Effect of co-doping of donor and acceptor impurities in the ferromagnetic semiconductor Zn$_{1-x}$Cr$_x$Te studied by soft x-ray magnetic circular dichroism

Y Yamazaki$^1$, T Kataoka$^1$, V R Singh$^1$, A Fujimori$^1$, F-H Chang$^2$, D-J Huang$^2$, H-J Lin$^2$, C T Chen$^2$, K Ishikawa$^3$, K Zhang$^3$ and S Kuroda$^3$

$^1$ Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan
$^2$ National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan, Republic of China
$^3$ Institute of Materials Science, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8573, Japan

E-mail: yamazaki@wyvern.phys.s.u-tokyo.ac.jp

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Abstract

We have performed x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) studies of the diluted ferromagnetic semiconductor Zn$_{1-x}$Cr$_x$Te doped with iodine (I) or nitrogen (N), corresponding to electron or hole doping, respectively. From the shape of the Cr 2p absorption peak in the XAS spectra, it was concluded that the Cr ions in the undoped, I-doped and lightly N-doped samples are divalent (Cr$^{2+}$), while Cr$^{2+}$ and trivalent (Cr$^{3+}$) coexist in the heavily N-doped sample. This result indicates that the doped nitrogen atoms act as acceptors but that doped holes are located on theCr ions. In the magnetic field dependence of the XMCD signal at the Cr 2p absorption edge, ferromagnetic behaviors were observed in the undoped, I-doped, and lightly N-doped samples, while ferromagnetism was considerably suppressed in the heavily N-doped sample, which is consistent with the results of magnetization measurements.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Diluted magnetic semiconductors (DMSs) [1] which show high ferromagnetic Curie temperatures (T$_{cs}$) are considered to be key materials for future applications of spintronics [2, 3]. The II–IV DMS Zn$_{1-x}$Cr$_x$Te is known to show ferromagnetism at room temperature, as confirmed by magnetization measurements and magnetic circular dichroism (MCD) measurements in the visible to ultraviolet region [4]. Recently, the effects of additional doping of atoms with different valencies in Zn$_{1-x}$Cr$_x$Te were investigated; that is, iodine which is expected to act as an n-type dopant enhances the ferromagnetism [5], while nitrogen which is expected to act as a p-type dopant suppresses it [6]. On the other hand, it has been predicted theoretically that spinodal decomposition causes the apparent ferromagnetic behavior of Zn$_{1-x}$Cr$_x$Te [7, 8]. Experimentally, indeed, spatially resolved energy-dispersive x-ray spectroscopy revealed that the Cr ions are distributed inhomogeneously in the I-doped samples, while they are distributed homogeneously in the N-doped samples [9]. The results of ab initio calculations of the total energies suggest that the valence state of Cr seems to be important for distribution of the Cr ions; that is, the Cr ions will be distributed inhomogeneously if the Cr ions are in the neutral 2$^+$ charge state, while they are distributed homogeneously if the Cr ions are in different $2^+$(2 $\pm \delta$) charge states [9, 10]. So far, x-ray magnetic circular dichroism (XMCD) studies have been performed on Zn$_{1-x}$Cr$_x$Te to investigate the electronic...
structure of the Cr ions and the Cr ions have been found to be in the 2+ state [11, 12]. It is necessary to know how the electronic state of the Cr ion is modified by the N- and I-doping to understand the mechanism of the spinodal decomposition. In order to investigate the effects of I- and N-doping, we have performed x-ray absorption spectroscopy (XAS) and XMCD experiments at the Cr 2p absorption edge of undoped, I-doped, lightly N-doped, and heavily N-doped Zn$_{1-x}$Cr$_x$Te thin films. XMCD is defined as the difference in XAS spectra between right-handed ($\mu^+$) and left-handed ($\mu^-$) circularly polarized x-rays, and is a powerful tool to investigate the ferromagnetism in DMSs [13–17], because it is element specific and sensitive to magnetically active components.

