Microstructure, magnetic, and spin-dependent transport properties of (Zn,Cr)Te films fabricated by magnetron sputtering

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Chromium doped zinc telluride thin films with various doping concentrations are fabricated by magnetron sputtering. These films are ferromagnetic and the Curie temperature increases with Cr concentration. X-ray diffraction, transmission electron microscopy, and magnetic circular dichroism characterizations show that the films are free of Cr$_{1-x}$Te$_x$ impurities and the ferromagnetism is intrinsic. The transport study shows that the resistivity and magnetoresistance are governed by variable range hopping at low temperatures. A negative magnetoresistance as large as ~57% is observed at 5 K. The magnetoresistance and its temperature dependence can be well explained by a model involving an increase in the localization length of carriers with a magnetic field in the hopping region. An anomalous Hall effect is also observed and a possible origin of the sign difference between the anomalous Hall resistance and ordinary Hall resistance is discussed.

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I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) have attracted a great deal of attention due to their fertile physics and promising applications in spintronic devices. With a DMS, a direct spin injection into a semiconductor becomes possible, and magnetoresistance can now be manipulated by ferromagnetic properties can now be manipulated by electrical or optical means. Many studies on DMSs were done in pioneering systems, such as Ga$_{1-x}$Mn$_x$As (Refs. 4–8) and In$_{1-x}$Mn$_x$As. Various efforts were also focused on transition metal doped II–IV compounds and oxides. Especially for Cr or V doped ZnTe, first principles calculations based on the density functional theory predicted an ferromagnetic ground state that is more favorable than the antiferromagnetic or spin-glass state. Indeed, Saito et al. found that the Curie temperature ($T_C$) in (Zn$_{1-y}$Cr$_y$)Te could be as high as 300 K and the ferromagnetism was proved by the magnetic circular dichroism (MCD) that originated from the s, p-d interaction of Cr ions and the ZnTe host. Later, this work was confirmed by Ozaik et al. Very recently, Ozaik et al. studied the carrier doping effect in (Zn$_{1-y}$Cr$_y$)Te and found that while the ferromagnetism was suppressed by a p-type doping, it was significantly enhanced by a n-type doping. In all of these reports, (Zn$_{1-y}$Cr$_y$)Te samples were fabricated by molecular beam epitaxy (MBE), and the transport properties were not studied in detail.

In this paper, we report the study of (Zn$_{1-y}$Cr$_y$)Te films fabricated by magnetron sputtering. Various characterizations show that these samples are free of Cr$_{1-x}$Te$_x$ impurities and the ferromagnetism is intrinsic. A more in-depth transport study demonstrates that at low temperatures the resistivity and magnetoresistance (MR) are governed by the Efros–Shklovskii (ES)-type variable range hopping (VRH). The anomalous Hall effect (AHE) is also observed.
TABLE I. Sample compositions determined by EDX.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn (%)</th>
<th>Cr (%)</th>
<th>Te (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>47.2</td>
<td>5.8</td>
<td>47</td>
</tr>
<tr>
<td>Sample B</td>
<td>43</td>
<td>6.8</td>
<td>50.2</td>
</tr>
<tr>
<td>Sample C</td>
<td>43</td>
<td>7.5</td>
<td>49.5</td>
</tr>
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III. RESULTS AND DISCUSSIONS

A. Structural characterization

The composition of the three samples in this study is summarized in Table I. Figure 1 shows the XRD patterns of these samples. The diffraction patterns clearly show the polycrystalline nature of the sputtered (Zn,Cr)Te films. All diffraction peaks are indexed as a zinc blende structure. For sample A with the lowest Cr concentration, the film shows a very strong [111] orientation. It is known that chromium and tellurium form a wide range of magnetic compounds Cr₁₋ₓTeₓ with Curie temperature ranging from 100 to about 350 K.\(^{22}\)

To confirm that there is no Cr₁₋ₓTeₓ phase, we performed high resolution TEM (HRTEM) studies. Figure 2(a) shows the plan-view HRTEM picture of the representative sample C. Grains with sizes of 10–15 nm can be seen in different orientations. No Cr₁₋ₓTeₓ clusters can be detected over a wide range of film areas. Figure 2(b) shows one of the selected area diffraction patterns (SADPs) from sample C. Again, all diffraction rings can be attributed only to the zinc blende structure. The area for SADPs is about 1 µm². All SADPs from the different parts of the sample show no existence of a secondary phase. Similar results have been observed in samples A and B.

