Advances in Magneto-Optics, Proc. Int. Symp. Magneto-Optics, J. Magn. Soc. Jpn. Vol. 11, Supplement, No. S1 (1987) 121–124.

MAGNETO-CIRCULAR DICHROISM SPECTRA IN SEMI-INSULATING GaAs: Cr AND InP: Fe

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ABSTRACT

Magneto-circular dichroism(MCD) spectra in semi-insulating (SI) single crystals of GaAs:Cr and InP:Fe have been measured between 0.7 and 1.4 eV with magnetic field about 10^6 A/m (13 kOe) at temperatures above 20 K. Relatively strong MCD signals were observed in the below-gap energy region where a strong photoionization absorption band appears. This strong MCD signal is suspected to be caused by the large oscillator strength of the charge transfer transition and the spin orbit splitting in the top of the valence band in these compounds.
Observed MCD peak-to-peak value normalized by transition atom (TA) concentration is about 5 times larger in GaAs:Cr than in InP:Fe. The ratio is comparable to that of valence band spin-orbit splitting between GaAs and InP; i.e. 0.35:0.11. We, therefore, conclude that the observed photoionization absorptions correspond to the transition from the valence band to the TA-level in both crystals.

1. INTRODUCTION

This paper describes magneto-optical studies of the photoionization transition in semi-insulating GaAs:Cr and InP:Fe. In these materials it has been known that a broad absorption band shows up below the fundamental absorption edge of the host material. Such a below-gap absorption has been assigned to photoionization transition from the valence band edge to the empty TA(transition atom)-related level or that from the filled TA-related level to the conduction band edge, depending on whether Fermi level is below or above the TA-level.[1,2] In addition, there appears in the same energy region an absorption band associated with the EL2 which is ascribed to antisite defect.[3] It is, therefore, needed to discriminate which mechanism is involved in the observed absorption. Since these absorption bands are very broad it is rather difficult to characterize from their line shapes or peak positions. Owing to the paramagnetic nature of these deep centers, application of magnetic field is thought to be helpful to distinguish one from the other. Especially, magnetocircular dichroism (MCD), which measures the difference between absorption for two different polarization, has inherently a derivative nature giving a sensitive tool for characterization of these defect-related optical transitions. We, therefore, measured MCD spectra on transition-atom doped single crystals of III-V compound semiconductors.

2. EXPERIMENTAL

Samples of TA-doped III-V semiconductors used in this study were single crystals of Cr-doped SI-GaAs grown by horizontal Bridgmann technique and Fe-doped SI-InP by LEC(liquid encapsulated Czochralski technique) supplied from Sumitomo Electric Co. Ltd. The specimens were cut parallel to one of the (100) planes and polished mechanochemically in both sides. Thickness of the samples were 5 mm for GaAs and 0.7 mm for InP. Concentration of Cr in GaAs was 0.3, 1.3 and 2.5 wtppm and that of Fe in InP 0.9 and 1.6 wtppm. Small amount of oxygen is co-doped in Cr-doped materials. For comparison, an undoped LEC semi-insulating crystal was also prepared. This crystal was grown at the Optoelectronics Joint Research Laboratory.

MCD spectra have been measured by means of the polarization modulation technique. The experimental setup for MCD measurements are schematically illustrated in Fig. 1: Light from a halogen tungsten lamp was dispersed with a Nikon P250 monochromator with a grating blazed at 750 nm, then chopped by a rotating sector at 210 Hz. The chopped monochromatic light was polarized linearly by a Gran prism polarizer, and modulated by a piezo-birefringent modulator. The output light from the modulator is right and left circularly polarized light alternating in 50 kHz. The modulated light was transmitted through a sample which is attached to a cold finger of a cryostat placed in an electromagnet with a perforation in its pole pieces. Most of the measurements were performed with liquid nitrogen cryostat; the sample temperature was varied between 90 K and 200 K. A cryostat using a helium refrigerator was also used, by which temperature down to 20 K was attained. The MCD spectra shown in Figs. 3 and 5 are measured by using the latter cryostat. The light through the sample was detected by a Ge PIN photo-diode or liquid nitrogen cooled InSb photo-cell and amplified by two lockin amplifiers; one tuned to modulating frequency and the other to chopping frequency. The maximum applied field was about 10^6A/m(13 kOe). Data were taken with the help of a microprocessor-based data acquisition system and the ratio of the outputs of the two lockin amplifiers was recorded. In order to eliminate spurious CD signal due to the optical elements, difference between two runs with opposite polarities of the magnetic field was calculated.

