Crystal growth and anomalous transport properties of $Cu_xBi_2Se_3$

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Topological insulators (TIs) have received considerable attention due to their potential to offer new platforms for the realization of novel states of quantum maters. TIs are characterized by their fully insulating gap in the bulk but necessarily gapless edge or surface states protected by time-reversal symmetry. Recently, the three-dimensional (3D) TIs were theoretically predicted and discovered by experiments, including binary $Bi_{1-x}Sb_x$ alloys, Bi_2Se_3, Bi_2Te_3, Sb_2Se_3 and Sb_2Te_3 compounds [1]. It was found that the 3D Bi_2Se_3 topological insulator has the simplest Dirac cone surface spectrum and the largest band gap, of ~0.3 eV, which indicates a true topological insulating behavior at room temperature and greatly increases potential applications in the future.

Superconductivity at T_c=3.8 K was induced in the $Cu_xBi_2Se_3$ compound by Cu intercalating the van der Waals gaps between the Bi_2Se_3 layers [2]. Because of this discovery, the compound was suggested to be one of the most promising candidates for realizing topological superconductivity, which has a full pairing gap in the bulk and gapless surface Andreev bound states. Recently, the existence of topological superconductivity in the $Cu_xBi_2Se_3$ compound has been investigated by transport, point-contact spectroscopy and angle resolved photoemission spectroscopy. Furthermore, the novel spin-triplet pairing with odd parity induced by strong spin-orbit coupling was proposed for the $Cu_xBi_2Se_3$ superconductor in both experimental and theoretical studies [3, 4].

In this study, single crystals of $Cu_xBi_2Se_3$ with various Cu doping contents were grown using a modified Bridgeman method. Electric transport and magnetic susceptibility measurements were performed on the samples. We found that the superconducting samples share a common anomalous temperature-dependent magnetoresistance feature in which a magnetic-field-tuned “crossover behavior” was observed. The results of IV (current-voltage) measurement were demonstrated to interpret the observed anomalous transport properties.

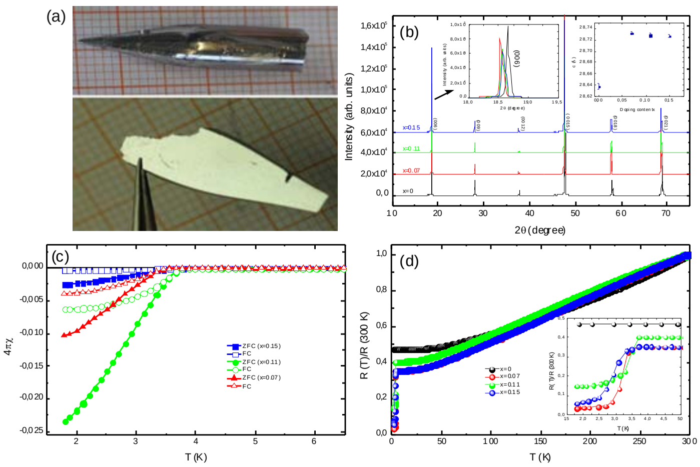

Figure 1: (a) The upper panel: Typical as-grown single crystal of $Cu_{0.11}Bi_2Se_3$, lower panel: as-cleaved crystal. (b) X-ray diffraction patterns show the (0 0 *l*) reflections. Left inset displays the shifting of the *(0 0 6)* patterns. Right inset is the Cu doping dependence of the *c* lattice parameters. (c) The temperature dependence of magnetic susceptibility with magnetic field H=10 Oe parallel to the *ab* plane. Both zero field (ZFC) and field cooled (FC) curves were recorded. (d) The temperature dependence of resistivity for $Cu_xBi_2Se_3$ with x=0, 0.07, 0.11, 0.15. The resistance is normalized to the value at 300 K.

The samples were prepared using high purity Cu (5N), Bi (5N), and Se (5N) lumps in the nominal composition $Cu_xBi_2Se_3$ (x=0, 0.12, 0.15 and 0.18) and sealed in an evacuated quartz ampoule. The ampoule was heated up to 1148 K for 48 h in a vertical tube furnace and then cooled down at a rate of 2.5 K/h to 833 K and maintained at that temperature for 24 h before quenching in cold water. The phase purity of obtained single crystals was examined by X-ray diffraction (XRD) measurements using a PHILIPS PW3710 diffractometer with Cu K_α radiation. The composition was determined by energy dispersive X-ray spectroscopy (EDX) in a Tescan Vega TS-5130MM scanning electron microscope (SEM), equipped with a NORRAN System 7 UltraDry Detector. In-plane resistivity measurements were performed on a physical property measurement system (PPMS-9, Quantum

Design) using the standard four wires with silver paste for the contacts. DC magnetic susceptibility was measured with a SQUID-VSM magnetometer (Quantum Design).

