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Article *in* Japanese Journal of Applied Physics · June 1988

DOI: 10.1143/JJAP.27.979

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JAPANESE JOURNAL OF APPLIED PHYSICS
VOL. 27, NO. 6, JUNE, 1988, pp. 979–982

Characterization of Below-Gap Absorption in Semi-Insulating GaAs:Cr by Magneto-Circular Dichroism Spectrum

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(Received February 18, 1988; accepted for publication March 26, 1988)

Magneto-circular dichroism (MCD) spectra in semi-insulating (SI) single crystals of GaAs:Cr have been measured between 0.7 and 1.4 eV with a magnetic field of 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. Assuming that this strong absorption is caused by the charge transfer transition from the top of the valence band to the Cr-related deep state, we have analyzed the observed data by a theoretical calculation using a model adopted by Martinez *et al.*, from which the Cr-related state was located 0.89 eV above the top of the valence band. The spin-orbit parameter used for the fitting is much smaller than that expected from the splitting in the top of the valence band. Modification of the theory used in this analysis is required.

KEYWORDS: magneto-circular dichroism spectrum, semi-insulating gallium arsenide, chromium-doped gallium arsenide, photoionization transition, below-gap absorption, EL2, spin-orbit splitting in the top of the valence band, quantum defect model

§1. Introduction

This paper describes magneto-optical studies of the photoionization transition in SI (semi-insulating) GaAs:Cr. In this material it has been known that a broad absorption band appears below the fundamental absorption edge of the host material. Such a below-gap absorption has been assigned to the photoionization transition from the VB (valence band) edge to the empty TA (transition atom)-related level or that from the filled TA-related level to the CB (conduction band) edge, depending on whether the Fermi level is below or above the TA-level.[1,2] In addition, there appears in the same energy region an absorption band due to the EL2 level which has been related to the antisite defect.[3] It is, therefore, necessary to determine which of these mechanisms is involved in the observed absorption. It seems rather difficult to judge one from the other only from their line shapes or peak positions, since these transitions result in considerably broad spectra. We have, therefore, been studying MCD (magneto-circular dichroism) spectra, which measure the difference between the absorption spectra for two different polarizations in the applied magnetic field, providing a sensitive tool for characterization of these defect-related optical transitions. Some of the experimental results have been published elsewhere.[4,5] In this paper experimental results as well as theoretical analyses on MCD spectra in SI-GaAs:Cr will be presented and discussed.

§2. Experimental

Samples used in this study were single crystals of Cr-doped SI-GaAs grown by a horizontal Bridgmann technique and purchased from Sumitomo Electric Co. Ltd. The specimens were cut parallel to one of the (100) planes and polished mechanochemically on both sides. Thickness of the samples was 5 mm for GaAs. Concentration of Cr in GaAs was 0.3, 1.3 and 2.5 wtppm. A small amount of oxygen has been co-doped in these Cr-doped materials. For comparison, an undoped LEC (liquid encapsulated Czochralski)-grown SI-GaAs 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 is schematically illustrated in Fig. 1. Light from a 150 W 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 alternates between right and left circularly polarized light at 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. The sample temperature was varied between 20 K and 200 K employing a cryostat using a helium refrigerator. The light through the sample was detected by a Ge PIN photo-diode or a liquid nitrogen-cooled InSb photo-cell and amplified by two lock-in amplifiers: one tuned to the modulating frequency and the other to the chopping frequency. The maximum applied field was about 10^6 A/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 lock-in amplifiers was recorded. In order to eliminate spurious CD signals due to the optical elements, the difference between two runs with opposite polarities of the magnetic field was calculated.