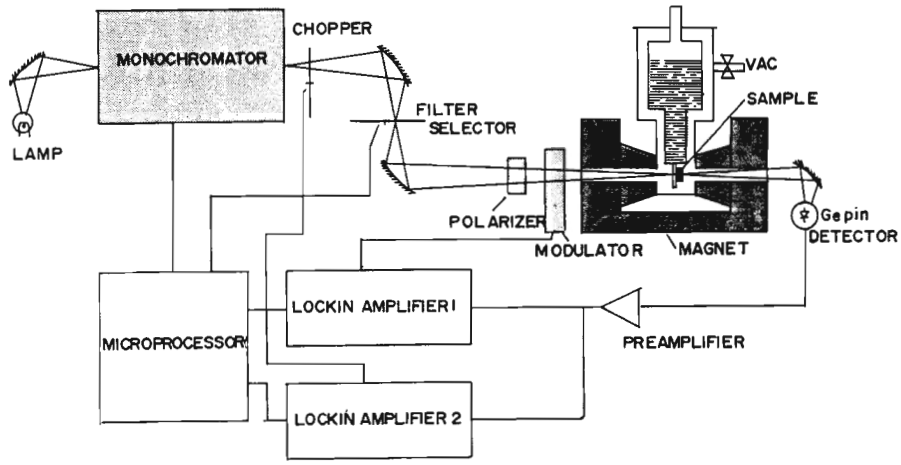

Fig. 1 A schematic diagram of the experimental setup used for MCD measurements.

3. RESULTS

In Fig. 2 absorption spectra of Cr-doped GaAs at 140 K are plotted for three samples with Cr concentration 0.3, 1.3 and 2.5 wtppm. Below the absorption edge of the host crystal, there exists a broad absorption band ranging between 0.7 and 1.4 eV with a broad shoulder around 1.1 eV. The below-gap absorption increases as Cr content increases. The absorption band which appears in this range of photon energy has been assigned to either the charge transfer transition from the valence band to the Cr-related level making Cr^{3+} into Cr^{2+} or the photoionization of an electron from the Cr-related center to the conduction band changing the Cr^{2+} into Cr^{3+}. By comparing the shape of the observed absorption spectrum with published data we have come to believe that the below-gap absorption is due to the transition from the valence band to the Cr level.

In Fig. 3 MCD spectrum of the 2.5 ppm Cr doped sample measured at 20 K under the magnetic field of 10^6 A/m is plotted. Considerably large MCD signal has been observed at the same energy region where the Cr-related photoionization absorption is observed. The MCD band starts at 0.8 eV and makes a peak around 1.01 eV, which is followed by a decrease starting at 1.05 eV and a minimum at 1.25 eV. The peak value amounts to 0.006 cm^{-1}. The MCD spectrum was considerably broad; no fine structures have not been observed even with the spectral resolution of 1 meV. No conspicuous change of line-shape was observed when the sample temperature was raised to 90 K except for the decease in the peak value.