B. Magnetic properties

Figure 3(a) shows the hysteresis loop of representative samples B and C measured by SQUID. The saturation moment per Cr atom for sample C is about 1µₘ at 5 K, which is much smaller than the reported value of 2.6µₘ in the MBE samples.\(^{12,15}\) The origin of ferromagnetism in (Zn,Cr)Te is believed to be the double-exchange interaction between the d electrons of Cr atoms, instead of the carrier-mediated mechanism as in (Ga,Mn)As since the ferromagnetism is suppressed by increasing hole concentrations.\(^{16}\)

Besides ferromagnetic double-exchange interaction, antiferromagnetic coupling between Cr ions could also exist in our samples. Due to the highly disordered nature of the polycrystalline films compared to the (Zn,Cr)Te fabricated by MBE, it is likely that substitutional Cr ions also antiferromagnetically interact with some interstitial Cr ions, which are similar to the antiferromagnetic coupling in (Ga,Mn)As due to Mn interstitial.\(^{8,26}\) Thus, the average Cr moment is reduced. The temperature dependence of the magnetization [Fig. 3(b)] shows the irreversible behavior between the zero-field-cooled (ZFC) and field-cooled (FC) measurements. This behavior was also reported in the (Zn,Cr)Te films grown by MBE,\(^{15,17}\) in which the effect was attributed to the inhomogeneity of ferromagnetic interaction in the samples.\(^{15}\)

In our case, this irreversible behavior could result from the coexistence of ferromagnetic and antiferromagnetic interactions (therefore, a possible micromagnetic or spin-glass phase), as reported before for (Zn,Co)O (Ref. 27) and (Zn,Mn)Te.\(^{28}\) It could simply be due to the applied magnetic field of 1000 Oe that is smaller than the coercive field (1350 Oe at 5 K). The fit of the magnetization versus temperature by Curie–Weiss law yields a Curie temperature of 205 K for sample C. The Curie temperatures of other samples are determined in the same manner. The insert of Fig. 3(b) shows that Tₐ increases with Cr concentration as expected.

In order to confirm that the observed ferromagnetic signal is from the interaction of substitutional Cr ions and ZnTe host, we performed the MCD measurement in the Faraday configuration with an applied field along the light propagation direction. In a DMS material, the strong hybridization of the conduction s-p carrier and localized d spins leads to a large Zeeman splitting \(\Delta E = (N\beta - N\alpha)x(S_z) + g^*\mu_B H\) between the dominant transition energies by \(\sigma^+\) and \(\sigma^-\) photons,\(^{29}\) where \(N\alpha\) and \(N\beta\) are, respectively, the s-d and p-d exchange constants, \(x\) is the concentration of the magnetic ions, \(S_z\) is the average moment of the magnetic ion along the field \(H, g^*\) is the factor for the diamagnetic host, and \(\mu_B\) is the Bohr magneton. The MCD signal, which is the reflection difference between \(\sigma^-\) and \(\sigma^+\) polarized photons, is directly proportional to \(\Delta E\) and \(dR/dE\), where the latter is the derivative of reflectivity with respect to the photon energy.\(^{30}\) The \(dR/dE\) term will have an extremum near the critical points of each material depending on the band structure. In our case, the MCD intensity is much enhanced near the critical point of ZnTe with the superposition of a strong Fabry–Pérot interference pattern, giving an oscillation behavior similar to what was observed in MBE grown (Zn,Cr)Te films.\(^{31}\)

The \(\Delta E\) term is proportional to the magnetization; thus, it is expected to see the ferromagnetic field dependence in the MCD intensity for a ferromagnetic DMS.\(^{29}\) Figure 3(c) shows the magnetic field dependence of MCD intensity for sample C at the photon energy very close to the \(\Gamma\) critical
point of ZnTe. Although the magnetic field in our measurement is not enough to saturate the magnetization, the field dependence of the MCD intensity exhibits a shape very similar to the $M-H$ curve. This indicates that the magnetization originates from the $s$, $p-d$ interaction of carrier and localized moment, which has a large magneto-optical effect at an energy near the $\Gamma$ critical point of ZnTe.\textsuperscript{12,15}

C. Transport properties

In this study, samples show typical semiconductor behaviors in the transport measurement [Fig. 4(a)]. The temperature dependence of the resistivity for all three samples at low temperature can be fitted by ES-type VRH, as shown in Figs. 4(b)–4(d). VRH is the main mechanism of conduction at low temperature for many DMS systems.\textsuperscript{7,32,33} In the ES-type VRH, the density of states is zero at Fermi energy ($E_F$) due to the Coulomb interaction between electrons.\textsuperscript{23} The room temperature resistivity in our polycrystalline sample containing 7\% Cr is more than an order of magnitude smaller than that of single crystalline MBE samples with 20\% Cr.\textsuperscript{14} The difference would be even larger if two types of samples have the same amount of Cr concentration because the resistivity is inversely proportional to doping concentration, as shown in Fig. 4(a) and as reported previously.\textsuperscript{12,14} The smaller resistivity in the polycrystalline samples could be caused by


