Room-Temperature Ferromagnetism in a II-VI Diluted Magnetic Semiconductor $Zn_{1-x}Cr_xTe$

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The magnetic and magneto-optical properties of a Cr-doped II-VI semiconductor ZnTe were investigated. Magnetic circular dichroism measurements showed a strong interaction between the *sp* carriers and localized *d* spins, indicating that $Zn_{1-x}Cr_xTe$ is a diluted magnetic semiconductor. The Curie temperature of the film with $x = 0.20$ was estimated to be 300 ± 10 K, which is the highest value ever reported for a diluted magnetic semiconductor in which *sp-d* interactions were confirmed. In spite of its high Curie temperature, $Zn_{1-x}Cr_xTe$ film shows semiconducting electrical transport properties.

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While semiconductor devices use *s, p* electrons, magnetic devices use *d* electrons to perform their functions. If the strong interactions between *s, p* electrons and *d* electrons could be used in a single semiconductor, new devices for information processing and data storage could be created by combining the functions of semiconductors and magnetic materials. In attempts to develop such spintronic devices [1], much effort has been made to find ferromagnetic semiconductors based on II–VI [2–4], III–V [5–7], and IV [8] compounds. $In_{1-x}Mn_xAs$ [5,6] and $Ga_{1-x}Mn_xAs$ [7] are pioneering examples of such diluted magnetic semiconductors (DMSs) with a long-range ferromagnetic order. However, if is difficult to control their magnetic and semiconducting properties independently because their ferromagnetism is induced by holes (10^{19}–10^{20} cm^{-3}) that are self-supplied from doped Mn ions. Such a large number of holes inevitably change their transport and optical properties from semiconducting to metallic. Even with heavy doping, the highest Curie temperature T_C of 110 K in $Ga_{1-x}Mn_xAs$ is still lower than room temperature (RT).

Recently, RT ferromagnetism was reported in GaN:Mn [9–11], GaN:Cr [12,13], TiO_2:Co [14], $CdGeP_2$:Mn[15], and ZnO:Co [16]. Although the ferromagnetism in those materials was attributed to the expected ferromagnetism of the DMSs on the basis of magnetization measurements and crystallographic studies, such as x-ray diffraction (XRD) analysis, it is still open to discussion whether the observed ferromagnetism comes from the DMSs or from magnetic precipitates. In resolving this controversy, we note that a critical distinguishing characteristic of a DMS is the *sp-d* exchange interaction [17]. Therefore, confirmation of the *sp-d* exchange interaction is essential in judging whether or not the synthesized material is a DMS. The *sp-d* interaction can be investigated by magneto-optical studies such as magnetic circular dichroism (MCD) spectroscopy because magneto-optical effects are directly related to the Zeeman splitting of the band structure caused by the *sp-d* exchange interaction [17,18]. MCD arises from the difference between the optical absorption for left and right-circular polarized light [18]. Its intensity linearly depends on the Zeeman splitting energy that is proportional to the magnetization. Thus, the magnetization process of a DMS can be obtained from the magnetic field dependence of the MCD intensity. Moreover, the MCD spectral shape provides a fingerprint of the material because the MCD intensity is strongly enhanced around the optical transition energies *E* corresponding to the critical points (CP) of the host semiconductor [18]. Thus, a DMS can be easily distinguished from the magnetic precipitates by analysis of the MCD spectral shape. We carried out a MCD study of several ferromagnetic materials. Our MCD studies showed that $Ga_{1-x}Mn_xAs$ [19] and $In_{1-x}Mn_xAs$ [20] are real ferromagnetic DMSs. Conversely, our studies clearly showed that the DMSs in ZnO:Co, ZnO:Ni [21], and GaN:Mn [22] are, in reality, paramagnetic. The observed ferromagnetism comes from some unidentified materials. These results suggest that XRD is not sensitive enough to exclude the presence of ferromagnetic precipitates.

