Evidence of the two surface states of 
\((\text{Bi}_{0.53}\text{Sb}_{0.47})_2\text{Te}_3\) films grown by van der Waals epitaxy

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The discovery of topological insulators (TIs) has led to numerous exciting opportunities for studying topological states of quantum physics and for exploring spintronic applications due to the new physics arising from their robust metallic surface states. Here, we report the high-quality topological insulator \((\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Te}_3\) thin films using a single van der Waals GaSe buffer layer. As a result, ultra-low surface carrier density of \(1.3 \times 10^{12} \text{ cm}^{-2}\) and a high Hall mobility of \(3100 \text{ cm}^2/\text{Vs}\) have been achieved for \((\text{Bi}_{0.53}\text{Sb}_{0.47})_2\text{Te}_3\).

T he discovery of two and three dimensional topological insulators (TIs) has generated strong activities in the condensed matter physics community1–5. Due to their Dirac-cone-like surface states and their relatively large bulk band gap, most research of 3D TIs has been based on \(\text{Bi}_2\text{Se}_3\) and \(\text{Bi}_2\text{Te}_3\)5–11. Despite the progress made to date, limited success has been achieved in reducing defects which causes high bulk conduction, overwhelming the surface charge transport. Only very recently, the research on ternary compound TIs, such as \(\text{BiTe}_2\text{Se}, \text{BiSe}_2\text{Te}, (\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Te}_3\) and \((\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Se}_3\)12–17, has demonstrated enhanced and tunable Dirac surface over bulk conduction. Among them, ternary compound of \((\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Te}_3\) is particularly interesting, because it reaches a record low 2D carrier density of \(2 \times 10^{11} \text{ cm}^{-2}\) in a 6 nm thin film15. And this compound with Cr-doping18 is also responsible for the newly demonstrated quantum anomalous Hall (QAH) effect.

Here, we report the use of a single GaSe van der Waals buffer layer on GaAs (111)B substrate to improve the growth of \((\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Te}_3\). The transport measurements show a clear ambipolar gating effect14 with top gate biases for all composition \(x\), and a high Hall mobility of \(3100 \text{ cm}^2/\text{Vs}\) from the surface electrons is observed. Shubnikov-de Haas (SdH) oscillations associated with the top and bottom surface states can also be observed and distinguished by the top gate biases. The results suggest that the van der Waals gap between the GaSe and \((\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Te}_3\) made it possible to observe the transport properties of the bottom Dirac Fermions of \((\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Te}_3\), and to improve the overall film quality.

Results

Cross-sectional TEM and EDX of \((\text{Bi}_{0.53}\text{Sb}_{0.47})_2\text{Te}_3\). For \((\text{Bi}_{x}\text{Sb}_{1-x})_2\text{Te}_3\) illustrated in Figure 1a, we first show the cross section high resolution TEM in Figure 1b. The quintuple layers (QLs) of TI films are clearly revealed on top of the GaAs substrate. Within each QL, five atomic layers are observed. A slightly darker gap represents the van der Waals gaps between TI quintuple layers, marked by the dashed blue lines in Figure 1b. We also notice there is a similar gap between the TI film and the substrate, which is consistent with the van der Waals epitaxy growth mode19,20. At the interface, the top atomic layer shows slightly brighter dots, compared with the rest of GaAs substrate, implying the presence of other heavier atoms. This is probably due to the fact that the top layer of As were substituted by Se during the de-oxidization annealing under Se-rich environment; a more solid evidence will be given by the space resolved EDX in Figure 1c–h. Since GaSe is a quadruple layered structure, with Se-Ga-Ga-Se alternative atomic layers along the c-axis21, and the coupling between two quadruple layers is



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SUBJECT AREAS:
CONDENSEDMATTER
PHYSICS
ELECTRONIC DEVICES

Received
19 September 2013
Accepted
12 November 2013
Published
3 December 2013

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SCIENTIFIC REPORTS | 3 : 3406 | DOI: 10.1038/srep03406
predominantly of the van der Waals type. After the formation of GaSe buffer layer, the top most Se atoms have no dangling bands, thus promoting the van der Waals epitaxial growth of TI films.

