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Electron delocalization and relaxation behavior in Cu-doped Bi₂Se₃ films

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Cu_xBi₂Se₃ is known for superconductivity due to Cu intercalation in the van der Waals gaps between the quintuple layers of Bi₂Se₃ at $x > 0.10$. Here we report the synthesis and transport properties of Cu-doped Cu_xBi₂Se₃ films prepared by chemical-vapor-deposition (CVD) method with $0.11 \geq x \geq 0$. It is found that the insulating-like temperature-dependent resistivity of polycrystalline Cu_xBi₂Se₃ films exhibits a marked metallic down-turn and an increase of carrier concentration below ~37K. There is also a time-dependent slow relaxation behavior in the resistance at low temperature. These effects might be related to the strong hybridization between Cu⁺ and Cu²⁺ conduction bands from the intercalated Cu⁺ and substituted Cu²⁺ sites in Bi₂Se₃ films. The findings here have important implications for the understanding and development of doping induced superconductivity in topological insulators.

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I. INTRODUCTION

A topological insulator is a material that has a bulk electronic band gap and gapless edge states for charges and spins, which are protected by time reversal symmetry [1,2]. Three dimensional (3D) topological insulator Bi_2Se_3 has the simplest Dirac cone surface spectrum and the largest band gap (0.3 eV) [3]. Bulk Bi_2Se_3 has a lot of native defects, including the Se vacancy (V_{Se}) and the Bi antisite (Bi_{Se}), which result in that the bulk carriers from defects are dominant over the surface carriers and give rise to its n -type conductivity [4]. The surface chemical potential and the bulk Fermi level of Bi_2Se_3 can be tuned by chemical doping. By doping Mn [5], Ca [6], Cd [7], or co-doping Sb and Pb [8], the carrier type of Bi_2Se_3 can be tuned from n -type to p -type. Especially in $\text{Cu}_x\text{Bi}_2\text{Se}_3$, Cu not only compensates Bi_2Se_3 native defects and reduces the bulk carrier density [9,10], but also intercalates into the van der Waals gaps between Se layers [11]. Superconductivity has been observed in Bi_2Se_3 by Cu [11] or Sr [12,13] doping, which are promising candidates for topological superconductor (TSC) researches. In $\text{Cu}_x\text{Bi}_2\text{Se}_3$ with $x>0.1$, topological order [14], quantum oscillations (the de Haas–van Alphen effect) [15], quantum anomalous thermal Hall effect [16], spin-rotation symmetry breaking [17] and odd-parity nematic superconductivity [18] have been observed, providing evidence that $\text{Cu}_x\text{Bi}_2\text{Se}_3$ is a TSC and opening up opportunities to realize Majorana fermions. However, there is very limited study on low Cu-doped $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x<0.1$). In $\text{Cu}_x\text{Bi}_2\text{Se}_3$ superconductors where $x>0.1$, Cu primarily intercalates between Se layers [11, 19-21]. The origin of the superconductivity in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ has been studied by many researchers. The tunneling spectrum of $\text{Cu}_{0.2}\text{Bi}_2\text{Se}_3$ shows that the density of states at the Fermi level is fully gapped without any in-gap states, being consistent with the Bardeen-Cooper-Schrieffer theory, which suggests that $\text{Cu}_{0.2}\text{Bi}_2\text{Se}_3$ is a classical s-wave superconductor [22]. This contradicting results might be reconciled by considering the evolution of the Fermi surface with carrier concentration [23] and the Dirac fermion states on the surface [24]. A subtle balance between two competing processes of electron and hole doping from Cu in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ single crystal was reported to be responsible for its superconductivity [21], and the disorder and

inhomogeneity effects in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ film were reported to suppress the superconductivity [25]. It was known that Cu atoms can not only intercalate into the van der Waals gaps as Cu^+ state and donate electrons to Bi_2Se_3 , but also substitute for Bi as Cu^{2+} state and act as an acceptor [26-28]. Recently, angle-resolved photoemission spectroscopy (ARPES) results indicated that when Cu concentration is at low level ($x < 0.05$), Cu predominantly intercalates into the van der Waals gap, while with further doping, Cu will replace Bi, causing the saturation of the carrier concentration [21]. Similar results were also obtained earlier by the reflectivity in infrared spectral region [26]. In addition to the two competing carrier doping effects and the disorder effect, the interaction of intercalated Cu^+ and substituted Cu^{2+} also plays an important role in the electrical transport property. Superconducting-like behavior has been observed in the layered chalcogenides CuS and CuSe when temperature is below 40 K due to a strong hybridization between Cu^+ and Cu^{2+} [29,30]. It has been noted that the conduction bands between two different site occupations of Cu in CuS take place a strong hybridization at low temperatures, resulting in the charge delocalization between these ions [30]. This behavior of CuS and CuSe is highly supported by two chemical characteristics: two dimensional structure and mixed valence of copper [29]. Bi_2Se_3 has a layered structure consisting of Se(1)–Bi–Se(2)–Bi–Se(1) quintuple layers (QLs), and it is bonded by weak van der Waals force between QLs [31]. It has a rhombohedral crystal structure (space group $D_{3d}^5(\text{R}\bar{3}\text{m})$), with $a = 4.14 \text{ \AA}$ and $c = 28.54 \text{ \AA}$ [25]. It is similar to CuS (or CuSe) crystal structure (space group $\text{P6}_3/\text{mmc}$, layered structure), with $a = 3.7938 \text{ \AA}$ and $c = 16.341 \text{ \AA}$ [32,33]. Therefore, it would be interesting to see that in Cu-doped Bi_2Se_3 , whether a strong hybridization will occur between the intercalated Cu^+ in quintuple layers and the Cu^{2+} substituting for Bi^{3+} at low temperatures.