$Zn_{1-x}Cr_xTe$ has been reported to be a DMS with a *sp-d* interaction in bulk [23] and film [24,25] samples. We confirmed the intrinsic ferromagnetism in $Zn_{1-x}Cr_xTe$ ($x = 0.035$) film [26,27] using MCD measurements. This material is the third real ferromagnetic DMS after $In_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$, in which the *sp-d* exchange interaction has been confirmed. T_c was about 15 K, which is much higher than the T_c (2–3 K) of a previously reported ferromagnetic Mn-doped II-VI DMSs [2–4]. While these II-VI DMSs with low T_c were heavily carrier doped, the carrier (hole) concentration of $Zn_{1-x}Cr_xTe$ ($x = 0.035$) was very low (1×10^{15} cm^{-3} at RT) [26]. $Zn_{1-x}Cr_xTe$ is expected to be a useful ferromagnetic DMS, in which the transport properties can be controlled by carrier doping.

In this study, we report RT ferromagnetism in a $Zn_{1-x}Cr_xTe$ film with higher Cr concentration. The film kept its semiconducting transport properties.

$Zn_{1-x}Cr_xTe$ films, 200 to 400-nm thick, with Cr concentration $x \leq 0.2$ were grown at 250–300 °C on 200-nm thick ZnTe buffer layers grown at 300 °C on semi-insulating GaAs (001) substrates using a molecular beam epitaxy (MBE) method. The reflection high-energy electron diffraction (RHEED) patterns of the ZnTe buffer layers were streaky. The $Zn_{1-x}Cr_xTe$ films showed a streaky RHEED pattern at $x < 0.04$ and spotted patterns at $x > 0.04$. The formation of twins was also observed at $x > 0.1$. To measure the MCD spectra at a photon energy higher than the optical band gap (2.4 eV) of ZnTe, a 80-nm thick $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film was grown on a very thin ZnTe buffer layer (several monolayers thick). No sign of a secondary phase was detected in any of the films by RHEED and x-ray diffraction. As a reference sample, a NiAs-type CrTe film (about 10-nm thick) was also prepared on a sapphire (0001) substrate at 300 °C using an MBE method. The Cr concentration x was determined by an electron probe microanalysis.

MCD spectra were measured using a spectrometer (JASCO J-600) with alternating circularly polarized light (50 kHz) produced by a quartz stress modulator. To measure the MCD in a transmission configuration, GaAs substrates of the samples were removed by chemical etching. A magnetic field $\mu_0 H$ was applied perpendicular to the film plane. Magnetization measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer in the magnetic fields applied perpendicular to the film plane. Resistivity was measured by the four-probe method using an apparatus designed for high-resistive samples up to 10^{12} Ω. The Ohmic behavior of the electrical contact using indium electrodes was confirmed up to a bias voltage of 10 mV.

Figure 1 shows the magnetization curves of $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film. The diamagnetic contribution from the substrate was subtracted. At a temperature of $T = 20$ K, a large ferromagnetic hysteresis loop was observed. The value of the magnetic moment at $\mu_0 H = 1$ T is about 2.6 μ_B per Cr ion, which is almost the same value as that of $Zn_{1-x}Cr_xTe$ ($x = 0.035$) film [26,27]. It should be noted that the ferromagnetic feature remains even at $T = 300$ K. To estimate the spontaneous magnetization M_s and T_c, the Arrott plot analysis of magnetization was used. The Arrott plot analysis is the most reliable method of obtaining accurate M_s and T_c because it only uses data under the higher magnetic fields where the effect of magnetic anisotropy and the formation of a magnetic domain can be neglected [28]. In the Arrott plot, the intercept of a linear extrapolation of M^2-$\mu_0 H/M$ plot to $\mu_0 H/M = 0$ from high magnetic fields corresponds to M_s^2. The Arrott plots of the film are given in an inset in Fig. 1. With increasing T, M_s decreases and disappears at $T = 300 \pm 10$ K, which corresponds to T_C.

