Magnetically doped semiconducting topological insulators

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The time invariant behaviors of topological insulators are expected to be changed with magnetic doping, which motivate the present study. Here, we show that for Bi2–xCrxSe3 (0.01 ≤ x ≤ 0.3) thin films grown on Si, the non-trivial topological surface state is weakened by the Cr dopants. The band gap of surface is opened and monotonically increased with Cr concentration up to ~100 meV at 10 K. Meanwhile, the semiconducting behavior is well-maintained in the bulk owing to the reduction of background doping by means of a modified growth strategy and an in situ passivation method. Besides, we also observe the existence of unconventional ferromagnetic ordering below 35 K, for which the Curie-Weiss Law and conventional/modified Arrott equations do not apply. These observations may further help us investigate extraordinary magneto-electric effect in topological insulators, and the result will also pave the way for realizing the quantized anomalous Hall effect.© 2012 American Institute of Physics.[http://dx.doi.org/10.1063/1.4754452]

Topological insulators (TIs) are drawn unparalleled attentions in recent research highlights.1–4 Exciting progress based on the time-reversal-invariant properties of TIs, such as high quality materials preparations5–10 and manipulation of surface states,11–14 has been made. Such efforts have accelerated the speed towards the demonstration of quantum spin Hall (QSH).15–19 To this end, the effort to break the topologically protected surface states by introducing magnetic ordering inside the TIs system would enable us to observe the quantized anomalous Hall (QAH).20–26 extraordinary magneto-electric (ME) effects, and perhaps other discoveries.27,28 Specifically, QAH is striking in terms of absence of itinerant carriers,22 and this proposal is contradicted to the behaviors of topological insulators, and the result will also pave the way for realizing the quantized anomalous Hall effect.© 2012 American Institute of Physics.[http://dx.doi.org/10.1063/1.4754452]

Efforts to dope tetradyrmite family materials with magnetic impurities were made before the discovery of their topological characteristics.29–32 However, the discussions of such magnetic doped materials at that time have been limited to the scope of conventional dilute magnetic semiconductors (DMS), despite that the doping concentration of magnetic impurities did obviously go far beyond the “dilute” regime. Most recently, ferromagnetism was proposed to exist in Cr/Fe doped TIs through the van-Vleck mechanism in the absence of itinerant carriers,22 and this proposal is contradictory to the s-d exchange interaction mechanism in standard DMS systems.33–35 This carrier-independent ferromagnetism was later observed in Bi1−xSbxTe3 system with different Cr doping concentrations.36 In addition, several groups have also experimentally prepared Mn/Fe/Cr doped Bi2Se3 by means of a modified Bridgman method,9 vapor-liquid-solid (VLS),37 and molecular beam epitaxial (MBE) growth.38 Extensive transport measurements were conducted in these systems, for instance, the crossover between weak localization (WL) and weak anti-localization (WAL) was found.38 However, these studies were either incomplete due to the limited Fe doping concentration (less than 2% as shown in Ref. 37) or due to the presence of heavy background n-type doping, i.e., metallic behavior in bulk.38 For the purpose of realizing of QAH in TIs, one should tune the magnetically doped TIs into bulk insulating states, and the relevant magnetic properties, such as phase transition information and relation of magnetism, with dopant/carrier concentration in these systems need to be comprehensively studied.

Following this motivation, we study the Cr doped Bi2Se3 epitaxial thin films grown using a solid source MBE system. We observe the band opening of the surface states below the Curie temperature (Tc ≈ 35 K). We demonstrate a well-established ferromagnetic ordering in the semiconductor background by combining both magneto-transport measurements and magnetic property measurements. Furthermore, we discover two exotic phenomena related to the “unconventional” ferromagnetism, which clearly contradict to the behaviors of the conventional s-d exchange mechanism in the DMS systems. Our findings in the Cr doped TI system within the semiconducting region may facilitate the associated understandings of intrinsic magnetic interaction mechanisms in the present systems.