Here, Cu-doped Bi_2Se_3 polycrystalline thin films were prepared by CVD method. It is found that the resistivity of the films changes from metallic in undoped samples to a non-metallic behavior upon Cu doping, and a resistivity abnormality is observed at 37 K in the films with high Cu concentration, which is independent of the application of

a magnetic field. We show that Cu atoms occupy both intercalated Cu^+ and substituted Cu^{2+} sites in Bi_2Se_3 films by Raman spectroscopy. We suggest that the metallic down-turn in the temperature-dependent resistivity and the carrier concentration increases at 37 K is due to a strong hybridization between the Cu^+ and Cu^{2+} conduction bands and the electron delocalization accompanying it. There is also a time-dependent relaxation behavior in electrical transport at low temperature, which is attributed to the electron delocalization.

II. EXPERIMENTAL

Cu-doped Bi_2Se_3 films were grown by CVD method on semiconductor Si substrates (with a thin amorphous SiO_2 layer on surface) with size of $\sim 1.5 \text{ cm} \times 1.5 \text{ cm}$ in H_2/Ar carrier gas with flow ratio of 10/40 sccm. Briefly, a high-temperature tube furnace (Lindberg Blue M) and a quartz tube of 1 in. diameter were used as the reactor for the synthesis with accurate control of temperature and carrier gas flow rate. 99.99% Bi_2Se_3 powder and 98.5% $\text{C}_{10}\text{H}_{14}\text{CuO}_4$ powder were used as precursor. The $\text{C}_{10}\text{H}_{14}\text{CuO}_4$ powder has a low sublimation and decomposition temperature, and works as a convenient source for Cu vapor. They were placed respectively at a distance of 2 cm and 12-18 cm upstream from the center of the furnace at 520°C . The Cu concentration can be controlled by the distance between the center of furnace and raw material of $\text{C}_{10}\text{H}_{14}\text{CuO}_4$ which determines the source temperature. The growth substrate was placed at a distance of 14-15 cm downstream from the center of the furnace. The pressure was kept at 24-30 Pa for 5 min to deposit the Cu-doped Bi_2Se_3 film. After that, the tube furnace was cooled naturally down to room temperature, and dark gray Cu-doped Bi_2Se_3 film was found on the Si substrates.

The phase structure of the Cu-doped Bi_2Se_3 films was confirmed by x-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu $\text{K}\alpha$ radiation. The analyses on the morphology and composition of sample were performed by field emission scanning electron microscopy (FESEM) and energy dispersive x-ray spectroscopy (EDS or EDX) (JSM 6301F). The site occupancies of Cu atoms in Bi_2Se_3 were checked by Renishaw in Via Raman Spectrometer equipped with a 633 nm excitation laser (17 mW). Transport properties were measured in a physical

property measurement system (PPMS, Quantum Design). Samples were cut into the shape with length about 1 cm and width of 3–4 mm. The resistivity versus temperature measurements were performed using a standard four-probe technique with silver paste as contacts. The Hall resistance versus temperature and magnetic field curves were collected with the Hall bar configuration.

III. RESULTS AND DISCUSSION

The temperature-dependent resistivity (R - T) of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ films were investigated in the temperature range from 300 to 2 K at zero magnetic field. The R - T curves of these four samples with respective $x=0, 0.07, 0.10$ and 0.11 are shown in Fig. 1. The Cu concentrations of all samples are determined by EDS measurements. The undoped Bi_2Se_3 film shows metallic R vs. T (Fig. 1(a)) which is similar to previous report [34-36]. The high temperature behavior of resistivity changes from metallic to a non-metallic insulating-like behavior with Cu doping in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ films, as shown in Fig. 1. However, we found that the resistivity shows a sharp drop at $\sim 37\text{K}$ at Cu concentration $x>0.066$, as shown in Figs. 1(b-d) and Fig. S1 in Ref. [37]. This phenomenon (a sharp decrease in the resistivity) has never been reported in $\text{Cu}_x\text{Bi}_2\text{Se}_3$. More results of other samples with different Cu concentrations are represented as Fig. S1 in the Supplemental Material [37]. The thin films are grown on Si substrate with a thin amorphous SiO_2 layer (about 10 nm by natural oxidation), as shown in Fig. S2. There is the van der Waals force between the thin film and the substrate. **It is indicated that no epitaxial strain exists in these films, so the epitaxial stain does not play a crucial role for the sharp drop in resistivity at $\sim 37\text{ K}$.** And from Fig. S1, we note that the metal-insulator transition temperature is almost the same with x increasing from 0.07 to 0.11. **In order to understand the annealing effect on transport properties of films, the prepared $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x=0.068$ and 0.071) thin films were annealed at 573 K (the temperature that Cu-doped Bi_2Se_3 thin films were deposited on substrates) for 5 hours. The R - T properties of the prepared thin films with and without annealing were measured.** As shown in Fig. 2, we can find that the decreasing amplitudes

$([\rho_{(37K)} - \rho_{(2K)}] / [\rho_{(37K)} - \rho_{(300K)}])$ of two R - T curves before and after annealing do not show much difference, indicating that Cu in prepared $\text{Cu}_x\text{Bi}_2\text{Se}_3$ thin film has a homogeneous distribution.