2. Experimental details

The samples used in this study were undoped Zn$_{1-x}$Cr$_x$Te with $x = 0.053$ ($T_c = 90$ K), I-doped Zn$_{1-x}$Cr$_x$Te with $x = 0.039$ ($T_c = 210$ K), lightly N-doped Zn$_{1-x}$Cr$_x$Te with $x = 0.043$ ($T_c = 60$ K), and heavily N-doped Zn$_{1-x}$Cr$_x$Te with $x = 0.047$ (no ferromagnetism). According to secondary ion mass spectroscopy (SIMS) analysis, the N concentrations in the lightly and heavily N-doped samples were $1.8 \times 10^{18}$ cm$^{-2}$ and $1.0 \times 10^{20}$ cm$^{-3}$, respectively. These values correspond to the ratios of substituting N for Te of 0.1% and 0.56%, respectively, when we assume that all the N atoms substitute for Te. These samples were grown on insulating GaAs(001) substrates by molecular beam epitaxy, as described elsewhere [9]. After depositing a 600 nm thick ZnTe buffer layer, the Zn$_{1-x}$Cr$_x$Te thin films of 300 nm thickness were grown. During the deposition, the substrate was kept at a temperature of 603–633 K. The sample surface was capped with a 3 nm thick Al layer to avoid oxidation of the Zn$_{1-x}$Cr$_x$Te layer. XAS and XMCD measurements were performed at the Dragon Beamline BL11-A of National Synchrotron Radiation Research Center (NSRRC), Taiwan. Spectra were measured in the total-electron-yield (TEY) mode and the total-fluorescence-yield (TFY) mode. Because the probing depths of the TEY and TFY modes are about 5 nm and 100 nm, respectively, one can consider that the TEY mode is surface sensitive and the TFY mode is bulk sensitive. The monochromator resolution was $E/\Delta E > 10,000$. In the XMCD measurements, the circular polarization of the incident photons was fixed and the direction of the applied magnetic field was changed. The XAS and XMCD measurements were made at a temperature of 20 K in an ultrahigh vacuum below $10^{-10}$ Torr.

3. Results and discussion

Figure 1 shows the Cr 2p XAS spectra of the undoped, I-doped, lightly N-doped, and heavily N-doped Zn$_{1-x}$Cr$_x$Te thin films taken in the TFY mode. For comparison, those of Cr$_2$O$_3$ and Zn$_{1-x}$Cr$_x$Te taken in the TEY mode are also shown. The Cr ions in Cr$_2$O$_3$ and Zn$_{1-x}$Cr$_x$Te are Cr$^{2+}$ and Cr$^{3+}$, respectively, as described elsewhere [12, 18]. The major two peaks in each spectrum are due to the 2p$_{3/2}$–2p$_{1/2}$ spin–orbit doublet of the Cr 2p core level. Due to the self-absorption effect of the TFY method, the intensity of the 2p$_{3/2}$ peak relative to the 2p$_{1/2}$ peak is reduced compared to one obtained by the TEY method. One can see from figure 1 that the spectral line shapes and the peak positions of the undoped, I-doped and lightly N-doped samples are similar to the spectra of Cr$^{2+}$. Considering that the TFY mode is bulk sensitive, one can conclude that Cr$^{2+}$ is dominant in the undoped, I-doped and lightly N-doped samples in the bulk region. On the other hand, the XAS spectra of the heavily N-doped sample showed clear peak shifts towards higher energies compared to the other samples and located between Cr$^{2+}$ and Cr$^{3+}$. This observation indicates that the N replacing Te atoms in the heavily N-doped sample supplied holes and worked as an acceptor and that Cr$^{3+}$ states were created.

Figure 2 shows the Cr 2p XAS and XMCD spectra of the undoped, I-doped, lightly N-doped, and heavily N-doped Zn$_{1-x}$Cr$_x$Te thin films taken at $T = 20$ K. Magnetic fields were applied perpendicular to the sample surfaces. We observed clear XMCD signals in the undoped, I-doped and lightly N-doped samples, while the heavily N-doped sample showed no clear XMCD signals, consistent with the magnetization measurements [9]. Figure 3(a) shows the XMCD spectra of the undoped, I-doped, lightly N-doped, and heavily N-doped Zn$_{1-x}$Cr$_x$Te thin films taken under 1, 0.5 and 0.1 T. The line shapes of the XMCD spectra are the same for all the samples, indicating that Cr$^{2+}$ ions contribute to the magnetism in these samples. Although the application of XMCD sum rules [19, 20] to TFY data does not give accurate results because of the self-absorption effect, we have attempted to deduce the magnetic moments of the Cr ions by applying the XMCD sum rules to the TFY data, in order to see relative changes with N- or I-doping. Figure 3(b) shows the magnetic...
Figure 2. Cr 2p XAS and XMCD spectra of the undoped, I-doped, lightly N-doped, and heavily N-doped Zn$_{1-x}$Cr$_x$Te thin films taken in the TFY mode at $H = 1$ T and $T = 20$ K. The XMCD spectra have been normalized to the XAS $[(\mu^+ + \mu^-)/2]$ peak height at around 576 eV.