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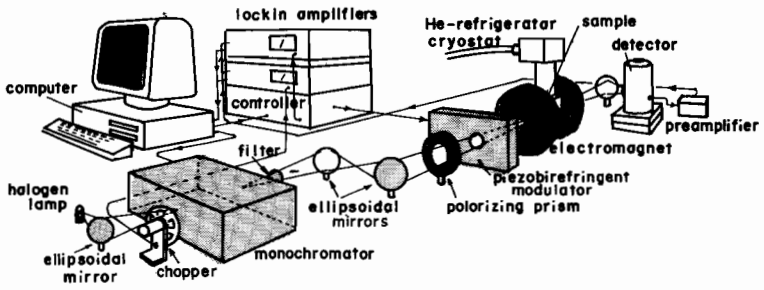

Fig. 1. A schematic diagram of the experimental setup used for the MCD measurements.

§3. Results

In Fig. 2, absorption spectra of Cr-doped GaAs at 140 K are plotted for three samples with Cr concentrations of 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 the Cr content increases. The absorption band which appears in this range of photon energy has been assigned to either the photoionization 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 Cr^{2+} to Cr^{3+}. By comparing the shape and intensity 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 VB to the Cr level.

In Fig. 3, MCD spectrum of the 1.3 wtppm Cr-doped sample measured at 20 K under a magnetic field of 10^6 A/m is plotted. A 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 peaks 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 0.013 cm^{-1}. The MCD spectrum was considerably broad; no fine structures have 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 decrease in the peak value.

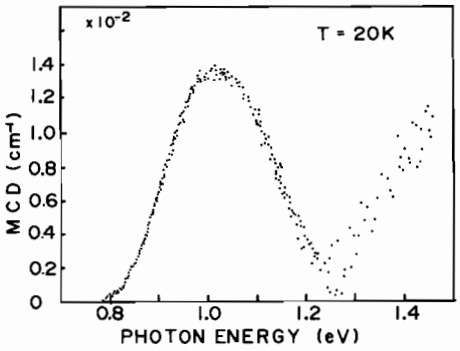

Fig. 3. MCD spectrum of GaAs doped with 1.3 wtppm Cr measured at 20 K with a magnetic field of 10^6 A/m.

The MCD spectrum of undoped semi-insulating GaAs was also measured. Figure 4 shows the MCD spectrum together 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 intensity 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.*[6] Our data showed no such fine structures as their result,

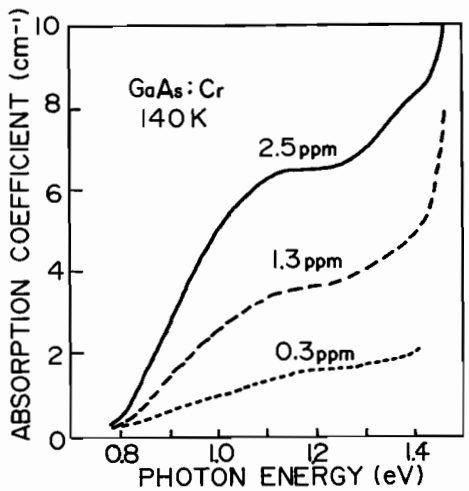

Fig. 2. Absorption spectra of GaAs:Cr with Cr concentrations of 0.3, 1.3 and 2.5 wtppm measured at 140 K.

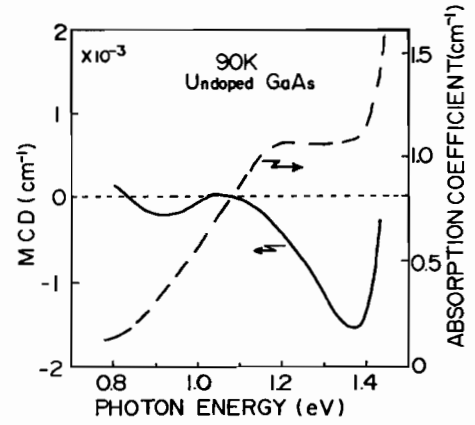

Fig. 4. MCD and absorption spectra in undoped semi-insulating GaAs measured at 90 K.

presumably because the temperature of our measurement was higher than that of theirs.

