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Magneto-photoluminescence of novel magnetic semiconductor $Zn_{1-x}Cr_xO$ grown by PLD method

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ABSTRACT The magneto-photoluminescence (PL) of novel magnetic semiconductor $Zn_{1-x}Cr_xO$ (ZCO) grown by the pulsed laser deposition (PLD) method was investigated. An ArF excimer laser and Cr_2O_3-mixed ZnO ceramic bulk targets were used for the PLD experiments. The PL peaks at room temperature are very sharp and there is no deep-level emission. The bound exciton peak at 4.2 K was very sharp and increased about three times with increasing applied magnetic field up to 1 T, and the peak wavelength was slightly blue-shifted. It is admirable that the magneto-PL peak was considerably modulated even at low magnetic field. From the peak shift energy of the magneto-PL, ΔE, effective Cr concentration x_{eff} was roughly estimated to be 0.001 on the basis of the electron (n)-type bound magnetic polaron (BMP) model.

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1 Introduction

Oxides have many excellent properties such as ferroelectricity, high permittivity, superconductivity, magnetism (including half metals) and photoelectricity. Owing to these superior properties, they have solely been used in many application fields. In oxide electronics, it has been expected to combine these excellent properties in the monolithic configuration and to make feasible the hyper-intelligent devices [1, 2]. So far, we have been studying semiconducting oxide materials that show ferromagnetic behaviors. ZnO based diluted magnetic semiconductors (DMS) have been investigated more and more actively, and become a matter of interest for many researchers with the keyword, "spintronics" [3–10]. To realize opto-spintronic devices, it is strongly requested that the semiconducting materials should have the magnetism with high Curie temperature (T_C) as well as the excellent optical (luminescence) properties. It is also necessary and of interest to create transparent magnetic semiconductors that can show optical emission.

We have reported the magnetic and optical properties of $Zn_{1-x}Cr_xO$ (ZCO) DMS thin films grown by pulsed laser deposition (PLD) method [11]. In the PL measurement at room temperature, the ZCO thin films showed brilliant luminescence from the bound-exciton level. The photoluminescence (PL) peak wavelength was 387 nm, which is slightly longer than that of ZnO (382 nm). In this study, we report the magneto-PL properties of ZCO DMS thin films, comparing with simulation for the bound magnetic polaron (BMP) model.

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2 Experimental

An ArF excimer laser ($\lambda = 193$ nm, pulse width 10 ns, laser fluence 1–3 J/cm^2 shot, repetition rate 10 Hz) (Lamda Physik, COMPex 100) and Cr_2O_3-mixed ZnO ($Zn/Cr = 0.70/0.30$) ceramic bulk targets were used for the PLD experiments. Most of the thin films were prepared on ZnO(0001) substrates and a few prepared on Al_2O_3(0001) substrates in 5×10^{-3} Torr pure O_2 gas ambient at substrate temperature of 350 °C. The film thicknesses of all samples are 400 nm. The crystallinity and the orientation of the grown films were examined by the X-ray diffraction (XRD) (Cu K_α) method (Rigaku, RINT). Magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL5U). To investigate the optical properties, we measured photoluminescence (PL) spectra and transmittance spectra in the UV-Vis range (only the samples on Al_2O_3(0001) substrates) at room temperature. PL measurements were carried out using a He-Cd laser ($\lambda = 325$ nm) as the excitation light source. The opto-spintronic properties of ZCO were characterized by magneto-PL measurement. Magneto-PL measurements were carried out using a cryostat with superconducting magnet at 4.2 K (Oxford Instruments, Spectromag 4000-8).

3 Results and discussion

The room temperature PL spectra for the ZCO thin films grown at deposition temperatures (T_d) of 450 °C and 350 °C are shown in Fig. 1. At a glance, the PL peaks are very sharp and there is no deep-level emission. The spectrum of the ZnO substrate is also shown as a reference in Fig. 1. As is well known, the 382 nm peak is assigned to the ZnO bound-exciton emission. Based on the comparison with this reference spectrum, it is understandable that all ZCO samples can also radiate the bound-exciton emission and that the peak wavelength is around 387 nm. The observed red-shift