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the so-called charge trapping effect, which is commonly observed in polycrystalline semiconductors.\textsuperscript{34–36} It is known that the charge (electron or hole) can be easily trapped by defects and dangling bonds at the grain boundaries, and sometimes, the resistivity of the whole sample is reduced due to relatively high conducting channels in the grain boundaries, as reported in polycrystalline Ge (Ref. 34) and GaSb (Ref. 35) films. The resistivity curve of sample A that crossed samples B and C at a lower temperature is noticed in Fig. 4(a). A similar crossing of resistivity curves between samples with different doping concentrations was also observed in other DMS systems.\textsuperscript{37,38} In our case, this behavior could be related to different stoichiometries of the films, as shown in Table I. Although achieving a nearly stoichiometric composition is generally very difficult for all DMS materials, sample A seems to contain more excessive Zn compared to the other two samples. It is known that Zn interstitials ($Zn_i$) or Zn vacancies often form shallow levels in the band gap, while the Cr dopant forms deeper levels at 0.2 eV above the valence band maximum.\textsuperscript{39–41} Moreover, all of these levels are subjected to a shift in the presence of a charge trapping effect of the grain boundaries in polycrystalline (Zn,Cr)Te samples.\textsuperscript{34,42} Therefore, the resistivity crossover of sample A is possibly due to the competition between the activation of $Zn_i$ and deeper dopant levels. At a low temperature, the activation from shallow $Zn_i$ in sample A dominates, resulting in a lower resistivity compared to the other two samples, while


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FIG. 2. (a) Plan-view HRTEM picture for sample C. (b) Selected area diffraction pattern for sample C.

FIG. 3. (Color online) (a) Hysteresis loops of samples B and C with applied magnetic field in the film plane. (b) FC and ZFC magnetizations as functions of temperature for sample C. The inset shows the Cr concentration dependence of $T_C$ for three samples and (c) magnetic field dependence of MCD intensity for sample C at 17 K.
the activation from the deeper dopant levels dominates at a high temperature in all three samples, giving rise to the proportionality between doping concentration and conductivity, as reported earlier.12,14

A similar negative MR was observed in all three samples. Figure 5(a) shows the negative MR (MR=[R(H)−R(0)]/R(0)), which is as large as −57%, observed in sample C at 5 K. The shape of the MR only changes a little when the applied external field changes from perpendicular-to-plane to parallel-to-plane (and parallel to the current), which is similar to what was previously observed in the (Zn,Cr)Te samples grown by MBE.14 Therefore, this MR is not the anisotropic magnetoresistance which is observed in traditional magnetic materials. At low fields, the MR exhibits a hysteretic behavior with maximum resistance at coercive fields, as shown in the inset of Fig. 5(a). The MR was negative at low temperatures and changes to positive at temperatures above TC in the MBE samples;14 while in our case, the MR is negative up to 300 K, as shown in Fig. 5(b). The MR for sample B at 35 K is displayed in the inset of Fig. 5(b), essentially showing the same behavior as sample C. A large negative MR was previously reported in many DMS systems such as (Ga,Mn)As,5−7,33 (In,Mn)As,9,10 and in MBE grown (Zn,Cr)Te.14 A couple of scenarios were proposed to explain the observed negative MR. One of them is based on the delocalization of carriers due to an applied field in the Anderson localization region.43 In this picture, the applied magnetic field will shift EF by gμBH because of the Zeeman effect. This Zeeman shift will introduce a decrease in [Ec−EF] for either the spin-up or spin-down subband, where Ec is the mobility edge. This will lead to an increase in conduction since the localization length is inversely proportional to [Ec−EF].4,6,33 Another scenario is based on the formation of bound magnetic polaron, where Mn spins near the localized holes are aligned through the p-d exchange interaction. These holes will become more mobile when most of the Mn spins in the sample are aligned by an external magnetic field, which is in contrast to the zero-field situation where the moving of polaron would involve flipping many Mn spins, thus making the polaron massive and immobile.6,33

However, no quantitative description of the large negative MR was given in the two cases above. Here, we demonstrate that the negative MR in our samples can be well fitted by a theory proposed by Medina et al.44,45 In this model, the hopping conductance is treated as the sum of all possible tunneling paths between impurities. In the diffusive conduction region, the negative MR is produced by the reduction in coherent backscattering when a phase shift of the electron wave function is introduced by the applied magnetic field. While in the VRH region, an electron experiences multiple elastic scattering in the course of hopping, which is fundamentally different from the normal diffusion process. In this strong localization region, the conduction is dominant by the forward scattering only and the backward scattering is not important. The applied magnetic field can suppress the interference between different scattering paths in the hopping process, thus leading to a negative MR.46 The numerical simulation in this model demonstrates that the localization length of the carrier will increase by the square root of the applied field.44 This theory predicts that the MR has the form

$$\rho(H) \propto \exp\left[PH^{1/2}\right].$$

(1)

where P is a constant for a specific temperature. As shown in Fig. 6(a), the MR can be well fitted by using Eq. (1). The
fitting parameter $P$ is linearly dependent on $T^{-1/2}$ as it should be for the conduction governed by ES-type VRH at a low temperature, giving further evidence to validate this model.