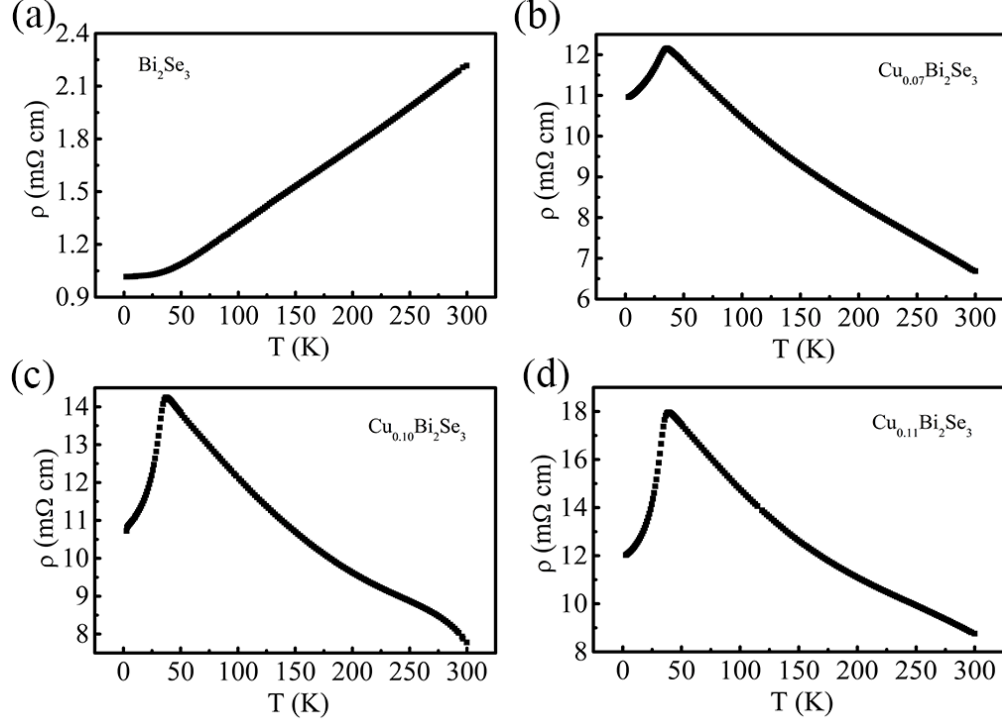


FIG. 1. Resistivity plotted as a function of temperature for four representative $\text{Cu}_x\text{Bi}_2\text{Se}_3$ thin film samples with respective $x=0, 0.07, 0.10, 0.11$, shown as (a), (b), (c) and (d).

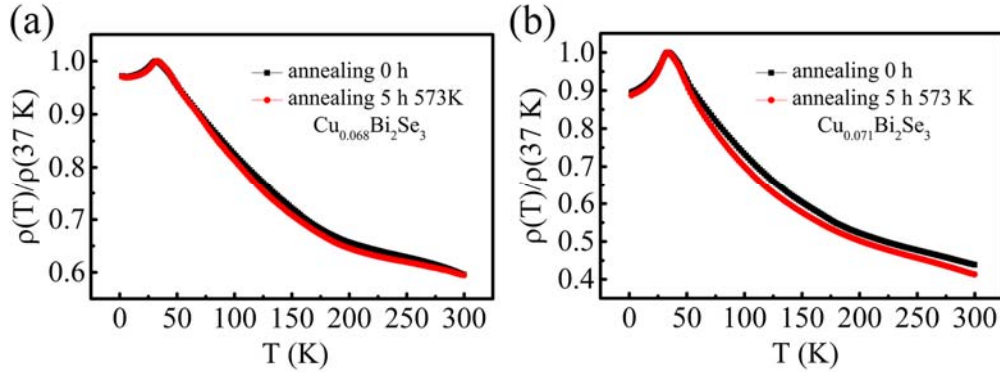


FIG. 2. Temperature dependence of resistivity of (a) $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x=0.068$) and (b) $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x=0.071$) before (black square) annealing and after (red circle) annealing at 573 K for 5 hours.