To confirm that the observed ferromagnetism originated from the $Zn_{1-x}Cr_xTe$ DMS, we analyzed the MCD spectral shape. Figure 2 shows the MCD spectra of the samples at $T = 20$ K and $\mu_0 H = 1$ T. Each sample shows a characteristic MCD spectral shape, reflecting its band structure. The RT ferromagnetic CrTe film [Fig. 2(a)] shows a broad spectrum reflecting its metallic nature, which is completely different from that of ZnTe and $Zn_{1-x}Cr_xTe$. A 100-nm thick ZnTe film [Fig. 2(b)] showed weak MCD signals around the Γ (2.4 eV) and L

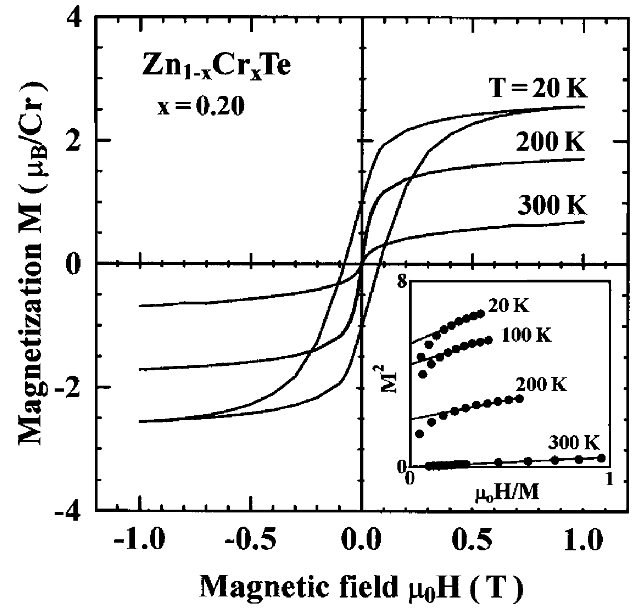

FIG. 1. Magnetization curves of $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film at various T. The inset shows the Arrott plots of the magnetization data.

(3.7 eV and 4.2 eV) critical points (CP) due to the diamagnetic Zeeman effect. An 80-nm thick $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film on a thin ZnTe buffer [Fig. 2(c)] also showed pronounced MCD structures at photon energies corresponding to the L-CPs of ZnTe, indicating that $Zn_{1-x}Cr_xTe$ shares a common band structure with ZnTe. It should be noted that the shape of the peak structures at the L-CPs of $Zn_{1-x}Cr_xTe$ is qualitatively different from that of ZnTe. While the polarities of the MCD peaks of ZnTe are positive at both L-CPs, the $Zn_{1-x}Cr_xTe$ film shows a positive MCD peak at 3.7 eV and a negative signal at 4.2 eV [18,24]. This characteristic MCD structure reflects the opposing polarities of the Zeeman splittings for the two L-CPs of $Zn_{1-x}Cr_xTe$ [18,24]. This is in accordance with the general character of the Zeeman splitting induced by the *sp-d* exchange interaction [29]. The polarities of the peaks correspond to the ferromagnetic *p-d* exchange interaction in agreement with previous studies of bulk [23] and film [18,24] samples. The $Zn_{1-x}Cr_xTe$ film was therefore confirmed to be a DMS.

Around Γ-CP, a broadened MCD spectral shape was observed in $Zn_{1-x}Cr_xTe$ film. To confirm that this broadened MCD spectrum also originated from the $Zn_{1-x}Cr_xTe$ DMS, we studied the magnetic field dependence of the MCD spectral shape. The normalized MCD spectra of $Zn_{1-x}Cr_xTe$ film on a thin ZnTe buffer at different magnetic fields are given in the inset of Fig. 2(c′). If the film contains magneto-optically active precipitates, the shape of the MCD spectrum should change with $\mu_0 H$ because of the different magnetization processes and different spectral shapes of $Zn_{1-x}Cr_xTe$ and the precipitates [21,30]. The spectra measured at any magnetic field can be superposed upon a single spectrum over