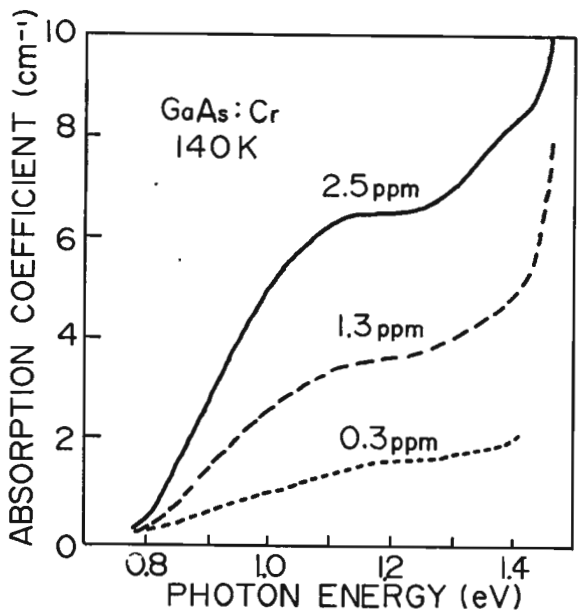

Fig. 2 Absorption spectrum of GaAs:Cr with the Cr concentration 0.3, 1.3 and 2.5 wtppm at 140 K.

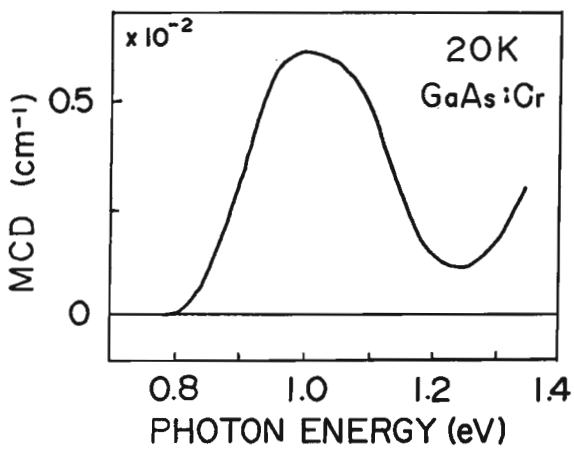

Fig. 3 MCD spectrum of GaAs:Cr measured at 20 K with the magnetic field 10^6 A/m.

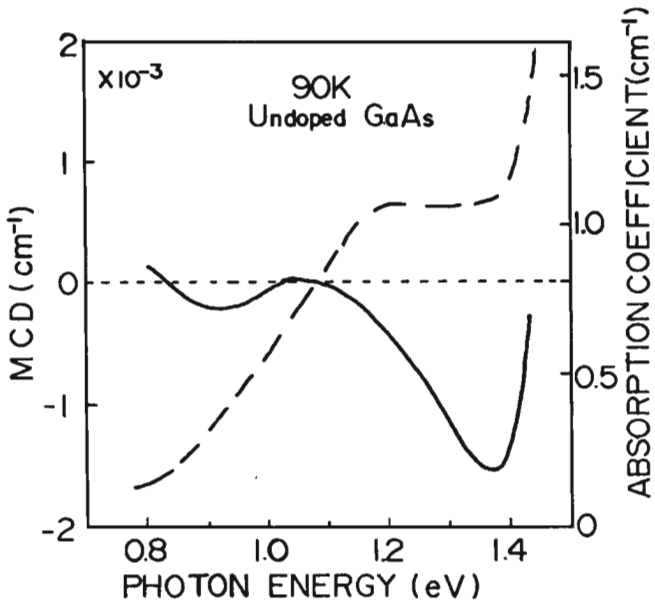

Fig. 4 MCD and absorption spectra in undoped semi-insulating GaAs.

MCD spectrum of undoped semi-insulating GaAs was also measured. Fig. 4 shows the MCD spectrum with the absorption spectrum. The absorption due to EL2 is clearly seen, from which concentration of the defect is estimated to be about 10^{16} cm^{-3} by comparison with published spectrum.[3] The MCD line-shape is completely different from that of Cr-doped samples. The peak value is much weaker than that of GaAs containing the same order of Cr concentration as the EL2 density of the undoped sample. It is clear from this result that the MCD signal seen in the Cr-doped samples is not relevant to the EL2 defect. Concerning the MCD study on EL2 there is a paper published by Meyer et al.[4] Our data showed no such fine structures as their result, presumably because the temperature of our measurement was higher than that of theirs.