To confirm the TI-GaSe-GaAs configuration (as shown in Figure 1a), energy dispersive X-ray spectroscopy (EDX) mapping in the Cs-corrected STEM (FEI TITAN) has been performed in this cross-section area. The distribution maps of each individual element are shown in Figure 1c–g. All the elements display a distinct distribution pattern: Bi, Sb and Te are located on the top half of the map; Se is located at the interface region; Ga and As are located in the bottom half. Specifically Figure 1h exhibits the average intensity profile for each element in Figure 1b; we can clearly see a sharp Se peak (red circles) at the film/substrate interface and Ga (blue dots) also extends to the interface area. Hence, this supports the former statement that a GaSe buffer is developed at the interface. We also notice that Bi (green triangles) and Te (blue squares) exhibit oscillating intensities with opposite phases. Bi demonstrates a peak in the center of TI layers (green line in Figure 1h), while Te shows a dip (blue line in Figure 1h), which could be understood as the following: for each QL of Te-Bi(Sb)-Te-Bi(Sb)-Te (Fig. 1b), Bi is accumulated in the center, while Te along the edges. The high crystal quality of the TI films also demonstrates exceptional electric properties as we will show below.

**Ambipolar conduction effect of (Bi0.53Sb0.47)2Te3.** (BiSb1−x)2Te3 is a non-stoichiometric alloy with Bi atoms randomly replaced by Sb, as illustrated in Figure 1a. We have studied the electronic properties of the thin films with various Bi concentration x, ranging from 0.32 to 0.77. Ambipolar effects have been observed for all the samples under gate biases (Supplementary Figure S2). At V_G = 0 V, the samples demonstrate a transition from p-type to n-type as the Bi concentration increases. At x = 0.53, the lowest bulk carrier concentration is achieved with high carrier mobility.

For the 10 QL (Bi0.53Sb0.47)2Te3 sample, the longitudinal resistance R_xx shows a semiconductor like temperature dependent relation with an activation energy of ~20 meV, estimated from the high temperature Arrhenius plot (supplementary Figures S4 inset), suggesting an impurity band positioned about 20 meV above the bulk valance band, similar to the reported value in bulk Bi2Te2Se.

R_xx saturates to a constant value down to 0.3 K (supplementary Figure S3), implying a temperature independent surface conductance.

At 0.3 K, typical gate voltage (V_G) dependence of the longitudinal resistance (R_xx) exhibits a broad peak (solid arrow in Figure 2a). It is about a few times greater than the resistance at large V_G far from the peak position. The high field (6 T) Hall coefficients, R_H, also reverse signs from negative to positive (hollow arrow in Figure 2b). This ambipolar field effect can be explained by a systematical change of the dominated conduction from the top and bottom surface electrons to bulk holes, which are confirmed from the Hall data as will be discussed later.

To explain transport data, we divide the range of top gate bias into three regions. In regions I (V_G < −3 V) and III (V_G > 4 V) (Figure 2a), bulk holes and surface electrons are the dominant carriers, respectively. The R_xx shows a linear dependence of the gate voltage, as indicated by the dashed lines in Figures 2a. The electron density reaches the lowest value at V_G = 4 V and furthermore, we also observe a high Hall mobility of 3100 cm²/Vs. In the mixed region II (−3 V < V_G < 4 V), the total conductance crosses from top and bottom surface electrons (n_top + n_bot) to bulk holes and

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**Figure 1** Cross-sectional TEM and EDX of (Bi0.53Sb0.47)2Te3. (a) A schematic diagram of the atomic layer structures of the TI film, interface and substrate. (b) High resolution TEM image exhibits QL of (Bi0.53Sb0.47)2Te3 film, GaAs substrate and the atomically sharp interface. Each QL is marked by the blue lines. A single GaSe layer is marked by the orange lines. (c–g) Distribution maps of individual elements: Bi/Sb (c), Te (d), Se (e), Ga (f) and As (g). (h) Average intensity profile of (b). The sharp peak of Se (red circles) confirms the presence of GaSe single layer.
bottom surface electrons \((p_{\text{bulk}} + n_{\text{bot}})\). As \(V_G\) is decreased from region III, \(n_{\text{top}}\) decreases and \(R_{\text{xx}}\) increases accordingly; upon further decrease of \(V_G\), \(p_{\text{bulk}}\) increases; hence the conductance of bulk holes increases, thus \(R_{\text{xx}}\) reaches a peak. The change of conductance from electrons to holes is also evidenced as \(R_{\text{xx}}\) changes sign. This is accompanied by the dramatic decrease of the Hall mobility due to the much lower mobility of bulk holes. It is worth noting that the maximum in \(R_{\text{xx}}\) does not completely coincide with that of the \(R_{\text{HH}}\) crossing zero\(^{14}\), nor with the \(R_{\text{HH}}\) maximum\(^{25}\). The small deviation may be attributed to the coexistence of three carriers conducting channels and the interplay of different carrier densities and their mobilities under different gate voltages.

