Magnetic and transport properties of Sb$_2$Te$_3$ doped with high concentration of Cr

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We report on the molecular beam epitaxy and properties of a magnetic topological insulator (TI): Cr-doped Sb$_2$Te$_3$. Composition analysis reveals that Cr replaces Sb, and X-ray diffraction confirms that a single-phase textured crystal structure can be obtained for (Cr,Sb)$_{1-x}$Te$_3$ with $x$ up to 0.44. A further increase in $x$ results in phase separation or precipitates in the material. The Curie temperature $T_C$ increases with $x$ up to 0.44 and reaches 250 K, which is the highest $T_C$ observed thus far in magnetically doped TIs. © 2017 The Japan Society of Applied Physics

Topological insulators (TIs) have become a research focus in condensed-matter physics owing to their intriguing properties resulting from gapped (insulating) bulk states and gapless (conducting) surface states. In the surface states, carrier spins are coupled with their momenta and are protected by the time-reversal symmetry (TRS).\(^1\)\(^2\) These unique surface states have been anticipated to exhibit various quantum phenomena, potentially contributing to developments in low-power spintronics.\(^1\)\(^2\) The TRS in these materials can be broken by doping magnetic impurities or by the ferromagnetic proximity effect, which results in the opening of a bandgap at the Dirac point.\(^3\)\(^4\) Ferromagnetism in TIs results in many exotic physical phenomena, such as the quantum anomalous Hall effect and magneto-electric effects.\(^5\)\(^6\) These properties stimulated interest in magnetically doped TIs to unlock further novel quantum phenomena to pave the way for future spintronics.

Magnetic TIs have been synthesized by doping non-magnetic TIs with 3$d$ transition metals such as V, Cr, Mn, Fe, and Cu. The doping induces various magnetic properties, such as ferromagnetism, antiferromagnetism, and superconductivity.\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\)\(^13\) To elucidate the nature of magnetism, one needs to vary the transition-metal concentration as well as the carrier concentration in the material. It has been observed that in the bulk matrix, the solubility of the transition metal is low under the equilibrium growth condition.\(^14\)\(^15\) Low-temperature molecular beam epitaxy (MBE) has allowed researchers to dope a higher concentration of transition metal because of its non-equilibrium growth nature, which helps to enhance the Curie temperature $T_C$.\(^16\) Among the ferromagnetic TIs, Cr-doped Sb$_2$Te$_3$, i.e., (Cr,Sb)$_{1-x}$Te$_3$, has exhibited ferromagnetism at a high $T_C$ of 190 K at a Cr composition $x$ of ~0.3.\(^3\)\(^4\) Sb$_2$Te$_3$ has a tetradymite crystal structure (space group $R\bar{3}m$) with quintuple (Te–Sb–Te–Sb–Te) layers piled up along the $c$-axis via a van der Waals interaction.\(^16\)\(^17\) To further investigate the composition dependence of the crystallographic, magnetic, and electrical properties of (Cr,Sb)$_{1-x}$Te$_3$, we study the MBE growth of (Cr,Sb)$_{1-x}$Te$_3$ and its properties by varying $x$ up to 0.61 and show that many properties of this system are similar to those of (Ga,Mn)As.

We grow (Cr,Sb)$_{1-x}$Te$_3$ films with different $x$ values on a semi-insulating GaAs (111)B substrate via MBE. The substrate is deoxidized by heating it to 700°C inside the MBE chamber with a base pressure of $<8 \times 10^{-8}$ Pa and then cooled to the growth temperature, which is fixed at 280°C. The beam equivalent pressure ratio between Sb and Te is maintained as $\sim 1:7$. We vary $x$ by tuning the Cr/Sb beam flux ratio by changing their source temperatures. The in situ reflection high-energy electron diffraction shows a streaky pattern throughout the growth, indicating two-dimensional growth of single crystals. After the growth, the film thickness $t$ (typically between 50 and 60 nm) is measured via cross-sectional scanning electron microscopy. The Cr composition $x$ is determined via energy-dispersive X-ray spectroscopy (EDX). $\theta$–$2\theta$ X-ray diffraction (XRD) measurements are performed using a Cu Kα radiation. Magnetic measurements as a function of the temperature and magnetic field are performed using a vibrating sample magnetometer. Transport measurements are performed using the van der Pauw method.