Typical single crystals of Cu-doped Bi_2Se_3 were obtained with the modified Bridgeman method, as shown in Fig. 1(a). The Cu content of the $Cu_xBi_2Se_3$ single crystals is determined to be x=0, 0.07, 0.11 and 0.15, respectively, less than the nominal compositions. The orientation of the large crystal surface was characterized via (*0 0 l*) reflections by XRD, as shown in Fig 1(b). The reflections shift towards the lower angle region with increasing Cu doping as seen in left inset of Fig. 1 (b), indicating that Cu atoms were intercalated into von der Waals gap between the Bi-Se layers. The *c*-axes were enlarged by the Cu doping. The lattice parameters are 28.638, 28.732, 28.728, and 28.726 Å for x=0, 0.07, 0.11 and 0.15, estimated using higher angle diffractions (*0 0 15*), (*0 0 18*) and (*0 0 21*). A significant increase of the *c*-axis by doping was observed. The doping dependence of the *c* lattice parameters shows a non-linear relationship. The fact is that the larger *c* expanded by Cu intercalation between Bi-Se layers, while smaller *c* caused by substitution for Bi accommodated in Bi-sites, due to the ionic radius of Cu^{2+} (57 Å) < Bi^{3+} (117 Å). The largest *c*-axis was estimated for x=0.07, shrinking with higher doping, as plotted in the right inset of Fig. 1(b). This result can be attributed to the Cu-atoms partly intercalated in Bi-Se layers and partly substituted for Bi-sites. The temperature dependence of magnetic susceptibility for these samples is plotted in Fig.1(c). The superconducting shield fraction was observed to be below 2.5%, indicating non-bulk superconductivity in the samples. Figure 1(d) shows the temperature dependence of resistivity. The highest $T_{c,onset}$~3.7 K is measured for $Cu_{0.11}Bi_2Se_3$ and zero resistance is not observed, consistent with magnetic susceptibility measurements.

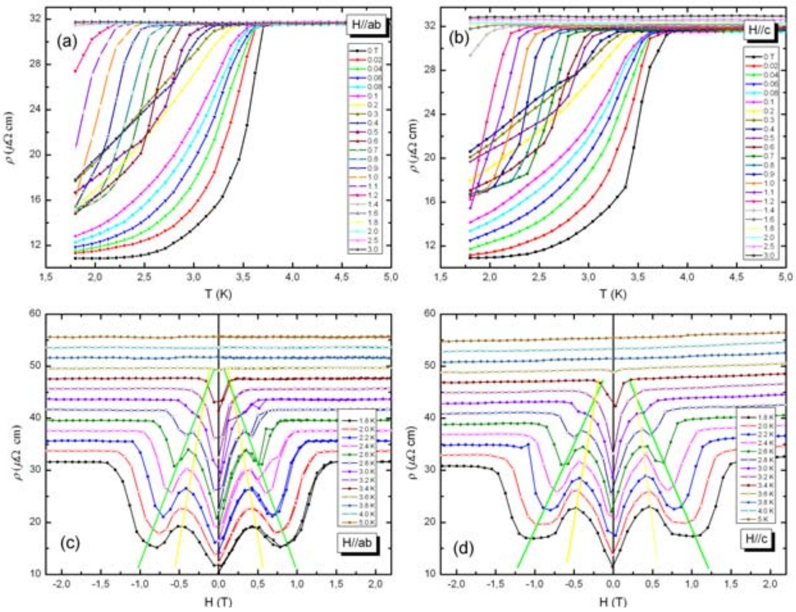

Figure 2: Magnetoresistance measurements of the $Cu_{0.11}Bi_2Se_3$ single crystal. The temperature dependence of resistivity under various magnetic fields at T=1.8 K with the configurations of H//ab (a) and H//c (b), respectively. The field dependence of resistivity at various temperatures with H//*ab* (c) and H//*c* (d), respectively. The green and yellow lines are guides to the eye.

The temperature dependence of resistivity was investigated under various magnetic fields with configurations of H//*ab* and H//*c* for the $Cu_{0.11}Bi_2Se_3$ single crystal, as shown in Figs 2(a) and (b), respectively. With increasing field, the superconducting transition temperature T_c was gradually suppressed and the transition width was broadened. It is noticed that an abrupt change in the superconducting transition occurs below the critical field H_{crt}~0.3 T, i.e., the crossover of resistivity curves was observed. This anomalous transport feature is different from the bulk superconducting $Cu_{0.29}Bi_2Se_3$ single crystal, which showed the "parallel transition" behavior with the increasing of fields, as reported by Kriener. et. al. [5]. In order to further investigate this feature, the magnetic field dependence of resistivity was measured under various temperatures and the results are plotted in Figs. 2(c) and (d), respectively. Intriguingly, there are apparent humps and valleys systemically appearing with positive and negative fields in the superconducting temperature region and more pronounced at the low temperature of 1.8 K. The humps and valleys correspond to the resistivity crossover curves. The results are reproducible in various Cu doping levels in our superconducting samples. When the temperature is higher than T~3.4 K this feature is no longer observed. For superconductivity at a non-zero resistance transition, it could be interpreted in one mesoscopic system with superconducting islands separated by the normal state region in an inhomogeneous compound. Nevertheless, this result suggests that superconducting Cooper pairs might play a key role in the resistivity crossover behavior.