Fig. 3 and Fig. S3 (see Fig. S3 in Ref. [37]) show the SEM images of typical samples. The thickness of all thin films can be estimated from the SEM images of sample taken from the side view (SEM images shown in Fig. S3(d)), which are 300 ± 20 nm. Fig. 3(a) is a typical SEM image of synthesized (undoped) Bi_2Se_3 film, showing interconnected grains of Bi_2Se_3 nanoplates. Figs. 3(b-d) are the SEM images of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ films with $x=0.07, 0.10$, and 0.11 . First, it is clear that the size of (undoped) Bi_2Se_3 nanoplates is bigger than that of $\text{Cu}_x\text{Bi}_2\text{Se}_3$. Moreover, with Cu doping, not only the lateral size of nanoplates along the ab plane becomes smaller, there are also more vertically grown nanoplates which likely cause stronger scattering in doped $\text{Cu}_x\text{Bi}_2\text{Se}_3$ films and the non-metallic R vs. T between 37K and 300K. It is similar to the non-metallic behavior in Bi_2Te_3 films [38] grown by CVD method, which is attributed to the structural disorder and porosity. However, the effect of the size of nanoplates can not cause the sudden metallic down-turn at 37K in our films. A similar non-metallic behavior is observed in the granular metals [39], which are arrays of metallic particles embedded into an insulating matrix. But the periodic granular array model [39] is different from the continuous film and the critical conductance theory of metal-insulator transition is not applicable to our case. In order to exclude Cu clusters effect in Cu-doped Bi_2Se_3 thin film, the energy dispersive x-ray spectroscopy (EDX) element mapping were measured to observe the element distribution of Cu-doped Bi_2Se_3 thin film sample ($x=0.071$). As shown in Fig. S4 of the Supplemental Material [37], we find that the Cu atoms in thin films had a homogeneous distribution.

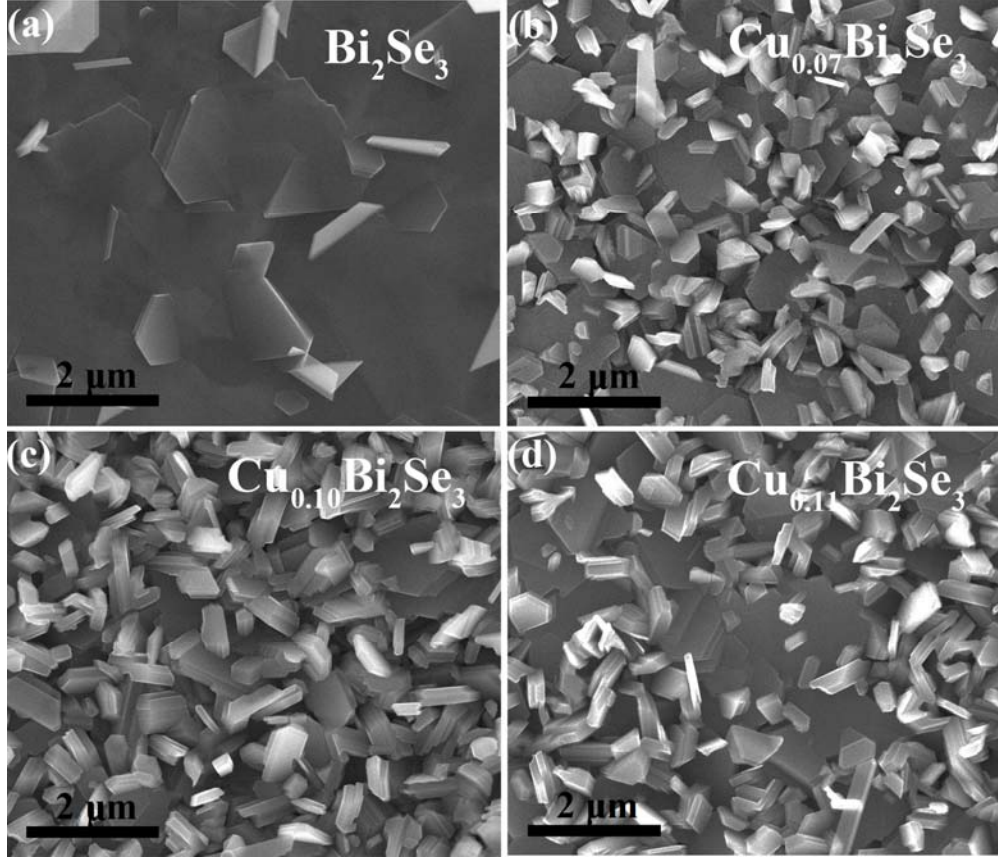


FIG. 3. SEM images of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ films with different Cu concentration. (a) A undoped sample ($x=0$). (b) A sample with $x=0.07$. (c) A sample with $x=0.10$ and (d) a sample with $x=0.11$.

Figs. 4(a-c) show the Hall resistance R_{yx} as a function of B (perpendicular magnetic field) at various temperatures for samples with $x=0$, 0.07, and 0.10. The sign of R_{yx} of all samples indicates n-type conduction. Fig. 4(a) illustrates that the R_{yx} of undoped samples is almost independent of temperature. Figs. 4(b)-(c) show that R_{yx} of doped $\text{Cu}_x\text{Bi}_2\text{Se}_3$ samples is temperature dependent, and the temperature-dependence becomes more pronounced with increasing Cu concentration. Additional Hall resistances for more samples are shown in Fig. S5 of the Supplemental Material [37]. We use the high field slope of $R_{yx}(B)$, i.e., dR_{yx}/dB to extract n_{total} , the total carrier concentration. The total carrier concentrations for the four typical samples with $x=0$, 0.07, 0.10, and 0.11 are presented in Fig. 4(d). The n_{total} is on the order of $10^{19}/\text{cm}^3$ for all the samples. We found that the carrier concentration variation with temperature is

interesting. For undoped samples, carrier concentration is hardly affected by temperature. The carrier concentration is almost unchanged with temperature decreasing from 200 to 2 K. In Cu-doped samples, the carrier concentration first decreases with lowering the T , and then increases at temperatures lower than about 37 K. The variation of carrier concentration is concomitant with the kink in R vs. T , suggesting a common origin for both phenomena.