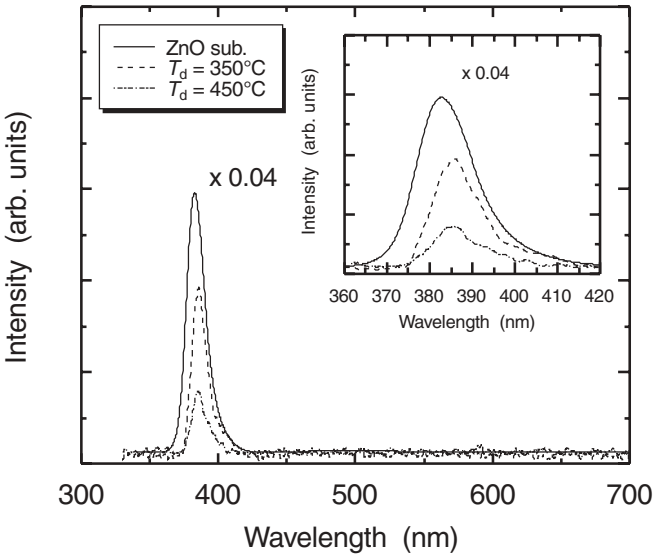

FIGURE 1 PL spectra of ZCO thin films at room temperature. ZnO data is magnified ×0.04. The PL peaks are very sharp and there is no deep-level emission

of the emission peak (from 382 to 387 nm) might be due to spin-correlated exciton formation and/or crystal deformation through Cr doping.

Temperature dependence of PL spectra of ZCO thin film are shown in Fig. 2. The zero phonon line of the bound exciton (I) and the phonon side band of the bound exciton (I-LO, I-2LO) were observed at 4.2 K. As temperature was increased, luminescence intensity of bound exciton line was decreased. The free exciton (Ex) and its phonon side band (Ex-LO, Ex-2LO) are dominant at temperatures above 90 K. From these results, the crystal deformation might occur through Cr doping.

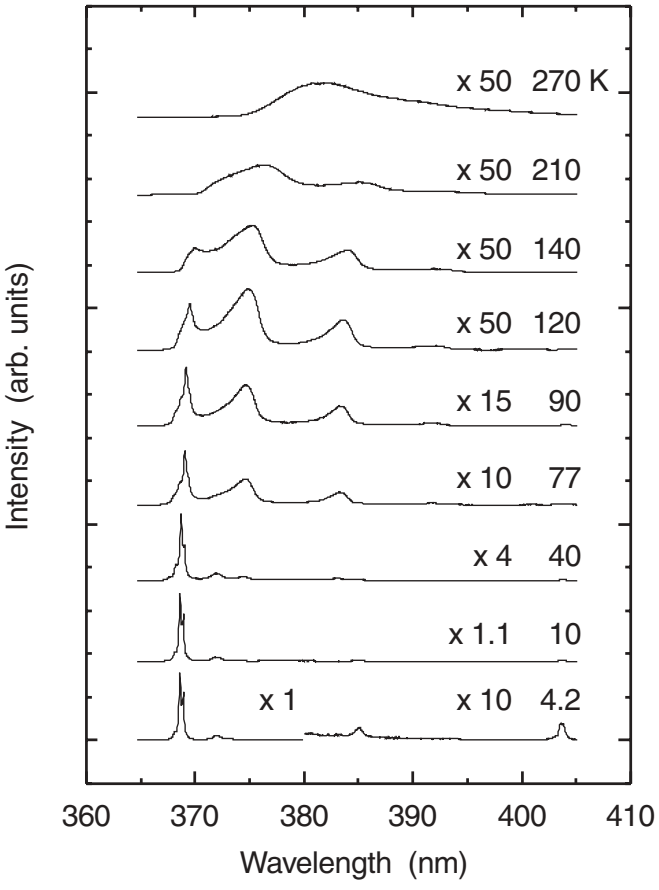

FIGURE 2 Temperature dependence of PL spectra of ZCO thin film. 4.2 K data is magnified ×10 at wavelength longer than 380 nm

Figure 3 shows magneto-PL of ZCO thin film at 4.2 K. The bound exciton peak is very sharp and increases about three times with an increasing magnetic field up to 1 T, and the peak wavelength was slightly blue-shifted. The bound exciton luminescence is caused by the transition from the state of exciton bound to a certain neutral center to the ground state of the neutral center.

To know more (in details) about this phenomenon, we estimated the shift energy ΔE from which the effective Cr concentration x_{eff} can be deduced. We calculated the shift energy for the electron (n)-type bound magnetic polaron (BMP) model expressed by following Eqns. [12]:

$$\Delta E = 4\pi N_0 a_{\mathrm{e}} x_{\mathrm{eff}} k_{\mathrm{B}} T\gamma \int_0^\infty r\mathrm{d}r \ln[F(f(r))] + \frac{2\pi N_0 a_{\mathrm{e}}^2 x_{\mathrm{eff}} k_{\mathrm{B}} T\gamma^2 \int_0^\infty \mathrm{d}r \ln[F(f(r))]}{1 + 4\pi N_0 a_{\mathrm{e}} x_{\mathrm{eff}} k_{\mathrm{B}} T\gamma \int_0^\infty r\mathrm{d}r \ln[F(f(r))]}, \quad (1)$$

where

$$F(x) = \frac{1}{5}\left(\mathrm{e}^{2x} + \mathrm{e}^{x} + 1 + \mathrm{e}^{-x} + \mathrm{e}^{-2x}\right), \quad (2)$$

