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Optical properties and functions of dilute magnetic semiconductors

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Abstract

The magneto-optical effect in dilute magnetic semiconductors (DMSs) is directly related to the interaction between the d electrons of the transition metal ions and the s, p electrons of the host semiconductor. We show the advantages of the magneto-optical effect of DMSs as regards fabricating magneto-optical waveguide devices that can be integrated with other semiconductor optical devices. We also discuss the advantages of magneto-optical spectroscopy for characterizing DMSs. Intrinsic ferromagnetism of $In_{1-x}Mn_xAs$, $Ga_{1-x}Mn_xAs$ and $Zn_{1-x}Cr_xTe$ is confirmed by using magnetic circular dichroism (MCD) spectroscopy. The MCD analyses also show that $Zn_{1-x}TM_xO$ (TM = Mn, Fe, Co, Ni or Cu), $Ga_{1-x}Mn_xN$ and $Ga_{1-x}Cr_xAs$ are paramagnetic DMSs with the s, p–d exchange interaction. Ferromagnetic behaviours observed in some transition metal doped ZnO, GaN and GaAs samples are attributed to unidentified precipitations not detectable by means of x-ray diffraction analysis.

1. Introduction

The most distinctive feature of dilute magnetic semiconductors (DMSs) is the strong exchange interaction (s, p–d exchange interaction) between the d spins of the magnetic transition metal ions and the sp carriers [1, 2]. By using this interaction, controlling electrical and optical characteristics of the semiconductor by magnetic field becomes possible. This interaction also enables one to change the magnetic characteristics of the material by electric and optical means. Moreover, it is understood that the appearance of the ferromagnetism observed in some DMSs, such as $Ga_{1-x}Mn_xAs$ [3], is due to this s, p–d exchange interaction. Therefore the confirmation of the s, p–d exchange interaction is the most important task to be carried out when new materials intended to be DMSs are synthesized. Characterization of the s, p–d exchange interaction has been a main topic for the II–VI based DMSs [1, 2]. Recently, controversial interpretations of the ferromagnetism observed in newly synthesized 'DMS' samples have

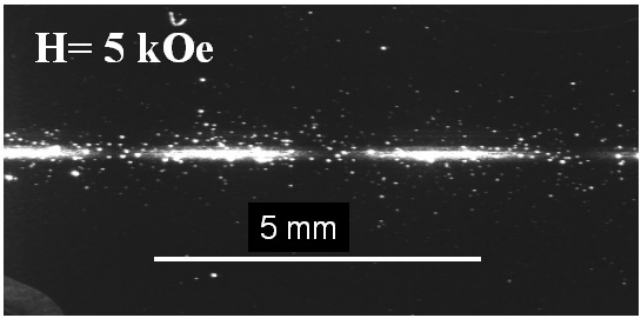

Figure 1. An optical streak of laser light ($\lambda = 730$ nm) propagating in a $Cd_{1-x}Mn_xTe$ waveguide on a GaAs substrate. The TE (transverse electric) mode component scattered from the waveguide surface is shown. Complete magneto-optical TE–TM (transverse magnetic) waveguide mode conversion is achieved at 300 K [12].

been reported [4–11]. One of the reasons for this controversy is a lack of clear data on the s, p–d exchange interaction. This paper reports how the magneto-optical effect induced by the s, p–d exchange interaction makes DMSs attractive materials for future optical communication systems use and how magneto-optical spectroscopy detects the s, p–d exchange interaction in various DMSs.

2. $Cd_{1-x}Mn_xTe$

$Cd_{1-x}Mn_xTe$ is a prototype II–VI DMS. While this DMS is paramagnetic at room temperature, its strong s, p–d exchange interaction induces a huge magneto-optical effect with a small applied magnetic field. This DMS is transparent for wavelengths longer than the optical band gap because the DMS is a semiconductor. And furthermore, its film can be grown directly on GaAs and InP substrates because they share the same zinc-blende-type crystal structure. By combining these unique features, a $Cd_{1-x}Mn_xTe$ waveguide with an optical loss less than 1 dB cm^{-1} and a high magneto-optical figure-of-merit of 200° dB^{-1} kG^{-1} was fabricated and complete magneto-optical waveguide mode conversion was demonstrated (figure 1) [12]. This result demonstrates the attractiveness of DMSs for monolithical integration of magneto-optical devices with other semiconductor optoelectronic devices.