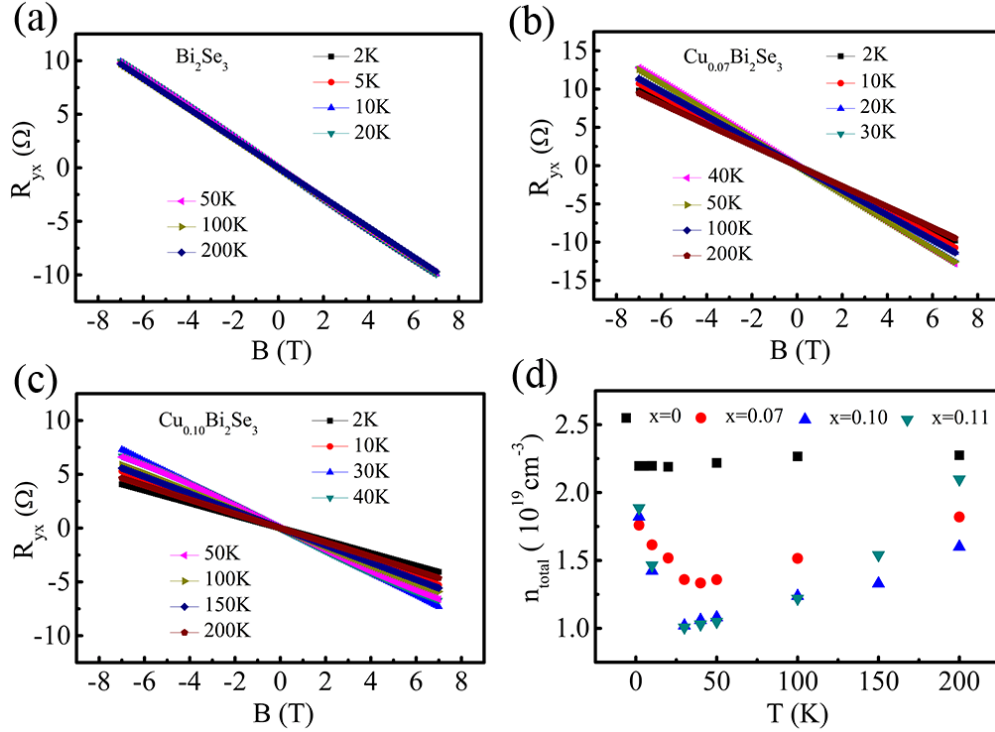


FIG. 4. Hall resistance data of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ thin film samples. (a) An undoped sample ($x=0$). (b) A sample with $x=0.07$ and (c) a sample with $x=0.10$. (d) Total carrier concentration of four typical samples ($x=0, 0.07, 0.10$ and 0.11) as a function of temperature.

In order to study the effect of Cu doping in Bi_2Se_3 , the structure and composition of these samples were investigated by XRD and EDS. XRD patterns of all samples show pure Bi_2Se_3 -type structure. As shown in Fig. 5(a), most of reflections are strong along the c -axis oriented (00 l) tropism in the undoped sample, which consists with the SEM image, reflecting that the (undoped) Bi_2Se_3 films display a continuous film with

triangular or hexagonal flakes laying on the substrate. Fig. 5(a) also shows that the doped $\text{Cu}_x\text{Bi}_2\text{Se}_3$ samples are polycrystalline without oriented (00 l) tropism. The lattice parameters are calculated by XRD analysis software MDI Jade 5.0 from the XRD patterns. Table 1 lists the lattice constants a and c obtained by XRD, and Cu concentration obtained by EDS for four samples with different x . From Table 1, we find that Cu doping causes the monotonic increase of the c -axis length. It suggests that Cu atoms are intercalated into the van der Waals gaps between QLs of Bi_2Se_3 . Moreover, Cu doping also leads to a slight decrease in the lattice along a -axis, compared with that of (undoped) Bi_2Se_3 , due to the Cu randomly substitutes for Bi within the host structure, as shown in Table 1. However, the lattice constant a is almost the same in samples with x from 0.07 to 0.11, suggesting that the difference in the lattice constant a is not significant in this Cu concentration range.