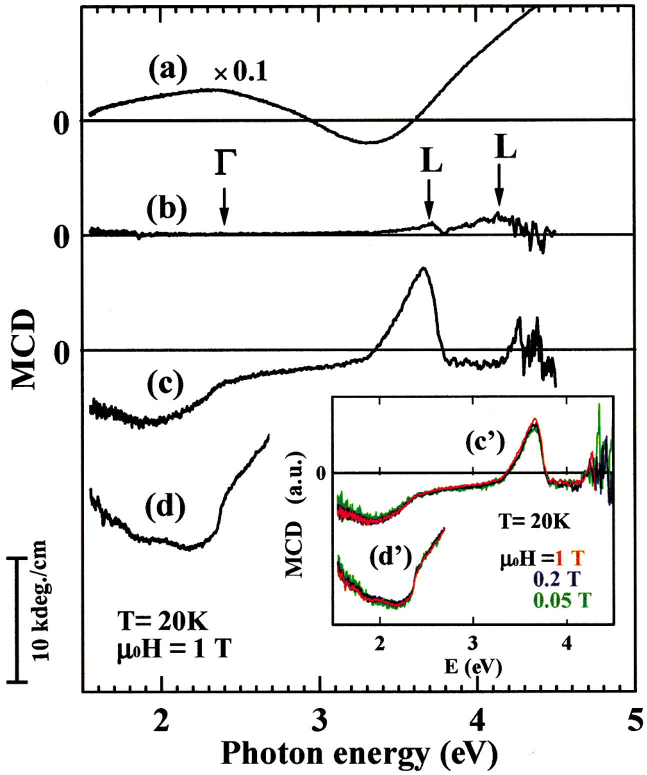

FIG. 2 (color). MCD spectra of (a) room-temperature ferromagnetic compound CrTe film, (b) 100-nm thick ZnTe film, (c) 80-nm thick $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film on ZnTe buffer with several monolayers, and (d) 400-nm thick $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film on 200-nm thick ZnTe buffer at $T = 20$ K and $\mu_0 H = 1$ T. MCD spectra of both 80- and 400-nm thick $Zn_{1-x}Cr_xTe$ ($x = 0.20$) films at $T = 20$ K measured in any magnetic fields can be superposed upon a single spectrum over the whole photon energy range [(c′) and (d′)].

the whole photon energy range. This indicates that the observed MCD spectra come from a single material, i.e., $Zn_{1-x}Cr_xTe$.

$Zn_{1-x}Cr_xTe$ ($x = 0.20$) film on a thick ZnTe buffer shows a similar MCD spectral shape [Fig. 2(d)] to a film with a thin buffer [Fig. 2(c)]. Because of the huge optical absorption above the band gap of the film on the thick ZnTe buffer, reliable MCD data were obtained only below 2.7 eV. A clearer step structure around the Γ-CP can be seen in Fig. 2(d). This indicates that $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film on a thick ZnTe buffer also has the same band structure as ZnTe and that its film quality is better than that of the film on a thin ZnTe buffer. The MCD spectra of a $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film on a thick ZnTe buffer in any magnetic field could also be normalized [Fig. 2(d′)].

The magnetic field dependence of MCD intensity for $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film on a thick ZnTe buffer near Γ-CP at $T = 20$ K and 293 K are shown in Fig. 3. As expected, the MCD data in Fig. 3 coincide with the magnetization curves measured using a SQUID (Fig. 1). Also, the MCD data showed that the ferromagnetic feature still remains even at around RT. Because the MCD signal is intrinsic to $Zn_{1-x}Cr_xTe$, Fig. 3 clearly shows

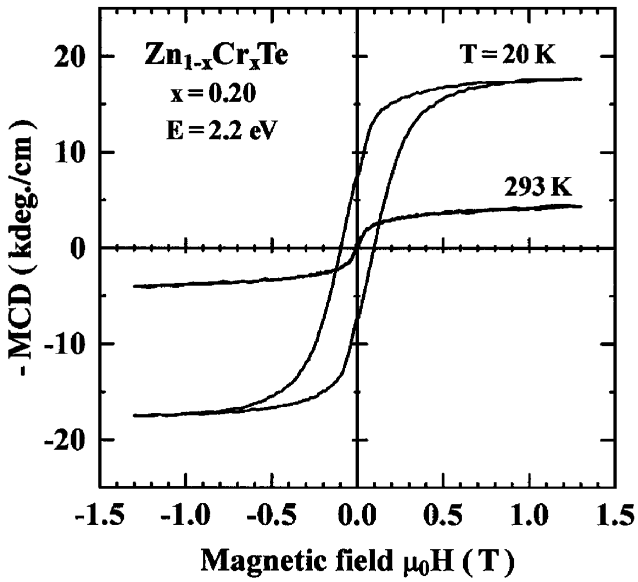

FIG. 3. Magnetic field dependence of MCD intensity of $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film at $E = 2.2$ eV and $T = 20$ K and 293 K.