Magneto-optical effects such as magnetic circular dichroism (MCD) also work as most powerful tools for detecting the s, p–d exchange interaction in DMSs [13]. MCD can be used to detect the difference in optical absorption or reflection for left and right circular polarized light caused by the Zeeman splitting. The circular polarized light was generated by combining a spectrometer and a photoelastic modulator. A magnetic field was applied along the light propagation direction (the Faraday geometry). One degree of MCD corresponds to 7% difference of the transmitted or reflected light intensity. Under a magnetic field, any material shows some Zeeman splitting. However, in DMSs, the Zeeman splitting is strongly enhanced by the s, p–d exchange interaction. Hence the MCD signal of $Cd_{1-x}Mn_xTe$ is much more pronounced as compared with that of a host semiconductor CdTe (figure 2). The arrows in figure 2 show the energies of the critical points (CPs) of the band structure. Because the CP provides a fingerprint for each material, we can identify the material that is responsible for the observed MCD signal. This feature of MCD spectroscopy is useful for discriminating between DMSs and second-phase materials that often appear in the synthesized materials. Details of the MCD spectroscopy can be found in [13].

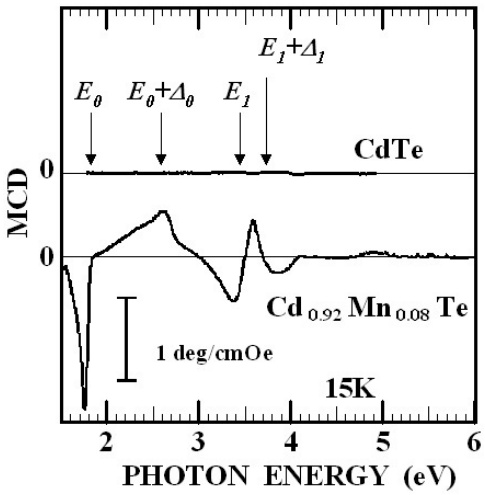

Figure 2. Transmission MCD spectra of CdTe and $Cd_{0.92}Mn_{0.08}Te$. Arrows show the energies of CPs [13].

3. $In_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$

The present enthusiastic interest in DMSs can be traced back to the discoveries of two ferromagnetic DMSs, $In_{1-x}Mn_xAs$ [14] and $Ga_{1-x}Mn_xAs$ [15]. The carrier–spin interaction in these DMSs has been verified by the appearance of the anomalous Hall effect. The MCD spectroscopy also confirms the intrinsic ferromagnetism of these DMSs. A reflection MCD spectrum of $In_{0.88}Mn_{0.12}As$ (figure 3) in remanence shows a strong signal at the photon energy corresponding to CPs of host InAs [16]. This experimental result means that this sample has the s, p–d exchange interaction and it shares the band structure of InAs. The magnetic field dependence of the MCD signal intensity shows clear ferromagnetic hysteresis [16]. A paramagnetic $In_{1-x}Mn_xAs$ sample also showed the same MCD spectrum with the same polarity. This means that the observed MCD hysteresis does not originate from the stray field from some possible ferromagnetic precipitates, because the stray field should be oppositely directed to the applied field. Thus we can say that the ferromagnetism detected by a superconducting quantum interference device (SQUID) magnetometer really comes from the $In_{1-x}Mn_xAs$ DMS. The same MCD spectral analyses also confirmed the intrinsic ferromagnetism of $Ga_{1-x}Mn_xAs$ [17].

4. $Zn_{1-x}Cr_xTe$: a room temperature ferromagnetic DMS

A SQUID measurement of an epitaxially grown $Zn_{0.8}Cr_{0.2}Te$ film shows a clear ferromagnetic hysteresis [18]. The ferromagnetic Curie temperature T_c estimated from the Arrott plot analysis is about 300 K. In order to establish whether the observed ferromagnetism really comes from the $Zn_{1-x}Cr_xTe$ DMS or not, we also analysed the MCD data [18]. Figure 4 compares the MCD spectra of host ZnTe, Cr doped ZnTe and NiAs-type CrTe. The ZnTe film shows MCD structures with the same polarity near the E_1 and $E_1 + \Delta_1$ CPs, indicating that the polarities of the Zeeman splittings at these two CPs are the same in ZnTe. This is due to a diamagnetic Zeeman splitting. (Zn, Cr)Te film also shows the MCD structures near the E_1 and $E_1 + \Delta_1$ CPs. While the MCD polarity of the E_1 CP is same as that of ZnTe, the polarity of the

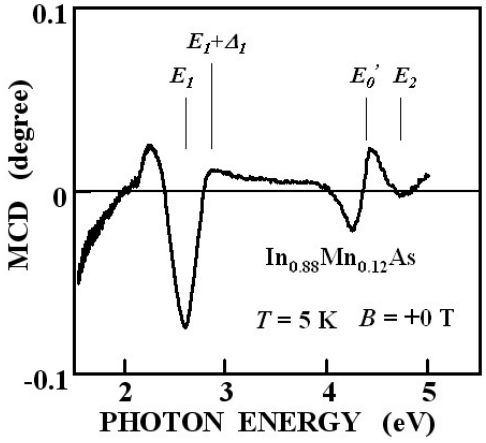

Figure 3. The reflection MCD spectrum of a $In_{0.88}Mn_{0.12}As$ film in the remanence state at 5 K [16].