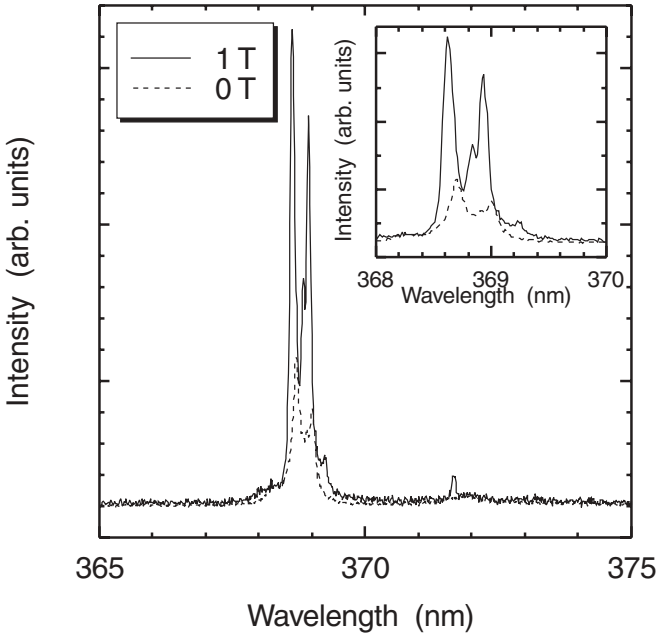

FIGURE 3 Magneto-PL spectra of ZCO thin film at 4.2 K. The bound exciton peak increases about three times with increasing magnetic field up to 1 T, and the peak wavelength was slightly blue-shifted

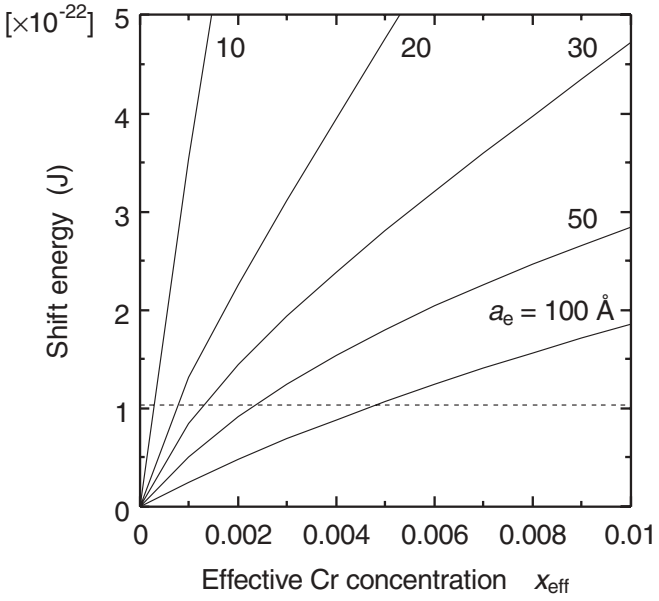

FIGURE 4 Zeeman shift energy vs. effective Cr concentration (*solid lines* are calculated data as functions of electron Bohr radius and *dashed line* is experimental data of magneto-PL measurement)

and

$$f(r) = \frac{J}{2k_B(T+T_{AF})}\left(\frac{e^{-2r/a_e}}{\pi a_e^3 \gamma^3}\right). \quad (3)$$

In (1), N_0 denotes the density of cation site, a_e denotes the electron Bohr radius. From these equations, the calculated results of the relationships between the shift energy ΔE and the effective Cr concentration x_{eff} are illustrated in Fig. 4. Since the main contribution to the BMP comes from Cr^{2+} ions within about one Bohr radius, which is about 14 Å for ZnO. In comparison with the experimental data (Fig. 4), from the peak blue-shift energy of the magneto-PL, $\Delta E = 0.6429$ meV, the effective Cr concentration x_{eff} is roughly estimated to be 0.001 on the basis of the electron (n)-type BMP model for the most probable parameters such that $J = 1$ eV, $T + T_{AF} = 5$ K.

Although the exchange interaction of the electron spin with the localized Cr magnetic spin is smaller than that of the hole spin, the exchange energy of the bound exciton may be smaller than that of the neutral donor center just after deexcitation, resulting in the blue-shift of the PL peak for the bound exciton. It is admirable that the PL peak is considerably modulated even at low magnetic field.

4 Conclusions

We have investigated magneto-photoluminescence of $Zn_{1-x}Cr_xO$ diluted magnetic semiconductor thin films grown by pulsed laser deposition method. The bound exciton peak is very sharp and increases about three times with an increasing magnetic field up to 1 T, and the peak wavelength was slightly blue-shifted. We calculated the shift energy and the effective Cr concentration for the electron (n)-type bound magnetic polaron model. It is admirable that the PL peak is considerably modulated even at low magnetic field.

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[1] In this work: Fig. 3, ×25 should be corrected as ×0.04.