The magnetoresistance \((MR = R_{\text{xx}}(B)/R_{\text{xx}}(0) - 1)\) also exhibits a strong gate-voltage dependence. It has a single peak of 2.6 at \(V_G = 3\) V, coincident with the \(R_{\text{xx}}\) maximum. A linear MR has also been observed in the bulk hole dominated region at high magnetic field, as indicated by dashed red lines in the Supplementary Figure S5, similar to other bulk dominated TI samples\(^{1,2,6-27}\). On the contrary, in the surface electron dominated region, linear MR is not observed.

At low magnetic field, sharp cusps of the weak antilocalization (WAL) effect can be seen. This weak antilocalization (WAL) effect is a signature of topological surface states associated with the helical states\(^{28-33}\). According to the Hikami-Larkin-Nagaoka (HLN) theory\(^{34}\), it can be described as

\[
\Delta \sigma = \frac{\alpha e^2}{2\pi h} \left[ \ln \left( \frac{h}{4eBl_p} \right) + \psi \left( \frac{1}{2} + \frac{h}{4eBl_p} \right) \right],
\]

where \(\Delta \sigma\) represents magnetoconductivity, \(l_p\) is the phase coherence length, \(\psi\) is the digamma function, and \(\alpha\) equals \(\frac{1}{2}\) for a single coherent channel. For multiple independent parallel channels, \(\alpha\) is equal to \(n \times \frac{1}{2}\) and \(n\) is the number of conducting channels\(^{27}\). In our analysis, \(\alpha\) shows a clear gate voltage dependence, as shown in Figure 2e.

A striking feature is that \(\alpha\) is close to 1 in region I, suggesting that there coexist two separate conductance channels (bulk holes and bottom surface electrons). In the transition region II, \(\alpha\) increases to 1.5 around the \(R_{\text{xx}}\) maximum, implying that bulk hole, top and bottom surface electrons constitute three separate channels. In region III, \(\alpha\) decreases to around 1.3 suggesting the system has mostly electrons from top and bottom surfaces with some mixed bulk holes. We have noticed there are some discrepancies between our results and other people, who have an alpha value changes between 0.5 to 1 from p-type to n-type region, depending on gate voltages\(^{35,36}\). We believe this is because in their films, the Fermi level of the far side surface (top surface) is buried inside the bulk valence band, which will not contribute too much to the total conduction. On the contrary, in our films the Fermi level of the far side surface (bottom surface) is pinned within the bulk band gap, thus it will contribute significantly to the conductance. Hence we have one more conducting channel compared with them. So \(\alpha\) changes from 1 to 1.5 as gate voltage changes.

Quantum oscillations from top and bottom surface states. At 0.3 K, oscillations can be seen in the longitudinal resistance after substrate a smooth background, as shown in the supplementary figure S6, at various gate voltages. To emphasize the gate dependent oscillations and to eliminate the MR background, we have used the second derivative of \(R_{\text{xx}}\) \((d^2R_{\text{xx}}/dB^2)\) in Figure 3a. The first thing to notice is that there are gate voltage dependent peaks as accentuated by the white dashed lines. These peaks (valleys) originate from the
Figure 3 | Shubinkov-de Haas oscillations from the top and bottom surface states. (a) $dR_{xx}/dB$ as a function of $1/B$ and $V_G$. Both gate dependent and independent peaks are observed. The features which change with $V_G$ originate from the formation of the Landau levels of Dirac fermions on the top surface states (white dashed lines, the Landau levels 2 to 5 are marked). The $V_G$-independent features come from the Landau levels of the bottom surface states (black dashed lines). (b) Landau fan diagram of the peaks. The peaks of the top surface states (solid symbols) show systematic changes depending on the gate voltages, while that of the bottom surface states are almost constant. Inset: The intercept $\gamma$ as a function of gate voltages. The black line indicates $\gamma = 0.5$. (c) The carrier density of the top (circles) and bottom (triangle) surface states as a function of Fermi energy $E_F$ extracted from the corresponding SdH oscillations for various gate voltages. A quadratic relationship is shown.
Methods