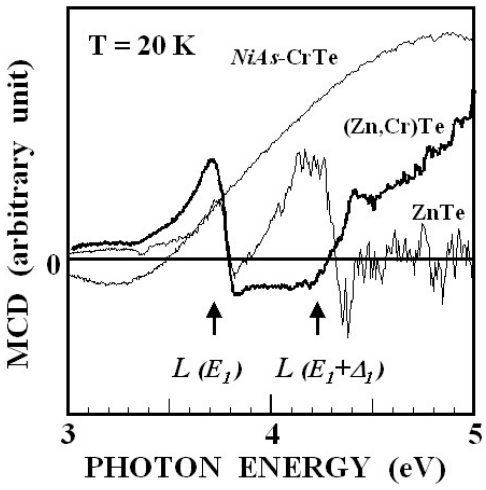

Figure 4. Transmission MCD spectra of ZnTe, (Zn, Cr)Te and NiAs-type CrTe.

$E_1 + \Delta_1$ CP is reversed. These opposite polarities are consistent with a theoretical result [19] that the Zeeman splittings induced by the s, p–d exchange interaction at the E_1 and $E_1 + \Delta_1$ CPs should have opposite polarities. Therefore we can say that the MCD spectral shape near 4 eV shown in figure 4 is a fingerprint of $Zn_{1-x}Cr_xTe$ DMSs. NiAs-type CrTe is the most possible ferromagnetic impurity in this Zn–Cr–Te system. However, as shown in figure 4, we can easily distinguish CrTe from $Zn_{1-x}Cr_xTe$ because the MCD spectrum of CrTe has no structures near 4 eV.

The MCD signal of $Zn_{0.8}Cr_{0.2}Te$ is much stronger than that of ZnTe and its spectral shape shows the characteristic spectral shape of the $Zn_{1-x}Cr_xTe$ DMS around 4 eV (figure 5). The MCD spectral signals at all photon energies show the same ferromagnetic field dependence [18], indicating that the MCD signal originates from a single material. Thus the MCD analyses confirmed the intrinsic ferromagnetism of the $Zn_{1-x}Cr_xTe$ DMS. The resistivity of the $Zn_{0.8}Cr_{0.2}Te$ film showed semiconducting behaviour and was several orders higher than that of $Ga_{1-x}Mn_xAs$ [20]. Therefore, at present, it is not clear whether the carrier-induced ferromagnetism model can explain the observed ferromagnetism of the $Zn_{1-x}Cr_xTe$ DMS.

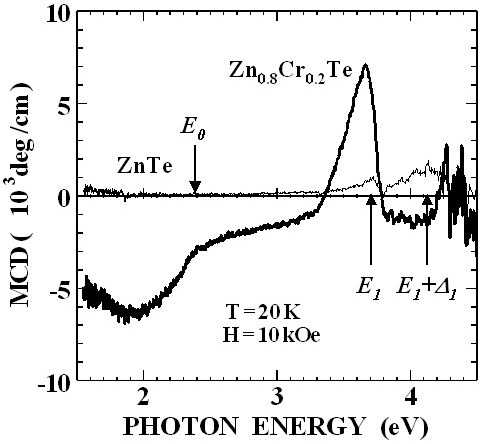

Figure 5. Transmission MCD spectra of ZnTe and $Zn_{0.8}Cr_{0.2}Te$ films [18].

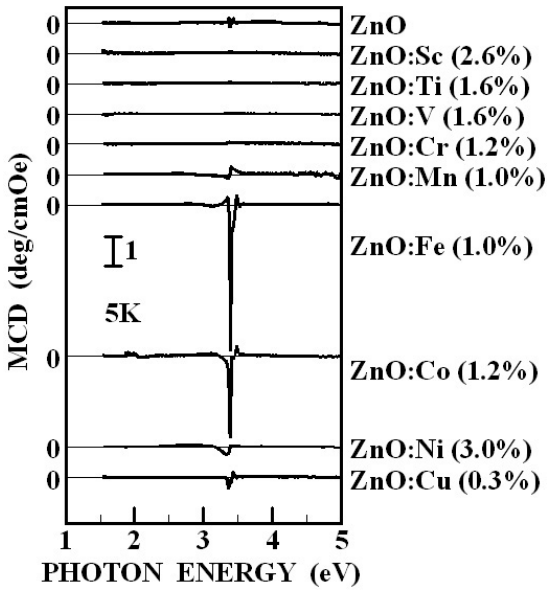

Figure 6. Transmission MCD spectra of ZnO and ZnO:TM (TM: transition metal).