§4. Discussion

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 VB and the TA-related state. The top of the VB consists of the fourfold degenerate $J_z=+3/2$ state and doubly degenerate $J_z=+1/2$ state, with the separation of spin-orbit interaction energy: 0.35 eV for GaAs. On the other hand, in the TA center the orbital angular momentum L is nearly quenched and for the initial approximation L can be treated as zero. Since TA impurities are paramagnetic, the applied external magnetic field increases the number of spins aligned toward the field direction. Then, we can assume only those electrons with $S_z=+1/2$ are involved in the magneto-optical transition.

According to Kane,[7] wave functions associated with the VB in the III-V materials can be described as follows:

$$\phi_{v1\alpha}=[(X+iY)\uparrow]/\sqrt{2}$$
$$\phi_{v1\beta}=[(X-iY)\downarrow]/\sqrt{2}$$
$$\phi_{v2\alpha}=(1/\sqrt{6})[(X-iY)\uparrow]+(\sqrt{2}/\sqrt{3})[Z\downarrow]$$
$$\phi_{v2\beta}=(1/\sqrt{6})[-(X+iY)\downarrow]+(\sqrt{2}/\sqrt{3})[Z\uparrow]$$
$$\phi_{v3\alpha}=(1/\sqrt{3})[(X-iY)\uparrow]-(1/\sqrt{3})[Z\downarrow]$$
$$\phi_{v3\beta}=(1/\sqrt{3})[-(X+iY)\downarrow]-(1/\sqrt{3})[Z\uparrow]$$

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

Since we have assumed that the angular momentum of the Cr-related deep level is zero, transitions contributing to the magneto-optical spectrum, which requires a change of the angular momentum quantum by $+1$, are those from the valence states with $L_z=+1$ or $L_z=-1$. It is, therefore, easily understood that the sign of the MCD signal for the transition from the heavy-hole band (v1) is opposite to that for the transitions from the light-hole (v2) and the split-off hole (v3) bands (Fig. 5).

The line-shape of the absorption line for each transition is calculated by using the quantum-defect model similar to that adopted by Martinez and coworkers,[1] in which the s-like wave function is assumed for the transition-atom-related center and parabolic wave functions for VB. Absorption cross sections for these three transitions σ_1, σ_2 and σ_3 are given as follows:

$$\sigma_1(\hbar\omega)=\frac{5.3\times10^{-14}}{n}\cdot\frac{E_g}{\hbar\omega}\cdot\frac{m}{m_c}\Gamma^{1/2}\left[E_0^{1/2}\right.$$
$$\left.\times\int_{-\beta}^{\infty}dx e^{-x^2}(\beta+x)^{1/2}\times\frac{\alpha_1^{1/2}}{[\hbar\omega+\Gamma x+E_0(\alpha_1-1)]^2}\right]$$

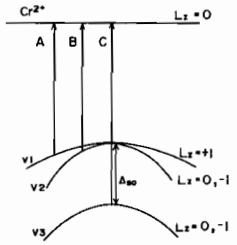

Fig. 5. A simplified energy band diagram used for the calculation.

$$\sigma_2(\hbar\omega)=\frac{5.3\times10^{-14}}{n}\cdot\frac{E_g}{\hbar\omega}\cdot\frac{m}{m_c}\Gamma^{1/2}\left[E_0^{1/2}\right.$$
$$\left.\times\int_{-\beta}^{\infty}dx e^{-x^2}(\beta+x)^{1/2}\times\frac{\alpha_2^{1/2}}{[\hbar\omega+\Gamma x+E_0(\alpha_2-1)]^2}\right]$$
$$\sigma_3(\hbar\omega)=\frac{5.3\times10^{-14}}{n}\cdot\frac{E_g}{\hbar\omega}\cdot\frac{m}{m_c}\Gamma^{1/2}\left[(E_0+\Delta)^{1/2}\right.$$
$$\left.\times\int_{-\beta_1}^{\infty}dx e^{-x^2}(\beta_1+x)^{1/2}\times\frac{\alpha_3^{1/2}}{[\hbar\omega+\Gamma x+(E_0+\Delta)(\alpha_3-1)]^2}\right]$$