Thin films of Cr doped Bi2Se3 are grown under an ultrahigh vacuum (UHV) system by MBE. High resistivity Si (111) wafers (ρ > 105 Ω·cm) are first cleaned with standard
Radio Corporation of America (RCA) clean method.\textsuperscript{39,40} The substrates are then treated by hydrofluoric acid wet etching so that the surface dangling bonds are saturated by a layer of hydrogen atoms and the (111) surface is $1 \times 1$ reconstructed to further enhance the film quality.\textsuperscript{41,42} The growth is conducted under the Se-rich environment with a nominal Se to Bi ratio approximately 10:1, which is expected to reduce the Se vacancy defects. In addition, the substrate is maintained at a relatively high substrate temperature (300°C to 350°C) to optimize both the surface migration rate and Cr solubility simultaneously.\textsuperscript{30} To inhibit the degradation introduced from ambient n-doping after growth, we use in-situ Al passivation method, which is to deposit 2 nm Al immediately after the TI thin film growth.\textsuperscript{43}

\textit{In situ} growth dynamics are monitored by reflection high energy electron diffraction (RHEED) measurements. Sharp streaky patterns in Figure 1(a) indicate a 2D pseudomorphic growth. Meanwhile, the intensity of zero-order pattern is tracked and the oscillations are evident in Fig. 1(b). The growth rate can thus be estimated as 0.56 quintuple layer (QL)/min.

The surface morphology of the thin film is examined by atomic force microscope (AFM). Typical triangular terraces are revealed without visible clusters even with the Cr doping concentration reaching to as high as 20%. Figure 1(c) illustrates the AFM image of a Cr$_{0.1}$Bi$_{1.9}$Se$_3$ sample with a film thickness of 50 QLs. The average terrace size is estimated to be 200 nm, which is comparable with the un-doped Bi$_2$Se$_3$ thin films grown on Si (111) substrates following a similar growth method.\textsuperscript{6} Further structural characterization is proceeded by using high resolution transmission electron microscopy (HRTEM) shown in Fig. 1(d), the layered structures of the 7 QL single-crystalline Cr$_{0.1}$Bi$_{1.9}$Se$_3$ thin film can be clearly seen and the lattice spacing between (0003) planes is measured to be $\sim$1 nm, corresponding to one quintuple layer. It also confirms that there are no clusters or second phase developed inside the crystalline structural matrix, within the resolution of the HRTEM. This result indicates that Cr atoms are most likely uniformly distributed inside the Bi$_2$Se$_3$ and the tetradymite quintuple layered structure is well maintained.

Energy dispersion relations of the Cr doped Bi$_2$Se$_3$ thin films are studied by angular resolved photoemission spectroscopy (ARPES). Atomically clean surfaces of the samples are obtained after mild annealing at 423 K for 2 h, and all photoemission data are collected at 10 K. To understand the evolution of surface states with the Cr doping level, we compare the band maps of un-capped Bi$_{2-x}$Cr$_x$Se$_3$ grown on Si (111) with same thickness (50 QL) but different Cr compositions, as given in Figures 2(a)–2(d). While a linear Dirac-cone-like dispersion relation can be clearly observed on the surface of the un-doped sample in Fig. 2(a), the gap of the surface states below the transition temperature is opened at the $\Gamma$ point and the electrons behave like massive Dirac fermions even without applying an external magnetic field in Figs. 2(b)–2(d). The change of surface state is mainly due to the factor that ferromagnetic ordering generated by the Cr dopants inside the material will break the time-reversal-symmetry (TRS) and thus force the surface opens the band gap. As Cr doping is increased, the magnetic moment gets enhanced, which further weakens the non-trivial topological surface states and enlarges the band opening. Furthermore, we can roughly estimate the amplitude of the surface gap $\Delta$ by means of projecting the photoemission intensity shown in Fig. 2 onto the energy spectrum. As indicated by the solid-yellow curves depicted in Figs. 2(b)–2(d), $\Delta$ are found to be around 5 meV, 35 meV, and 100 meV for Bi$_{2-x}$Cr$_x$Se$_3$ with $x = 0.02$, 0.1, and 0.2 at 10 K, respectively. The relation of the Berry phase to $\Delta$ in the presence of magnetic ordering perpendicular to the surface can also be determined as follows:\textsuperscript{44}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{(a) RHEED pattern along [1120] direction of an as-grown surface of Bi$_{2-x}$Cr$_x$Se$_3$ with a thickness of 7 QLs. (b) RHEED oscillations of intensity of the specular beam. The oscillation period is found to be 108 s, corresponding to a growth rate of $\sim$0.56 QL/min. (c) AFM image of the Cr-doped Bi$_2$Se$_3$ thin film with the size of 0.3 $\mu$m $\times$ 0.3 $\mu$m. (d) HRTEM of a Bi$_{1.8}$Cr$_{0.2}$Se$_3$ grown on a Si (111) substrate.}
\end{figure}
\[ \delta \varphi = \pi \left( 1 + \frac{\Delta}{2E_F} \right) \]