Field dependence of the approximate Cr magnetic moments of these samples, estimated using the XMCD sum rules. If the XMCD intensities are extrapolated to $H = 0$ T, one can see finite magnetization at $H = 0$ T in the undoped, I-doped, and lightly N-doped samples, indicating that the ferromagnetism in these samples is of intrinsic bulk origin. In addition, a higher magnetic moment was observed in the I-doped sample than in the undoped sample. Although the application of the XMCD sum rules to TFY data does not give accurate magnetic moments, the observation of finite magnetization at $H = 0$ T and the relative changes of magnetization with N- or I-doping are real and can be used to study the ferromagnetism of the undoped, I-doped, and lightly N-doped samples and the influence of N- or I-doping on the magnetic state of Cr.

The recent atomic-scale analysis using energy-dispersive x-ray spectroscopy has shown a close correlation between the spatial homogeneity of the Cr distribution and the ferromagnetic properties [9]; an inhomogeneous distribution, possibly due to spinodal decomposition, enhances the ferromagnetism while a homogeneous distribution suppresses it. According to a theoretical model [10], the valence state of the Cr ions is important for the spinodal decomposition. In the intrinsic situation, the valence state of the Cr ions substituting for Zn is 2$^+$, being electrically neutral with the same charge state as Zn$^{2+}$, and the strong attractive interaction between the electrically neutral Cr ions makes the Cr distribution inhomogeneous. When the Cr charge state deviates from 2$^+$, the repulsive force of the electrostatic origin created between the Cr ions makes a homogeneous distribution. In the actual samples grown by MBE, it is considered that the Cr valence state in the undoped Zn$_{1-x}$Cr$_x$Te slightly increases from 2$^+$ to the formation of Zn vacancies, which act as shallow acceptors, while the Cr valence state returns to 2$^+$ in the I-doped Zn$_{1-x}$Cr$_x$Te due to the compensation of these Zn vacancies by the donor impurities. This model explains the experimentally observed inhomogeneous/homogeneous Cr distribution and the resultant enhancement/suppression of ferromagnetism in the I-doped/undoped Zn$_{1-x}$Cr$_x$Te. In either case, the dominant Cr ions are in the valence state of 2$^+$, which is consistent with the result of the XAS measurements in the I-doped and undoped samples. On the other hand, the co-doping of nitrogen, which acts as an acceptor impurity when substituting for Te, converts the Cr valence state from 2$^+$ to 3$^+$. As a result, in the heavily N-doped sample the Cr valence state becomes mixed valence or an intermediate valence between Cr$^{3+}$ and Cr$^{2+}$, as demonstrated in the XAS spectra. The disappearance of ferromagnetism in the heavily N-doped sample can be attributed to this conversion of the Cr valence state in addition to the homogeneous Cr distribution. In the lightly N-doped sample, the conversion of the Cr valence state is not sufficient to induce an apparent shift of the XAS spectra. Our experiment thus gives the

Figure 3. Magnetic field dependence of the XMCD spectra (a) and magnetic moments (b) of the I-doped, undoped, lightly N-doped, and heavily N-doped Zn$_{1-x}$Cr$_x$Te thin films at $T = 20$ K.

(a)  
(b)
first microscopic support for the model that acceptor doping changes the valence of Cr and this change influences the ferromagnetism in Zn$_{1-x}$Cr$_x$Te.

4. Conclusion

In conclusion, we have performed XAS and XMCD measurements on undoped, I-doped, lightly N-doped, and heavily N-doped Zn$_{1-x}$Cr$_x$Te. From the XAS measurements, the Cr ions were found to be in the Cr$^{2+}$ state in the undoped, I-doped and lightly N-doped samples, while Cr$^{3+}$ and Cr$^{2+}$ states were formed in the heavily N-doped sample. In the XMCD measurements, it was found that the magnetic moment of the Cr$^{3+}$ state contributes to the ferromagnetism in the undoped, I-doped and lightly N-doped samples, while the XMCD signals at the Cr 2p edge were not observed in the heavily N-doped sample. The magnitude of the magnetic moment was found to be larger in the I-doped sample than in the undoped one, consistent with the results of the magnetization measurements.

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