Growth of (Bi_{0.53}Sb_{0.47})_{2}Te_{3} thin films. The GaAs (111)B substrates have been cleaned by acetone with ultrasonic for 10 minutes before loaded into the growth chamber. Then the substrates were annealed to 580 °C and cooled to growth temperature, under Se rich environment. During this anneal procedure a strained GaSe single buffer layer was formed on the surface. The film growth was performed at about 200 °C, with Bi, Sb, and Te shutters opened at the same time. The flux ratio of Bi:Se:Te was about 1:4:20 for the compound of (Bi_{0.53}Sb_{0.47})_{2}Te_{3}, ex-situ estimated by EDX. The growth mode was via layer-by-layer, monitored by the RHEED intensity oscillations (supplementary Figure S1), through which accurate film thickness could be achieved. There was a deposition of 2 nm Al immediately after the growth of Ti film in MBE chamber to protect the film for environmental doping.

Device fabrication. The MBE-grown Ti thin films were first patterned into a microlens array, followed by photolithography and a subsequent CHF_{3} dry-etching of 15 s. Hall bar contacts were defined by photolithography and followed by e-beam evaporation of 10 nm Titanium (Ti) and 100 nm Gold (Au). A 15 nm thick Al_{2}O_{3} dielectric layer was conformally deposited by ALD at 250 °C to serve as the high-k gate dielectric. Another step of photolithography was needed to open window, and dry etching was carried out to etch the Al_{2}O_{3} in the contact area with subsequent dip in 5% diluted HF. Finally, the top-gate electrode and Hall channel contacts were defined and followed by metal deposition of Ti/Au (10 nm/100 nm).

Electrical measurements. The devices were cooled down using a He3 insert at Cell 8 and 12 at the National High Magnetic Field Laboratory at Florida. The DC magnetic field used was up to 35 T and the base temperature was 0.3 K. The electrical characteristics were measured using a lock-in technique (magnetotransport) with a constant AC current of 0.1 μA at 13 Hz plus a 5 μA DC bias current by Keithley 6221. The gate bias was provided by a Keithley 2401.

TEM characterizations. The observations of the atomic structure and atomic EDX mapping at the interface between (Bi_{0.53}Sb_{0.47})_{2}Te_{3} and GaAs were conducted using a FEI TITAN Cs-corrected ChemiSTEM, operating at 200 kV. This instrument incorporates the spherical aberration corrector and ChemiSTEM technology, and can achieve the resolution to 0.8 nm. The cross-sectional samples for TEM were prepared by a dual beam by gallium ion milling (Quanta 3D, FEG, FEI). All parameters were carefully optimized to avoid the gallium injection.

Acknowledgments

The authors would like to thank the support from Defense Advanced Research Projects Agency (DARPA) with grants N66001-12-1-4034 and N66001-11-1-4105. K.W. also acknowledges the support of the Raytheon endowed chair professorship. F.X. would like to acknowledge financial supports from the National Young 1000 Talents Plan and Pu Jiang Talent Plan in Shanghai. Y.W. acknowledges support from Natural Science Foundation of China (11174244) and Zhejiang Provincial Natural Science Foundation of China (LR12A04002) and National Young 1000 Talents Plan.

Author contributions

L.H. and K.W. conceived the idea and supervised the overall research. L.H. and X.K. synthesized the thin films. M.L., T.N. and W.J. fabricated the devices. L.H., X.K. and E.S.C.
carried out low-temperature transport measurements. Y.J. and Y.W. performed the structural analysis. L.H., Y.F. and F.X. contributed to the analysis. L.H., Y.F., F.X. and K.W. wrote the paper with help from all other co-authors. L.H., X.K., and M.L. contributed equally to this work.

Additional information
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: He, L. et al. Evidence of the two surface states of (Bi0.53Sb0.47)2Te3 films grown by van der Waals epitaxy. Sci. Rep. 3, 3406; DOI:10.1038/srep03406 (2013).