The MCD spectrum in 1.6 ppm Fe doped semi-insulating InP was measured at 20 K. The result is illustrated in Fig. 5 together with the absorption spectrum at 90 K. Absorption spectrum similar to the one in GaAs:Cr was observed. Such a absorption band has been assigned to the charge transfer transition from the valence band to the Fe related state changing the valence state of Fe from trivalent to divalent.[5] The MCD spectrum of InP:Fe is considerably different from that of GaAs:Cr; the MCD spectrum of InP:Fe shows two peaks with energy separation about 0.3 eV.

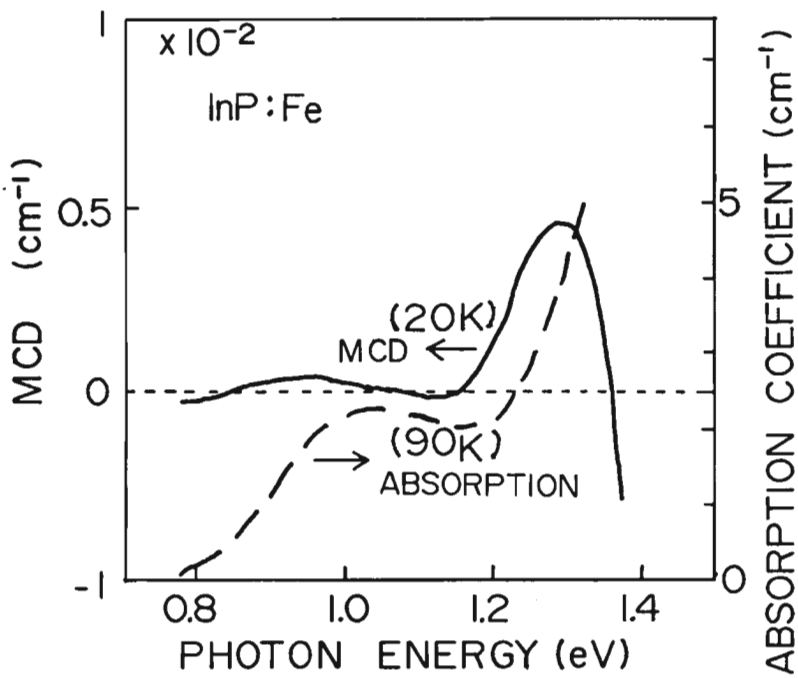

Fig. 5 MCD spectrum at 20 K and absorption spectrum at 90 K in semi-insulating InP doped with Fe at 90 K.

4. DISCUSSIONS

There have been no theoretical treatments on the spectral shape of MCD of the charge transfer transition concerning deep levels introduced by TA impurities. We, therefore, treat it in a rather simplified manner. The threshold energy of the charge transfer transition is assumed to be the energy separation between the top of the valence band(VB) and the TA related state. The top of the VB consists of the fourfold degenerate J=3/2 state and doubly degenerate J=1/2 state, with the separation of spin-orbit interaction energy; 0.35 eV for GaAs and 0.11 eV for InP. On the other hand, in TA center the orbital angular momentum L is nearly quenched and at zeroth approximation L can be treated as zero. Since TA impurities are paramagnetic, the applied external magnetic field increases the number of spins alligned toward the field direction. Then we can assume only those electrons with S=+1/2 are involved in the magnetooptical transition.