5. Other DMSs

5.1. ZnO:TM

Figure 6 shows the MCD spectra of (0001) oriented $Zn_{1-x}TM_xO$ (TM: transition metal) films [21]. The high quality of the ZnO film grown on a lattice-matched $ScAlMgO_4$ substrate leads to a small but clear MCD structure at the band gap (3.4 eV). Other films were grown on lattice-mismatched Al_2O_3 substrates. ZnO films doped with Mn, Fe, Co, Ni and Cu show clear MCD structures near 3.4 eV. Therefore we can say that ZnO doped with at least Mn, Fe, Co, Ni or Cu is a DMS. The magnetic field and temperature dependences of the MCD spectra show that all of these films are paramagnetic.

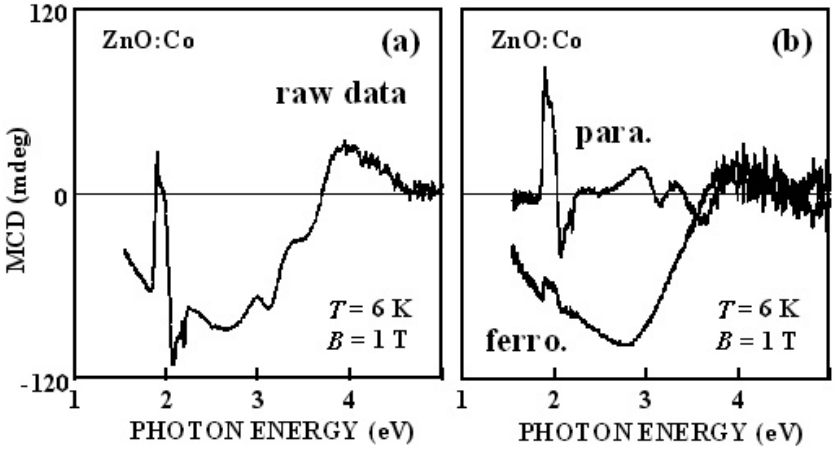

Figure 7. The transmission MCD spectrum of ferromagnetic ZnO:Co (a) can be decomposed into paramagnetic and ferromagnetic components (b). The structure near 2 eV in the ferromagnetic component is artificial [22].

Some ZnO based DMSs were reported to be ferromagnetic [4]. Figure 7(a) shows a MCD spectrum of a ferromagnetic ZnO:Co film [22], for which T_c is higher than 300 K. The sharp structure near 2.0 eV is a fingerprint of d–d* intra-ionic transitions from $^4A_2(F)$ to $^4T_1(P)$, $^2E(G)$ of Co^{2+} ions situated in the T_d symmetry sites. Another structure near 3.4 eV corresponds to the band gap of ZnO. These two structures can be also observed in paramagnetic $Zn_{1-x}Co_xO$ films [23] as shown in figure 6. These results show that the sample contains $Zn_{1-x}Co_xO$ DMS. However, in addition to these two MCD structures, a broad signal is observed for the ferromagnetic sample. The temperature and magnetic field dependences reveal that the MCD spectrum of figure 7(a) can be decomposed into paramagnetic and ferromagnetic components (figure 7(b)) [22]. The paramagnetic component apparently comes from the $Zn_{1-x}Co_xO$ DMS. The second-phase material that is responsible for the ferromagnetic MCD component has not been identified yet. Since the ferromagnetic MCD spectrum does not show noticeable structures near 2.0 and 3.4 eV, which would be the fingerprints of $Zn_{1-x}Co_xO$, the electronic structure of the ferromagnetic material contained in the ferromagnetic ZnO:Co sample seems to have no relation with that of ZnO. Co metal is a possible candidate for being the second-phase material [24]. However, the MCD spectral shape of the ferromagnetic component (figure 7(b)) is different from that of Co metal [25].