Fig. 5(b) presents Raman spectra for $\lambda = 633$ nm excitation at 295 K. When Cu intercalates between the QLs of Bi_2Se_3 , both peaks of the bulk phonon modes ($E_g(2)$ and $A_{1g}(2)$) will shift to lower frequencies [40,41]. However, $E_g(2)$, $A_{1g}(1)$ and $A_{1g}(2)$ modes are expected to shift to higher frequencies when Bi is substituted by other small atoms [42]. High frequency modes are out-of-phase movements of the outer Bi and Se atoms which are attracted by the strongest bonding forces in the crystals [42]. Therefore, interactions between the QLs are weakened by the intercalation of Cu atoms and the substitution of Cu atoms strengthens the interlayer van-der-Waals forces. As shown in Fig. 5(b), $A_{1g}(1)$ mode peak does not shift clearly with increasing Cu concentration due to its low frequency nature. $E_g(2)$ and $A_{1g}(2)$ mode peaks first shift to lower frequencies at low Cu concentrations, and then shift to higher frequencies with further increasing Cu concentration. It indicates that Cu atoms occupy the intercalative sites between the QLs at low Cu concentrations, and take the substitutional sites of Bi atoms gradually with increasing Cu concentration, which is similar to the previous report [21]. These findings confirm that the substitution Cu and the intercalation Cu atoms are both present in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ polycrystalline thin films. When Cu intercalates into the van der Waals gap, it can donate an electron to Bi_2Se_3 as Cu^+ state, and the substituted Cu is in the Cu^{2+} state and acts as an acceptor

[26-28].

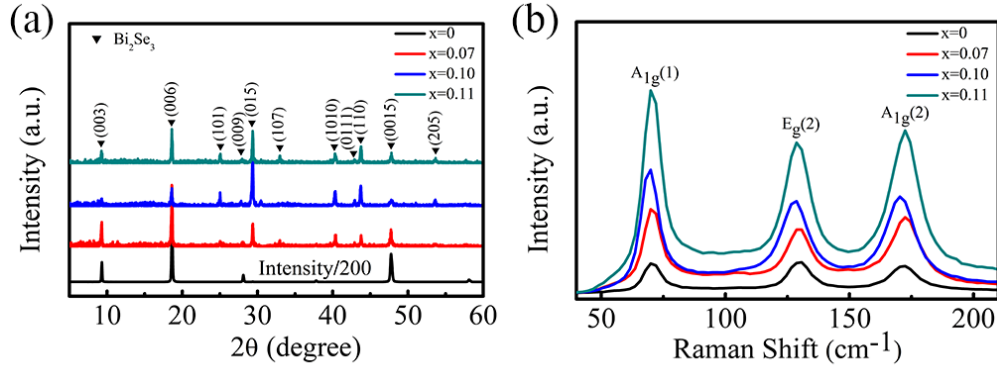


FIG. 5. (a) XRD patterns of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ thin film samples with respective $x=0, 0.07, 0.10, 0.11$. (b) Raman spectra of the four samples in (a).

TABLE I. Lattice constants a and c , and the Cu concentration in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ thin film samples obtained by XRD and EDS.

	a (\AA)	c (\AA)	Doping level x
Sample 1	4.152 ± 0.002	28.54 ± 0.01	0
Sample 2	4.135 ± 0.002	28.55 ± 0.01	0.07
Sample 3	4.135 ± 0.002	28.60 ± 0.01	0.10
Sample 4	4.136 ± 0.002	28.64 ± 0.01	0.11

By analogy of other similar layered selenides [29], we infer a structural diagram of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ with both intercalated Cu sites and random substitutional Cu sites, as schematically shown in Fig. 6(a). In our work, Cu is also found to randomly substitute for Bi within the host structure, which differs from the bulk $\text{Cu}_x\text{Bi}_2\text{Se}_3$ single crystals reported with superconductor phase, suggesting that the site occupancy of Cu in Bi_2Se_3 depends on the process of sample growing [11].

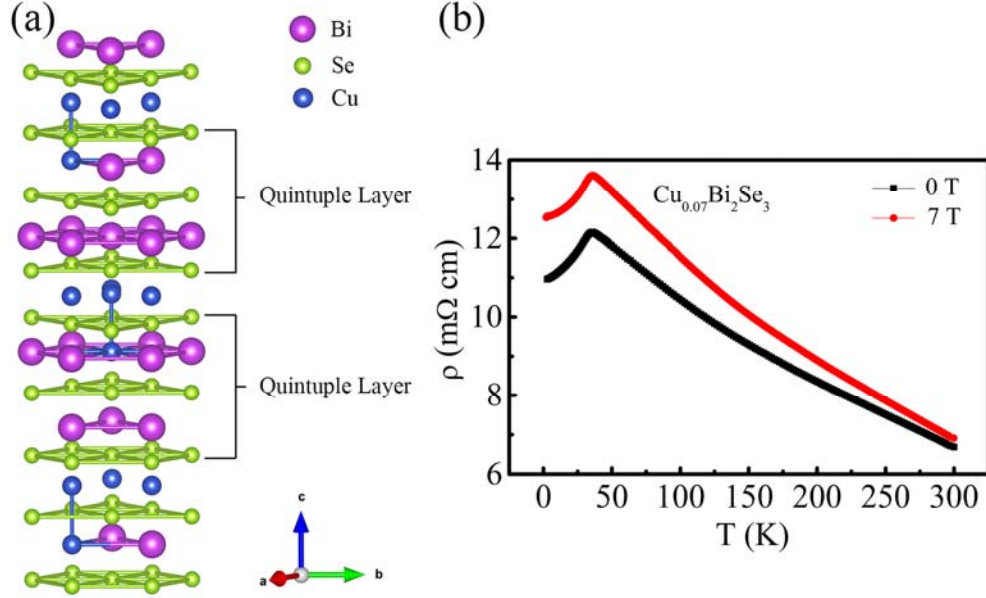


FIG. 6. (a) Crystal structure of Cu-doped Bi₂Se₃, including both intercalated Cu and substitutional Cu. (b) The temperature-dependent resistivity of a Cu_xBi₂Se₃ ($x=0.07$) thin film with an applied magnetic field of 7 T and zero field.