In order to further understand the observed anomalous transport phenomenon, IV measurements were performed to detect a possible Josephson-like effect in the $Cu_{0.11}Bi_2Se_3$ single crystal. The results are plotted in Figs. 3(a-d). As seen in Fig. 3(a), the shape of the IV curve is similar to that of the Josephson junction [6], whereas a non-zero dynamic resistance is observed for each curve in the superconducting state (<3.7 K). This indicates that the dissipation of a Josephson supercurrent might occur in the $Cu_{0.11}Bi_2Se_3$ sample. This agrees with the non-zero resistance transition in Fig. 1(d). As the temperature increases, the critical current I_c decreases gradually and eventually disappears when the temperature is higher than 3.7 K, as shown in Fig. 3(b). Figure 3(c) shows the IV curves measured under different external fields and an apparent hysteretic behavior is observed between the 1^{st} and 2^{nd} cycle. This hysteretic behavior could be the result of phase instability, which typically appears in the capacitively and resistively shunted Josephson junction or due to the heating effect. The slope of each IV curve is different, i.e., has different resistivity, indicating that the differential resistivity, as defined by *dV/dI*, could be tuned by the external field. The field-tuned fluctuations of dynamic resistance correspond to the resistivity crossover behavior, supported by the data in Figs. 2(a-d). The magnetic-field dependence of critical current I_c was performed by two cycles (1^{st} and 2^{nd}) at T=1.8 K, as shown in Fig. 3(d). An apparent kink occurs at H~0.3 T for both cycles and non-linear dependence is observed between the critical current and magnetic-field. This feature might be related to the mesoscopic superconductivity in which sample contains numerous Josephson-like junctions with the existing of superconducting Cooper pairs. The IV results suggest an important role of superconducting Cooper pairs tunneling between the normal state region and superconducting islands, as resulted in the observed feature of anomalous transport properties.

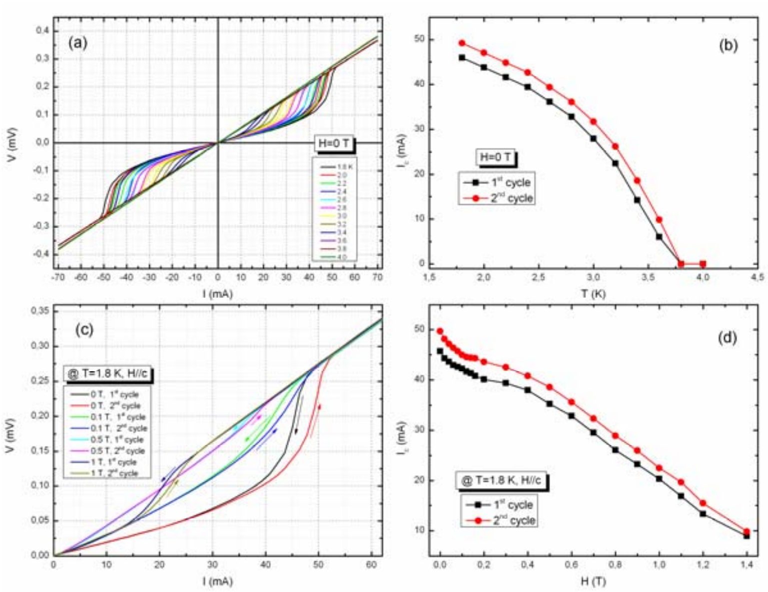

Figure 3: (a) The IV curves of the $Cu_{0.11}Bi_2Se_3$ sample obtained at various temperatures. (b) The temperature dependence of critical current I_c, and two branches of I_c, were plotted. (c) The IV curves obtained under the fields of H=0 T, 0.1 T, 0.5 T, 1 T at T=1.8 K, showing the apparent hysteresis behavior between two cycles, respectively. (d) The magnetic field dependence of critical current I_c at T=1.8 K, and two sets of I_c were plotted.

In summary, we have prepared single crystals of $Cu_xBi_2Se_3$ (x=0, 0.07, 0.11, 0.15) using a modified Bridgeman method. The results of transport measurements indicate that the superconducting samples share a common anomalous temperature-dependent magnetoresistance feature, in which a magnetic-field-tuned "crossover behavior" was observed. The crossover behavior could be interpreted with IV results, assumed the superconducting Cooper pairs tunneling between the normal state region and superconducting islands, as resulted in the anomalous transport phenomenon. However, more experimental and theoretical work have to be performed to elucidate the intrinsic physical origin of this anomalous transport behavior.

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