where \( E_F \) is the energy gap between the Fermi level measured from the Dirac cone. For \( \text{Cr}_{0.1}\text{Bi}_{1.9}\text{Se}_3 \) as one example, we subsequently obtain a perturbed Berry phase of 7.6% deviating from the ideal \( \pi \) phase. Moreover, higher Cr doping concentration will also damage the crystalline structure of \( \text{Bi}_{2-x}\text{Cr}_x\text{Se}_3 \) films and introduce strong electron scattering in these samples. This along with the Berry phase deviation will further degrade the ARPES spectrum, and in our experiments the surface states of Cr doped \( \text{Bi}_2\text{Se}_3 \) films can no longer be detected by ARPES when the doping composition of Cr exceeds 0.3. Meanwhile, it should be noted that the Fermi levels almost remain the same regardless of Cr doping concentration in the ARPES images. However, this does not have any direct relation with the intrinsic carrier densities. Instead, we credit such Fermi level pinning to un-intentional ambient doping, band bending, and photoemission gating effects brought during the ARPES measurements.

The material challenges for 3D TIs at the current stage lie in the effort to sustain the bulk insulating states. However, doping concentrations in \( \text{Bi}_2\text{Se}_3 \) based materials are usually and inevitably high because of intrinsic Se vacancy defects. Consequently, the Fermi level is pinned up in the conduction band, and thus introduces undesirable metallic behaviors in TI materials. In our experiment, by modifying the cleaning procedure, optimizing growth conditions, and with \textit{in-situ} Al passivation, we successfully suppress these drawbacks. In Fig. 3(a), the temperature dependence of the longitudinal resistance \( R_{xx} \) are...
displayed. The monotonic increase in $R_{xx}$ as the decrease in
temperature (from 300 K) reveals typical semiconductor behavior ($dp/dT < 0$ in the phonon scattering dominant region) in the
sample. Similar to other doped semiconductor systems, the
transport characteristic in a high temperature insulating phase
follows the Emin-Holstein theory:

$$p(T) = p_0 T^a \exp(E_a/k_BT).$$  \hspace{1cm} (2)

Here $E_a$ is the activation energy and $k_B$ is the Boltzmann constant. With linear fitting in the high temperature region
($T > 200$ K) as shown in the inset of Fig. 3(a), the exponent $a$
is found to be 3/2 and thus corresponds to the non-adiabatic
small polaron hopping (SPH), with a small polaron bandwidth; $E_a$ is estimated to be 35 meV.

The magnetic properties of the 50 QL Bi$_{1.9}$Cr$_{0.1}$Se$_3$ thin
film sample are investigated by superconducting quantum inter-
ference device (SQUID). The phase transition information
and the relation of magnetization as a function of temperature
can be obtained by performing the zero-field cooling (ZFC)
and field cooling (FC) measurements. An external magnetic
field of 50 Oe is applied perpendicular to the sample plane
during these measurements. The bifurcation of ZFC and FC
curves at 8 K in Figure 3(b) corresponds to a blocking temper-

Here, we adopt modified Arrott-Noakes equation of state$^{54}$

$$\left( \frac{H}{M} \right)^{1/\gamma} = \frac{T - T_C}{T_1} + \left( \frac{H}{M} \right)^{1/\beta}. \hspace{1cm} (4)$$

Provided that the linearized parallel straight lines are
observed, one can thus experimentally determine the underly-
ing dominant interaction by reploting $M-H$ curves$^{54,55}$ for
example, in the long range mean field model, these exponents are $\gamma = 0.5$, $\beta = 1$, while in the nearest neighbor 3-D Heisen-
berg model, the corresponding values change to $\gamma = 0.37$, $\beta = 1.39$. However, as depicted in Figs. 4(b) and 4(c), rather
than displaying the parallel straight lines, both plots display
some continuous curvatures, even in the saturation region up
to 8000 Oe, and these effects turn to exclude the dominant
long range interactions, as well as preclude us from giving an
accurate estimation of the transition temperature.$^{54,47,56}$ In