AHE is also detected in sample C, as shown in Fig. 7. A distinguishable feature of an intrinsic ferromagnetic semiconductor is the exchange interaction between the carriers and localized moments. The observation of AHE gives further evidence of the intrinsic nature of our samples. It is worth noting that AHE was not observed in the (Zn,Cr)Te films grown by MBE.\textsuperscript{14} Although the exact origin of this discrepancy is not clear at this time, it is possibly related to the presence of the large amount of defects and disorders in the polycrystalline samples; as it has been reported in many studies that defects and disorders play a very important role in DMS.\textsuperscript{47} Another reason might be the large resistivity at low temperatures in MBE films. Usually, AHE is only observed in DMS samples with relatively small resisitivities,\textsuperscript{4,10,33,48} since experimentally it is very hard to distinguish the AHE signal from the large longitudinal resistance at low temperatures.\textsuperscript{33,49,50}

Generally, the Hall resistance can be expressed as $R_{\text{Hall}} = R_{\text{OH}} + R_{\text{AH}} = R_B + 4\pi MR_S$. The ordinary Hall resistance $R_{\text{OH}}$ and the anomalous Hall resistance $R_{\text{AH}}$ are proportional to the external field $B$ and the magnetization, respectively. As mentioned above, the Hall effect is hard to measure in the hopping region due to its large longitudinal resistance. In our case, the measured Hall voltage inevitably picked up some MR signal due to the finite size of the voltage leads of the Hall bar, giving rise to the slight asymmetric curve. After subtracting the MR signal at large fields ($>5$ T), we determined that the carrier is $p$ type and the hole density is estimated to be $2 \times 10^{16}$ cm\textsuperscript{-3} at 10 K. It is interesting to note that the $R_{\text{AH}}$ part is electronlike (negative), while the $R_{\text{OH}}$ part is holelike (positive). The electronlike carrier type in the AHE region in a $p$-type sample was also observed in (In,Mn)Sb (Ref. 51) and (Ga,Mn)As.\textsuperscript{33,50} A possible origin of this behavior can be understood by a model developed by Burkov and Balents,\textsuperscript{24} which has been used to study the AHE in DMS materials such as MnGe (Ref. 37) and (Ga,Mn)P.\textsuperscript{52} In this model, the origin of AHE was attributed to the phase that carriers gained during hopping conduction in the presence of spin-orbital interaction and background magnetization of localized moment. Specifically, it predicts

\[ R_{\text{AH}} \propto B f_1(T) \exp(T_0/T)^\beta, \]

\[ R_{\text{OH}} \propto M f_2(T) [d \ln(N_0)/dE]^{-1} \exp(T_0/T)^\beta, \]

where $B$ is the magnetic induction, $M$ is the magnetization, $N_0$ is the density of states at $E_F$, $f_1(T)$ and $f_2(T)$ are the power law functions, and $\beta=1/4$ or 1/2, corresponding to Mott-type VRH and ES-type VRH, respectively.\textsuperscript{24,50} Equation (2) shows that while the sign of $R_{\text{OH}}$ is fixed for $E_F$ throughout the impurity band, the sign of $R_{\text{AH}}$ is dependent on the logarithmic derivative of the density of states at $E_F$. Therefore, $R_{\text{AH}}$ could have both positive and negative signs, depending on the location of $E_F$ with respect to the extremum of the density of states, e.g., the sign of $R_{\text{AH}}$ is determined by the slope of the density of states at $E_F$. Indeed, both positive and negative $R_{\text{AH}}$ were observed in samples prepared under different conditions.\textsuperscript{50} In our case, $E_F$ is determined by many factors, such as defects, doping concen-
transport, compensation, and so on. Therefore, it is possible that the slope of the density of states is negative at $E_F$ and thus gives the negative sign of $R_{AH}$.

IV. CONCLUSION

We presented a study on chromium doped zinc telluride films fabricated by magnetron sputtering, XRD, TEM, and MCD characterizations reveal that these films contain no secondary phases and the ferromagnetism comes from the intrinsic diluted magnetic semiconductor (Zn,Cr)Te. Transport study shows that resistivity and magnetoresistance are governed by variable range hopping at low temperatures. The large negative magnetoresistance can be well explained by a model involving the expansion of localization length with a magnetic field in the hopping region. The anomalous Hall effect is also observed and the sign difference between the anomalous Hall resistance and ordinary Hall resistance is discussed.

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