As known, strong hybridization between the adjacent Cu⁺ and Cu²⁺ conduction bands takes place at low temperature, as observed in the 2D regime of CuS and CuSe [29,30]. It indicates that charge delocalization between these ions can occur in the 2D regime [29]. As shown in Fig. 4(d), the carrier concentration of Cu_xBi₂Se₃ thin films increases significantly below 37K, which probably originates from the delocalized electrons by the strong hybridization between adjacent Cu⁺ and Cu²⁺ conduction bands. This scenario appears to be compatible with the resistivity drop at 37 K, as shown in Figs. 1(b-d). One may suspect that these features come from the CuSe phase due to the superconducting-like property of CuSe. To address this possibility, we studied the effect of magnetic field and ruled it out since the superconducting-like behavior of CuSe is sensitive to magnetic field (such as 7 T) [29]. We compare the R - T behaviors of Cu_xBi₂Se₃ ($x=0.07$) in zero field vs a magnetic field of 7 T, as shown in Fig. 6(b). The kink of R vs T at 37K does not change, but there is a magnetoresistance. More data are shown in Fig. S6 of the Supplemental Material [37]. This positive magnetoresistance is a normal phenomenon in topological insulator,

such as in Bi_2Se_3 [43], Bi_2Te_3 [38] and nonmagnetic Sn doped Bi_2Te_3 film [44]. Furthermore, we measured the current-voltage (I-V) curves of two representative samples with $x=0.10$ and 0.11 by using the current value far smaller than the one used in the R - T curves. Both of them show a linear I-V characteristics at 2 K, 50 K below and above 37 K, see Fig. S7 in Ref. [37]. These are not the characteristics expected for superconductors. The effect of the structural phase transition is excluded by temperature-dependent x-ray diffractometer (XRD) using Empyrean PIXcel 3D produced by PANalytical. We measured the XRD patterns of a typical sample ($x=0.081$) at 20 K, 50 K and 298 K, respectively, see Fig. S8 in Ref. [37]. It is noted that the sample was kept at 20 K for two hours to stabilize the phase before measurement. The kink is observed in R - T curve at about 37 K, see Fig. S8 (a) in Ref. [37]. As shown in Fig. S8 (b) of the Supplemental Material [37], there is no indication for structural phase transition at 37 K. With decreasing temperature, all peaks in the XRD spectrum shift to higher angles with a small range, which indicates that its lattice constants exhibit a slight decrease at low temperature. These results indicate that our case is different from superconducting-like behavior in CuSe and there is no structural phase transition around 37 K, but a more likely explanation is the strong hybridization between the adjacent Cu^+ and Cu^{2+} conduction bands in Cu-doped Bi_2Se_3 polycrystalline thin film, which causes the electron delocalization.

Further study reveals that a time-dependent relaxation phenomena is in electronic transport at low temperature. Fig. 7(a) shows the temperature dependence of resistivity at zero magnetic field of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x=0.076$) before and after relaxation at 2 K. The R - T curve (black squares) was measured with decreasing temperature from 300 to 2 K, and then the sample was kept at 2 K for 29 hours without any external excitation. Then the resistivity (red circles) was measured with increasing temperature from 2 to 300K, as shown in Fig. 7(a). From Fig. 7(a), it is noted that the kink of resistivity at 37 K is more pronounced after the sample is allowed to stabilize at low temperature for a long time and the two resistivity curves do not show much deviation above 37K. As it is unlikely that the thermal contact between sample and environment suddenly changes at 37K, these data exclude the poor thermalization (or

thermal contact) of sample as the explanation for the relaxation phenomenon below 37K.