5.2. GaN:Mn

We have also measured the MCD spectra of a ferromagnetic GaN:Mn film [26]. SQUID magnetization data showed a clear ferromagnetism at room temperature. X-ray diffraction analysis did not detect any precipitation. We observed a clear MCD spectral peak at the band gap of GaN (figure 8), indicating that $Ga_{1-x}Mn_xN$ is a DMS. The very sharp MCD line shape indicated the high quality of the sample. However, the MCD signal showed paramagnetic behaviours. No ferromagnetic feature was detected by the MCD spectroscopy. The contradiction between the results obtained from the SQUID data and the MCD data means that the sample contains a ferromagnetic material which is not magneto-optically active. This example indicates that the x-ray diffraction is too poor for detecting the precipitations, while SQUID magnetization measurement is so sensitive that it is disturbed by the ferromagnetic precipitations.

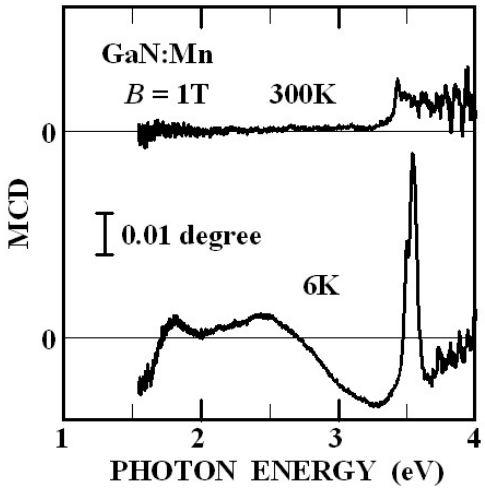

Figure 8. Transmission MCD spectra of ferromagnetic GaN:Mn at different temperatures [26].

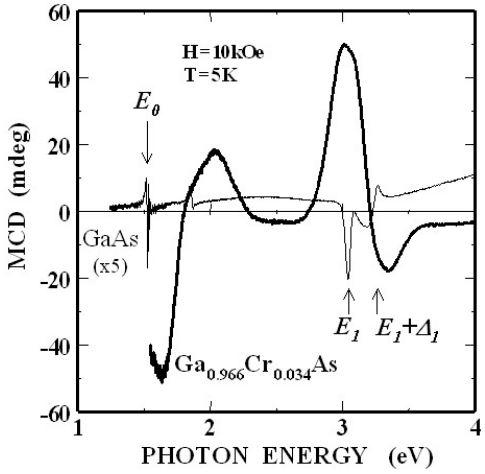

Figure 9. Reflection MCD spectra of a GaAs substrate and a $Ga_{1-x}Cr_xAs$ film [8].

5.3. GaAs:Cr

Figure 9 compares the MCD spectra of GaAs and $Ga_{1-x}Cr_xAs$ ($x = 0.034$) [8]. Enhanced MCD structures are clearly observed for $Ga_{1-x}Cr_xAs$ at the CPs of the host GaAs. This indicates that $Ga_{1-x}Cr_xAs$ is a DMS with the s, p–d exchange interaction. While the ferromagnetic interaction between Cr ions was observed [8], no long-range magnetic order was observed. Some samples with Cr concentration higher than about $x = 0.10$ showed ferromagnetic SQUID data. However, at the same time, the MCD signal intensity decreased or disappeared. Since there is no way to explain the absence of the magneto-optical activity in DMSs at present, we attributed the observed ferromagnetism to some ferromagnetic impurity not detectable by means of x-ray diffraction. $Ga_{1-x}Cr_xAs$ and CrAs were claimed to be ferromagnetic in some of the literature [9, 11], which reported SQUID magnetization data. As described for GaN:Mn, the SQUID data do not always offer decisive evidence of intrinsic ferromagnetism of DMSs. Further examinations of the ferromagnetism in this Ga–Cr–As system involving detecting the s, p–d exchange interaction are desired.

6. Conclusions

We have shown how the s, p–d exchange interaction is essential both for applications and characterizations of DMSs. The MCD spectroscopy confirms the intrinsic ferromagnetism of $In_{1-x}Mn_xAs$, $Ga_{1-x}Mn_xAs$ and $Zn_{1-x}Cr_xTe$. The MCD analyses also show that $Zn_{1-x}TM_xO$ (TM = Mn, Fe, Co, Ni or Cu), $Ga_{1-x}Mn_xN$ and $Ga_{1-x}Cr_xAs$ are paramagnetic DMSs with the s, p–d exchange interaction. Ferromagnetic SQUID data observed for some $Zn_{1-x}TM_xO$, $Ga_{1-x}Mn_xN$ and $Ga_{1-x}Cr_xAs$ samples were contradictory to the MCD data. This contradiction indicates that the theoretical predictions of very high T_c for GaN and ZnO based DMSs [27, 28] and half-metallic CrAs [9] have not been experimentally confirmed yet. Further studies, both theoretical and experimental, are needed to understand the ferromagnetism in DMSs.

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