The EDX results indicate that we obtain (Cr,Sb)$_{1-x}$Te$_3$ with the nominal highest $x$ of 0.61. The ratio of ([Cr] + [Sb]) : [Te] is nearly $2:3$, indicating that Cr atoms replace Sb. The XRD pattern of the (Cr,Sb)$_{1-x}$Te$_3$ films up to $x$ = 0.44 shows (003) family peaks along with GaAs(111) substrate peaks, which confirms a tetradymite structure with growth along the $c$-axis [Fig. 1(a)]. The $c$-axis lattice parameter for Sb$_2$Te$_3$ is determined to be 3.04 nm from Bragg’s law using the peak position, which is close to the reported value.\(^1\)\(^5\) The peaks shift slightly to a higher $2\theta$ angle when $x$ is increased to 0.44, as shown in Fig. 1(b), indicating the decrease of the $c$-axis lattice parameter, which is consistent with a previous report.\(^9\)\(^13\) The sample with $x$ = 0.61 exhibits almost the same peak positions as those for (Cr,Sb)$_{1-x}$Te$_3$ with $x$ = 0.33 and has additional peaks at $2\theta$ values of approximately 30 and 60° (marked by arrows), as shown in Fig. 1(c). This suggests phase separation or precipitation in (Cr,Sb)$_{1-x}$Te$_3$ with a high $x$. The Cr composition dependence of the $c$-axis lattice parameter is summarized in Fig. 1(d).

Figure 2(a) shows the temperature dependence of the magnetization $M$. The sample is cooled from room temperature to the lowest measured temperature (5 K) in the presence of 0.1 T applied normal to the film plane, and then data are recorded while the sample is heated to 400 K under 2 mT, i.e., a field to compensate the remnant field in the magnetometer.\(^1\)\(^6\) Upon heating, the magnetization decreases monotonically and exhibits a magnetic phase transition from ferromagnetic to paramagnetic at $T_C$ ($T_C$ is marked with an arrow). When $x$ increases, the magnetization increases, and $T_C$ shifts to higher temperatures reaching 250 K for (Cr,Sb)$_{1-x}$Te$_3$ with $x$ = 0.44. Further increase of $x$ results in a...
compositions of (a) under perpendicular and in-plane magnetic fields. The arrows indicate additional peak positions. (d) Magnetic moments \( M \) per Cr as a function of \( x \) for (Cr,Sb)\(_2\)Te\(_3\) with \( x = 0.12, 0.33, \) and 0.44, respectively. The values of \( M \) and \( H_c \) increase with \( x \). The sample with \( x = 0.61 \) exhibits hysteresis with steps, indicating the presence of two ferromagnetic phases, as detected by the temperature dependence of \( M \). To investigate how \( T_C \) varies with respect to \( x \), we plot \( T_C \) vs \( x \) in Fig. 2(c), where \( T_C \) increases almost linearly with \( x \) up to 0.44, similar to what was reported for (Ga,Mn)As.\(^{17,18}\) This observation appears to be consistent with the theoretical calculation, which shows that the ferromagnetic interaction is mediated by a Te anion between Cr atoms as well as carriers.\(^{19}\) The magnetic moment \( \mu \) per Cr atom determined from \( M_S \) is between 2\( \mu_B \) and 3\( \mu_B \) [Fig. 2(d)], where \( 2 \mu_B \) is the Bohr magneton, showing that Cr is electrically neutral (Cr\(^{3+}\)) or acts as a donor (Cr\(^{4+}\)). Figure 2(e) shows the magnetization curves for (Cr,Sb)\(_2\)Te\(_3\) with \( x = 0.44 \) at 5 K under fields applied along the out-of-plane and in-plane directions. The film has an easy axis of magnetization parallel to the \( c \)-axis and a hard axis of magnetization in the \( ab \)-plane, similar to previous reports on ferromagnetic TIs.\(^{8}\) The anisotropy field is as large as \( \sim 2 \) T.