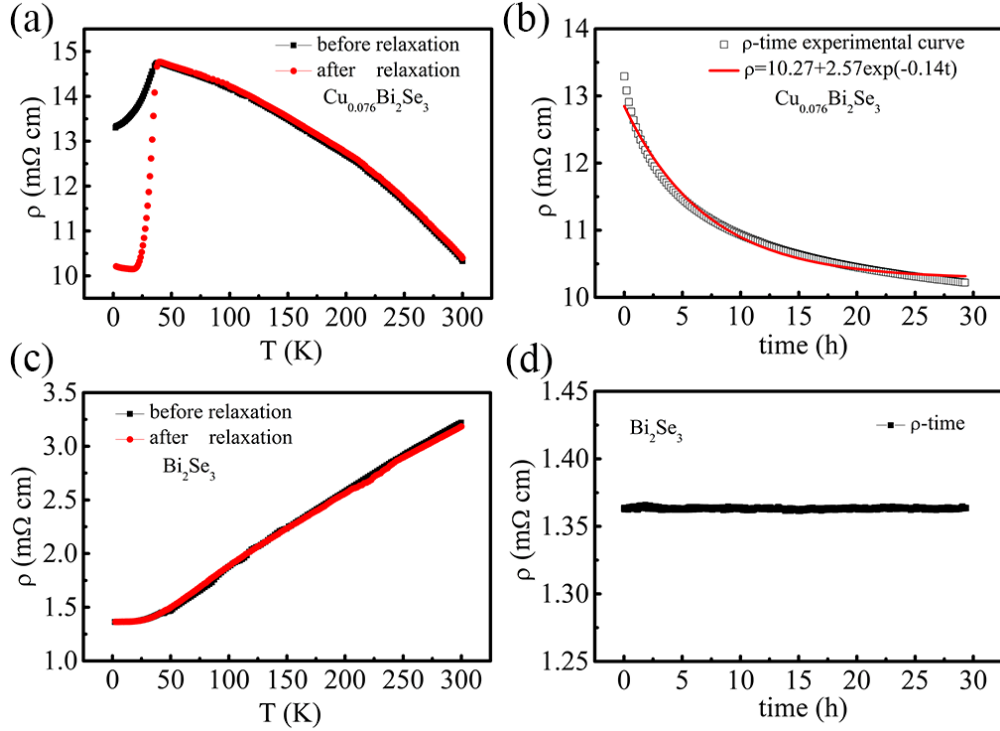


FIG. 7. Temperature dependence of resistivity of (a) $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x=0.076$) and (c) undoped Bi_2Se_3 before (black square) and after (red circle) relaxation at 2 K for 29 hours. Time dependence of resistivity of (b) $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x=0.076$) and (d) undoped Bi_2Se_3 at 2 K for the relaxation process of 29 hours.

Although the exact mechanism of the slow dynamics observed below 37K remains unknown, we performed more characterizations to gain more understanding. Fig. 7(b) shows the resistivity relaxation process with time at 2 K. The red line is the fitting curve to following formula [45,46],

$$\rho(t) = \rho(\infty) + [\rho(0) - \rho(\infty)] \exp(-Et), \quad (1)$$

where t is the relaxation time, $\rho(0)$ is the initial resistivity, $\rho(t)$ is the time-dependent resistivity, $\rho(\infty)$ is the saturation resistivity and E is the relaxation rate. More data on additional samples are given in Fig. S9 of the Supplemental Material [37]. For comparison, temperature-dependent resistivity and relaxation behavior of undoped

Bi_2Se_3 film are shown in Fig. 7 (c) and (d) respectively. The time-dependent slow relaxation behavior is clearly absent in undoped Bi_2Se_3 film. In addition, the dependence of resistivity vs. time at 2 K for $\text{Cu}_x\text{Bi}_2\text{Se}_3$ films with different Cu concentrations is shown in Fig. 8. When the Cu concentration increases, the relaxation rate E decreases (relaxation becomes slower). Meanwhile, the magnitude of the resistivity change during relaxation also increases at higher doping level, accompanying the slower relaxation dynamics.

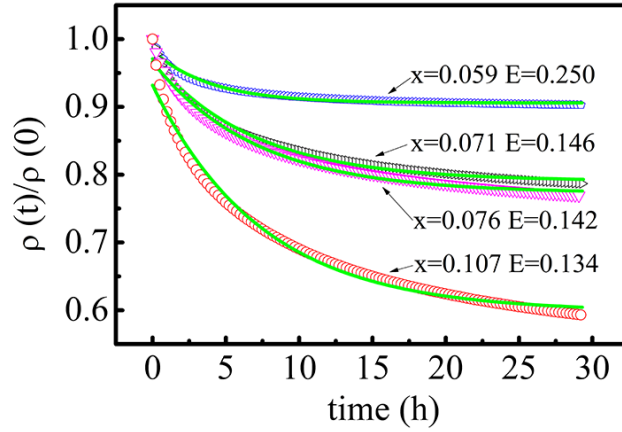


FIG. 8. Time dependence of resistivity at 2 K for different Cu concentrations of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ ($x=0.059, 0.071, 0.076, 0.107$). Solid lines (green) are best fits to formula (1): $\rho(t)/\rho(0) = \rho(\infty)/\rho(0) + [\rho(0) - \rho(\infty)]/\rho(0) \exp(-Et)$.

IV. CONCLUSION

In conclusion, we have performed a structure and transport property study of $\text{Cu}_x\text{Bi}_2\text{Se}_3$ polycrystalline thin films with $0.11 \geq x \geq 0$ prepared by the CVD method. Raman analysis shows that there are both intercalated Cu^+ and substituted Cu^{2+} in $\text{Cu}_x\text{Bi}_2\text{Se}_3$. Due to disorder, Cu-doped Bi_2Se_3 polycrystalline thin films exhibit non-metallic temperature-dependent resistivity between 37K and 300K. However, an unexpected sign change in dR/dT is observed at 37K. It is suggested that the hybridization effect between Cu^+ and Cu^{2+} conduction bands is responsible for the metallic behavior at $T < 37\text{K}$. Moreover, a relaxation behavior was observed in the time dependence of resistivity in the metallic state below 37K, calling for the further

understanding of the dynamics in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ polycrystalline thin films.

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