where σ is given in cm^2, when energies are expressed in cm^{-1}, E_g is the energy gap, n the refractive index, and $\alpha_1=m/m_{v1}$, $\alpha_2=m/m_{v2}$, $\alpha_3=m/m_{v3}$, Δ the spin-orbit splitting and Γ the broadening parameter. Then, the MCD spectrum will be expressed by the product of the degree of spin polarization and the linear combination of these three absorption spectra;

$$\Delta\alpha_{MCD}=\frac{M(H,T)}{M_s}(a_1\sigma_1+a_2\sigma_2+a_3\sigma_3)\cdot N_0$$
$$=\frac{gS\mu_BH}{kT}(a_1\sigma_1+a_2\sigma_2+a_3\sigma_3)\cdot N_0$$

where N_0 represents the concentration of absorbing centers (cm^{-3}). We determined the weight (a_1, a_2, a_3) for each contribution by fitting to the experimental MCD spectrum, in which a_1 was assumed to be positive and a_2 or a_3 negative. The best fit was attained when we adopted parameters as follows: Chromium level from the top of the valence band $E_0=0.89$ eV, spin-orbit splitting parameter $\Delta=0.2$ eV, and weights for three transitions $a_1=0.2$, $a_2=-0.4$ and $a_3=-1.3$. In Fig. 6 are shown the experimental spectrum and the theoretical fit as well as the contributions from the three transitions. The fit seems quite satisfactory except for the energy region above 1.2 eV, where an MCD structure due to higher-lying state starts. Thus the position of the Cr level has been determined as 0.89 eV above VB at 20 K. However, the fitting procedure requires a much reduced value of the spin-orbit parameter of the VB, i.e. 0.2 eV, compared to 0.35 eV known as the value at the Γ-point. Such

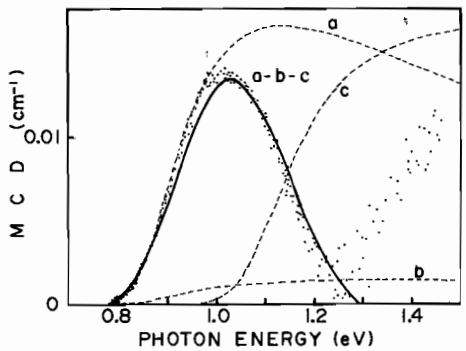

Fig. 6. Calculated MCD spectrum in GaAs:Cr. Dotted curves denoted with a, b and c are contributions of transitions from the three valence bands v1, v2 and v3, respectively, to the energy level of Cr.

discrepancy may be attributed to an overly simplified model adopted in our treatment and also due to neglect of the angular momentum in the chromium-originated deep state. Therefore, an alternative model should be investigated that enables a more appropriate treatment of the angular momentum in the chromium level, to replace the quantum-defect model.

§4. Conclusion

Magneto-circular dichroism spectra in semi-insulating GaAs doped with Cr have been measured for the first time. These spectra showed relatively large MCD signals at the energy region where the Cr-related below-gap absorption exists. Assuming the absorption is caused by the charge transfer transition from the VB to the Cr-related level, the MCD line-shape has been calculated theoretically and fit to the experiment. A satisfactory fit has been obtained and the position of the Cr level has been determined as 0.89 eV above VB. The spin-orbit parameter $\Delta = 0.2$ eV determined by our analysis is greatly reduced from the value 0.35 eV expected for VB at the Γ-point. Further theoretical studies are necessary for a more detailed interpretation of the observed magneto-optical spectra.

Acknowledgments

We are much obliged to Professor T. Kambara of Electro-communication University for kind discussions. Thanks are also due to Kogaku-Giken Ltd. for cutting and mechanochemical polishing of the samples. This work has been partially supported by a Grant-in-Aid for Scientific Research (Category: B, No. 61460061) from the Ministry of Education, Science and Culture.

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