According to Kane[6], wave functions associated with the VB of the III-V materials can be described as follows:

$$\phi_{v1\alpha} = [\,(X + iY)\uparrow\,]/\sqrt{2}$$
$$\phi_{v1\beta} = [\,(X - iY)\downarrow\,]/\sqrt{2}$$
$$\phi_{v2\alpha} = (1/3)^{1/2}\,[\,(X - iY)\uparrow\,]/\sqrt{2}\,] + (2/3)^{1/2}\,[Z\downarrow]$$
$$\phi_{v2\beta} = (1/3)^{1/2}\,[-(X + iY)\downarrow\,]/\sqrt{2}\,] + (2/3)^{1/2}\,[Z\uparrow]$$
$$\phi_{v3\alpha} = (2/3)^{1/2}\,[\,(X - iY)\uparrow\,]/\sqrt{2}\,] - (1/3)^{1/2}\,[Z\downarrow]$$
$$\phi_{v3\beta} = (2/3)^{1/2}\,[-(X + iY)\downarrow\,]/\sqrt{2}\,] - (1/3)^{1/2}\,[Z\uparrow]$$

Here notation v1, v2, and v3 refer to heavy-hole, light-hole, and split-off hole bands, respectively. From these expressions one can easily understand that for up-spin (S=1/2) states, the heavy hole band is described by the orbital state of L=+1, while the light hole band by those of L=-1 and L=0. Each contribution is $1/\sqrt{2}$, $1/\sqrt{6}$ and $1/\sqrt{3}$, respectively. On the other hand, the split-off band consists of the states of L=-1 and L=0 with contribution of $1/\sqrt{3}$ and $1/\sqrt{3}$, respectively.

Therefore, in the lowest (threshold) transition, the weight of the transition with $\Delta L=-1$ is 1/2 and that with $\Delta L=+1$ is 1/6, and in the next lowest transition, the weight of $\Delta L=+1$ transition is 1/3, if the same transition probability is assumed for both transitions. Then we can predict that MCD spectrum will have two absorption threshold with opposite signs with the separation of the spin-orbit splitting energy. The observed MCD spectrum of GaAs:Cr shows such a behavior; the first threshold is 0.8 eV and the second one 1.05 eV. The observed separation 0.25 eV, however, is about 0.1 eV less than the value expected from the spin orbit splitting of the valence band. This discrepancy may result from ambiguity in the evaluation of the second threshold from the observed spectrum. Theoretical calculation is now under study to get improved fitting.

In InP:Fe two couples of thresholds were observed; one at 0.82 and 0.95 eV and the other at 1.15 and 1.28 eV. Each separation 0.13 eV is very close to the spin-orbit splitting in the VB of InP and the energy difference between two couples, i.e. 0.3 eV should be compared with the crystal field splitting 0.35 eV of Fe^{2+} in InP.[7]

The peak-to-peak value of the MCD signal per TA concentration in the first peak in InP:Fe was found to be about 1/5 of that in GaAs:Cr. The ratio is close to the ratio of the spin-orbit splitting in the top of the valence band in InP and GaAs, i.e. 1/3.2. This result is consistent with the assumption that the below-gap absorption is due to the charge transfer transition from the VB to the empty TA related states.

4. CONCLUSION

Magneto-circular dichroism spectra in semi-insulating GaAs doped with Cr and InP doped with Fe have been measured for the first time. These spectra showed relatively large MCD signals at the energy region where the charge transfer transition from the VB to the TA related level exists. Two MCD thresholds with opposite signs were observed with energy separation nearly equal to the spin-orbit splitting of the VB states in these compound semiconductors.

Further experimental and theoretical studies are necessary for the interpretation of the observed magneto-optical spectra.

ACKNOWLEDGMENT

The authors are much indebted to Sumitomo Electric Co. Ltd. for supplying semi-insulating InP:Fe, and to Kogaku-Giken Ltd. for cutting and mechanochemical polishing of the samples. This work has been partly supported by Grant-in-Aid (Category General Research B) from the Ministry of Education, Science and Culture, which is deeply appreciated.

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