that the observed ferromagnetism comes solely from $Zn_{1-x}Cr_xTe$, not from the precipitates. The Arrott plots of the MCD data also indicate the ferromagnetic state up to RT (Fig. 4). The inset in Fig. 4 shows the temperature dependencies of MCD intensity at $\mu_0 H = 0$ T obtained by the Arrott plots, together with that of M_S. MCD data showed the same T_C as that obtained from the magnetization data of 300 ± 10 K. These results clearly indicate that $Zn_{1-x}Cr_xTe$ is a real RT ferromagnetic DMS. $Zn_{1-x}Cr_xTe$ film on a thin ZnTe buffer also shows

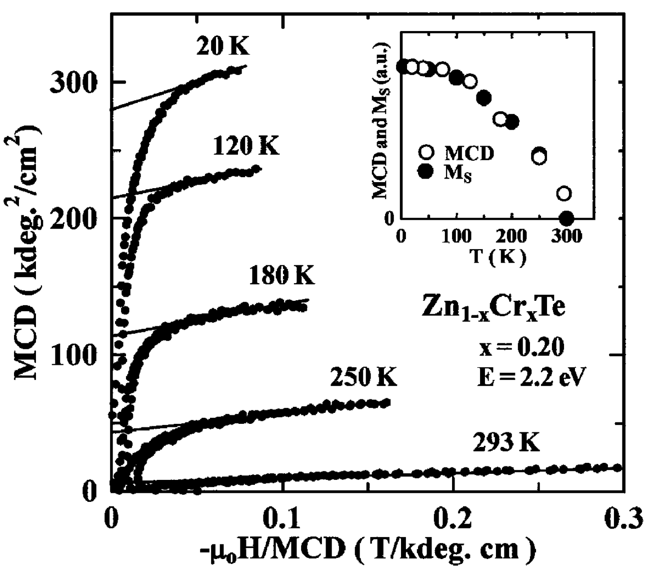

FIG. 4. Arrott plots of MCD intensity of $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film at $E = 2.2$ eV and various T. The inset shows the temperature dependence of MCD intensity (open circles) extrapolated to $\mu_0 H = $ T obtained by the Arrott plot, together with that of M_S (solid circles).

ferromagnetic behavior, but its magnetic moment (about 1.2 μ_B/Cr at $\mu_0 H = 1$ T, $T = 5$ K) and T_C (about 200 K) is lower than those of films on a thick buffer. The magnetic properties seem to sensitively depend on the quality of the film. By optimizing the growth conditions, a higher T_C could be realized.

The temperature dependence of the resistivity for $Zn_{1-x}Cr_xTe$ ($x = 0.20$) film on a thick ZnTe buffer was measured. Contributions from the GaAs substrate and ZnTe buffer layer could be neglected since the resistivity of a semi-insulating GaAs substrate (0.36×10^9 Ω cm at RT, according to a certificate of quality) and a ZnTe buffer layer (1.0×10^5 Ωcm at RT, according to this study) is several orders higher than that of a $Zn_{1-x}Cr_xTe$ layer. The resistivity of the $Zn_{1-x}Cr_xTe$ film shows semiconducting behavior, that is, a monotonous increase with decreasing T. The resistivity of the film at RT and 100 K are 58 and 280 Ω cm, respectively, which is several orders higher than that of $Ga_{1-x}Mn_xAs$ [31] and comparable to that of $Zn_{1-x}Cr_xTe$ ($x = 0.035$) film [26,27]. For $Zn_{1-x}Cr_xTe$, both the carrier-induced [32,33] and superexchange [34] interactions were theoretically predicted to be ferromagnetic. At present, it is not clear which interaction is responsible for the observed ferromagnetism.

In summary, we found that $Zn_{1-x}Cr_xTe$ ($x = 0.20$) is a diluted magnetic semiconductor with room-temperature ferromagnetism. The observed T_C (300 ± 10 K) is the highest value ever reported for a ferromagnetic DMS in which *sp-d* exchange interactions were confirmed. The high resistivity of $Zn_{1-x}Cr_xTe$ suggests that the transport properties in this DMS can be controlled.

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