thus, we find that our achievement of more insulating-like behavior in Bi$_2$Se$_3$ is not a simple matter of lowering the electron concentration below a certain point, but also lowering the mobility of the bulk electrons as well as increasing the contribution of positive carriers, through concentration and higher mobilities.

Using the estimated carrier concentrations, we calculate the 2D and 3D Fermi momenta $k_F$ for each sample. Using the obtained $k_F$ values and the measured ARPES band structure, we map the calculated $E_F$ energies for both bulk and surface states onto the measured bulk and surface band dispersions in Fig. 3. As expected, the bulk $E_F$ values for all samples lie at the bottom of the bulk conduction band. From this and previous studies it seems that the bulk $E_F$ is strongly pinned to either the conduction or valence band and cannot be pushed into the gap for bulk samples by growth techniques alone. The surface $E_F$ values are distributed over a wider range, however the nonmetallic sample values lie within the range of the Dirac point where charge pudd-
FIG. 3: (a) Electronic band structure of Bi₂Se₃ obtained from photoemission data [51], showing the positioning of bulk (dashed lines) and surface (dotted lines) chemical potential values \( E_F \) extracted from two-carrier analysis of data for samples A and V (see text). Panel b) presents a schematic of the difference between downward and upward band bending near the surface, providing an explanation for the positioning of surface chemical potentials of samples V and A near the Dirac point, consistent with an upward band bending picture.

The analysis of SdH oscillations observable in higher carrier density samples allows for an independent check of our analysis. Samples V and H both exhibit SdH oscillations as usual for moderately doped samples [26], but the latter sample exhibits a rare case of two oscillatory components as clearly seen in the beating modulation presented in Fig. 3b). Fourier transform analysis confirms two oscillation frequencies of 85 T and 95 T, corresponding to 3D carrier densities of \( 4.4 \times 10^{18} \text{ cm}^{-2} \) and \( 5.3 \times 10^{18} \text{ cm}^{-2} \), respectively, matching the concentrations extracted from Hall data shown in Fig. 3a).

Applying the standard Lifschitz-Kosevich formalism with an assumed typical effective mass of \( 0.1m_e \) [26], we are able to successfully model the oscillations and perform a full Dingle-Berry analysis, yielding Dingle temperatures as well as Berry’s phase information for both samples (see Supplemental Information for fit results). From the Dingle analysis, carrier mobilities also compare favorably between SdH analysis and Drude transport fit results. More surprising, the SdH analysis yields Berry’s phases for the two oscillatory components that are offset by approximately \( \pi \) from one another, suggesting that the component with a non-trivial Berry’s phase is a TI surface state. This is extraordinary, considering that quantum oscillations of surface states in Bi₂Se₃ have so far only been observed in very high (pulsed) magnetic fields in samples with enhanced bulk scattering [36]. In our case, the corresponding mobility is much enhanced for the component with non-trivial Berry’s phase, approaching a value of 7,850 cm²/Vs that is remarkably similar to the surface carrier values obtained for sample V above.

Finally, the significant enhancements in measured mobilities of TI surface states in stoichiometric Bi₂Se₃ are surprising in comparison to prior extensive work on this material, but perhaps not unfounded given the unique material preparation technique that yields a band bending direction opposite to that commonly observed. This is confirmed by our observations of changes in the transport data as a function of time (see SI). The suppression
of measured resistivity with air exposure time, in particular in the most insulating-like samples that exhibit hole-type behavior, is consistent with a significant downward shift in the energy bands at the surface, in agreement with previous studies of the electronic structure evolution at the surface of Bi$_2$Se$_3$ [23, 42]. Furthermore, the model of Se buildup at the surface of samples causing upward band bending is supported by findings that the carrier concentrations in samples increase with mechan- 

ical exfoliation [28, 55]. Overall, while true insulating bulk behavior in stoichiometric Bi$_2$Se$_3$ remains difficult to achieve, our observations of greatly enhanced mobilities and ambipolar transport without atomically perfect thin films or fabricated gate structures suggests that engineering of electronic band bending near the surface of crystals via new routes of materials synthesis and preparation promises a new route to optimizing applications of the simplest three-dimensional topological insulator.

Methods

Single crystals of Bi$_2$Se$_3$ were grown using ultrapure (≥99.999%) elemental Bi and Se, using a self-flux technique [26] subject to high gas pressures (further details of the growth procedure are included in the Supplemental Information section). The average crystal size varied from (0.5×1) mm$^2$ to (3×3) mm$^2$. Longitudinal and Hall resistance measurements were performed simultaneously on all samples using a six-wire configuration with two voltage contacts in standard longitudinal configuration and two voltage contacts in a transverse (Hall) configuration, both sharing the same current contacts. All samples were measured in a commercial cryostat from temperatures of 2 K to 300 K and magnetic fields up to ±14 T.

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* Electronic address: paglione@umd.edu

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