![FIG. 4. (a) M-H loops of the 50 QL Bi$_{1.9}$Cr$_{0.1}$Se$_3$ thin film at 5 K, 10 K, 15 K, 20 K, 30 K, and 35 K. Inset: zoom-in hysteresis loop at 5 K, the coercivity field is started to be around 150 Oe. (b) Arrott plots of $H/M$ versus $M^2$ for magnetic isotherms from 14 K to 26 K. (c) Modified Arrott-Noakes plots of $(H/M)^{1/3}$ versus $M^{1/3}$ for data in (b). The applied magnetic field is always perpendicular to the sample surface, and the field range which covers from $-8000$ Oe to $8000$ Oe is high enough to saturate the magnetic moment.](image-url)
addition, the absence of “S” shape in the Arrott plot suggests the underlying phase transition is of second order. Given the above observed abnormal inverse susceptibility shown in Fig. 3(b), as well as applicability of the modified Arrott-Noakes equation of the state, we suggest that these behaviors should result from the intrinsic magnetism in Cr doped Bi$_2$Se$_3$ systems where the major contribution of spin susceptibility is brought by a strong coupling between the intrinsic magnetism and local valence electrons.\textsuperscript{55} Clearly, this needs to be further studied.

Finally, the FM phase and its relation with Cr doping can also be confirmed by the magneto-transport measurements. Standard Hall bars structures on different Bi$_{2-x}$Cr$_x$Se$_3$ samples with 0.01 $\leq x \leq 0.3$, with the same thickness of 50 QL and device size of 10 $\mu$m ($L$) $\times$ 40 $\mu$m ($W$), are fabricated using photolithography. As we can observe in Figure 5(a), the overall two-dimensional (2D) Hall carrier density decreases modestly when more Cr atoms are increasingly introduced. Given the intrinsic n-type behavior caused by Se-vacancies in undoped Bi$_2$Se$_3$ thin films, the suppression of electron concentration in Bi$_{2-x}$Cr$_x$Se$_3$ suggests that a majority of Cr atoms are incorporated within the crystal lattice with the form of Cr$^{3+}$ state, and therefore substitute on the Bi sublattice in the TI matrix.\textsuperscript{57,58} On the other hand, the degradation of conduction mobility reveals the factor that extra impurity scattering centers will form in the bulk due to Cr doping and thus hamper the electron transport under low temperature.

Provided there is close correlation between magnetism and transport in magnetic materials, anomalous Hall effect (AHE) is utilized to confirm the prevailing ferromagnetism.\textsuperscript{59} Other than a linear slope of ordinary Hall resistance $R_{xy}$ in non-magnetic semiconductors, the magnetization induced by the exchange field modifies $R_{xy}$, leading to the following empirical relation:\textsuperscript{59}

$$R_{xy} = R_0 H + R_A M(H),$$

where $R_0$ is the ordinary Hall coefficient and is solely connected to the carrier density; the anomalous Hall coefficient $R_A$ is affected by the longitudinal resistance $R_L$ depending on the dominant intrinsic/extrinsic scattering mechanisms.\textsuperscript{60,61} From $R_{xy}$ (Eq. 5), we can relate the same hysteretic behavior to that of the SQUID measurement due to the existence of remnant magnetization within the FM phase. By extracting the linear ordinary Hall component $R_{xy}$, we plot the dual-loop anomalous Hall data $R_A M$ as a function of applied field at 1.9K in Fig. 5(b). With the increase in Cr composition, more distinct hysteresis behavior can be found, and both the saturation magnitude of anomalous Hall component and coercivity field $H_C$ as shown in the inset will become enhanced.

In conclusion, we have demonstrated the presence of FM ordering in the epitaxial Bi$_{2-x}$Cr$_x$Se$_3$ thin films on Si substrate using MBE growth. The Cr can be fully incorporated into the Bi$_2$Se$_3$ matrix without altering the quintuple layer structure. The ARPES result shows the magnetic doping can also drive the topologically protected surface states into the massive Dirac fermions region. Furthermore, magnetization measurements confirm that the ferromagnetic ordering forms below $T_C \approx 35$ K. In addition, the semiconductor behavior and the presence of Anomalous Hall Effect are all revealed by transport measurements. It is important to approach the bulk insulating state by decreasing the carrier concentration. The Fermi level also needs to be engineered in the surface states band gap with the fabrication of gated devices. By combining them together, we can verify the intrinsic magnetic mechanisms inside the Cr doped TI systems and forward a crucial step towards the realization of critical QAH effect and magneto-electric coupling based applications.

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