Figures 3(a) and 3(b) show the field dependence of the Hall resistivity \( \rho_{\text{Hall}} \) at 5 K and the temperature dependence of the longitudinal resistivity \( \rho \) under zero magnetic field for (Cr,Sb)\(_2\)Te\(_3\) with different \( x \) values, respectively. The \( \rho_{\text{Hall}} \) in magnetic materials can be expressed as \( \rho_{\text{Hall}} = R_{\text{Hall}} H + R_S M \) with the ordinary Hall coefficient \( R_H \), the anomalous Hall coefficient \( R_S \), and permeability in the free space \( \mu_0 \). (Cr,Sb)\(_2\)Te\(_3\) with \( x = 0 \) shows the ordinary Hall effect, as indicated by the linear dependence of \( R_{\text{Hall}} \) with \( H \), while (Cr,Sb)\(_2\)Te\(_3\) with \( x = 0.12 - 0.44 \) exhibits the anomalous Hall effect (AHE) because of the magnetic contribution. The positive slope of \( \rho_{\text{Hall}} \) in the high-field region, where AHE becomes saturated, indicates that hole-type carriers are dominant in these films, possibly owing to native defects.

Figure 2(b) shows the magnetization curves for (Cr,Sb)\(_2\)Te\(_3\) with different \( x \) values at 5 K under perpendicular magnetic fields, in which the diamagnetic contribution from the substrate is subtracted from the total magnetization using a linear fit in high fields. A clear hysteresis loop with a coercive field \( H_C \) of \( \sim 53 \) to \( 91 \) and \( \sim 167 \) mT and saturation magnetization \( M_S \) of \( \sim 39 \), \( \sim 130 \), and \( \sim 135 \) mT are observed for \( x = 0.12, 0.33, \) and 0.44, respectively. The values of \( M_S \) and \( H_C \) increase with \( x \). The sample with \( x = 0.61 \) exhibits hysteresis with steps, indicating the presence of two ferromagnetic phases, as detected by the temperature dependence of \( M \). To investigate how \( T_C \) varies with respect to \( x \), we plot \( T_C \) vs \( x \) in Fig. 2(c), where \( T_C \) increases almost linearly with \( x \) up to 0.44, similar to what was reported for (Ga,Mn)As.\(^{17,18}\) This observation appears to be consistent with the theoretical calculation, which shows that the ferromagnetic interaction is mediated by a Te anion between Cr atoms as well as carriers.\(^{19}\) The magnetic moment \( \mu \) per Cr atom determined from \( M_S \) is between 2\( \mu_B \) and 3\( \mu_B \) [Fig. 2(d)], where \( 2 \mu_B \) is the Bohr magneton, showing that Cr is electrically neutral (Cr\(^{3+}\)) or acts as a donor (Cr\(^{4+}\)). Figure 2(e) shows the magnetization curves for (Cr,Sb)\(_2\)Te\(_3\) with \( x = 0.44 \) at 5 K under fields applied along the out-of-plane and in-plane directions. The film has an easy axis of magnetization parallel to the \( c \)-axis and a hard axis of magnetization in the \( ab \)-plane, similar to previous reports on ferromagnetic TIs.\(^{8}\) The anisotropy field is as large as \( \sim 2 \) T.

(a) Temperature \( T \) dependence of the magnetization \( M \) of (Cr,Sb)\(_{1-x}\)Te\(_3\) films with Cr compositions of (a) \( x = 0 \), (b) \( x = 0.44 \), and (c) \( x = 0.61 \). The vertical dotted lines are a visual guide for observing the slight shift in the peak positions that occurred when the Cr concentration \( x \) was varied. The arrows in (c) indicate additional peak positions. (d) Magnetic moments \( \mu \) per Cr as a function of \( x \) for (Cr,Sb)\(_2\)Te\(_3\) with a uniform Cr distribution and the unfilled symbol for with phase separation or precipitates.
such as Sb antisites acting as acceptors.\textsuperscript{20} The hole concentration $p$ in $\text{(Cr,Sb)}_2\text{Te}_3$ determined from the slope is summarized in Fig. 3(c), which suggests that the introduction of Cr promotes the formation of electrically active defects and increases the hole concentration. The inset of Fig. 3(a) shows the magnetic-field dependence of $\rho_{\text{Hall}}$ and $M$ measured at 5 K for the film with $x = 0.44$. The hysteresis loop in $\rho_{\text{Hall}}$ is more square than that. Similar behavior was reported in (Ga,Mn)As.\textsuperscript{21} The difference between the two hysteresis loops arises from the difference in the two measurements of the sample. In magnetic measurements, $M$ comes from spins throughout specimen, whereas in transport measurements, $\rho_{\text{Hall}}$ detects the magnetization from the conducting region, where current flows more easily than in the less conducting region.\textsuperscript{21} However, we obtain the same $T_C$ from the Arrott plots using the Hall resistance data as from the magnetization data.

Figure 3(d) shows double-logarithm plots of the Hall conductivities $\sigma_{xx}$ vs the longitudinal conductivities $\sigma_{xx}$ (stars), along with those obtained previously for (Ga,Mn)As and (Ga,Mn)Sb.\textsuperscript{22,23} The plots obey an empirical scaling relationship, $|\sigma_{xy}| \propto \sigma_{xx}^{1.6}$, as observed for numerous materials, including typical ferromagnetic semiconductors.\textsuperscript{24} As shown in Fig. 3(b), below 25 K, the $\rho$ of the Cr-doped films starts increasing upon further cooling. This low-temperature rise becomes more pronounced as $x$ increases. This feature can be explained by two mechanisms. One is the freezing of bulk carriers at low temperatures, where the bulk becomes insulating and the surface states dominate.\textsuperscript{25} The other is weak localization.\textsuperscript{26} We observe negative magnetoresistance at low temperatures, which suggests that the low-temperature increase in $\rho$ is due to weak localization in TIs.\textsuperscript{27} Again, similar behavior was observed for (Ga,Mn)As.\textsuperscript{17,26} Both the magnetic and transport properties of (Cr,Sb)$_2$Te$_3$ are thus similar to those reported for (Ga,Mn)As, which suggests that (Cr,Sb)$_2$Te$_3$ is another useful material for investigating the spin–orbit coupling-related phenomena in magnetic materials.\textsuperscript{28} In addition to this, the bulk conduction in the system under study can be suppressed by applying electrical gating or chemical substitution. This can provide information on the mechanism of the observed ferromagnetism\textsuperscript{29} and make this high-$T_C$ material a candidate for applications in low-power spintronics.

In summary, we grow (Cr$_{1-}\text{Sb}_{1}\text{Sb}_1$)$_2$Te$_3$ with different $x$ values on a semi-insulating GaAs (111)B substrate using MBE. The structural, magnetic, and transport properties do not indicate any secondary phase for (Cr,Sb)$_2$Te$_3$ with $x$ up to 0.44. The magnetic and transport properties are very similar to those of (Ga,Mn)As and reveal robust ferromagnetic ordering in these films. The Curie temperature increases with the Cr composition $x$ and reaches $\sim 250$ K for (Cr,Sb)$_2$Te$_3$ with $x = 0.44$. A further increase in $x$ results in phase separation or precipitates in the material and does not further enhance the Curie temperature.

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