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Effects of hole doping in the ferromagnetic semiconductor Mn-doped ZnO thin film studied by x-ray magnetic circular dichroism

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1. Introduction

Diluted magnetic semiconductors (DMSs), where magnetic ions are doped into semiconductor hosts, continue to attract considerable attention due to the possibility of utilizing both the charge and spin degrees of freedom in the same materials, allowing us to design a new generation spin electronic devices with enhanced functionalities [1,2]. In this field of spintronics, a semiconducting and ferromagnetic material at room temperature has been desirable. Theoretical studies on the basis of Zener's *p-d* exchange model have shown that wide band gap materials such as ZnO-based DMSs, which tend to have smaller lattice constants and hence strong *p-d* hybridization, are predicted to have high Curie temperatures (T_c) [3]. First-principle calculations by Sato and Katayama-Yoshida [4] have also predicted that ZnO-based DMSs exhibit ferromagnetism, and room temperature ferromagnetism in Mn-doped ZnO (ZnO:Mn) thin films has indeed been reported [5]. The understanding of ferromagnetic interaction in the ZnO:Mn system has been obtained from the theoretical prediction and experiments with native defects such as vacancies [6,7]. Following the spin-split donor impurity band model suggested by Coey *et al*., [8], the long ferromagnetic exchange coupling can be mediated by polaronic percolation of bound magnetic polarons created by oxygen vacancies. The defect-induced shallow donor levels are hybridized with the transition-metal 3*d* levels and thus stabilize the ferromagnetic ground state for such materials. On the other hand, First-principle calculations [9] have predicted the necessity of additional hole doping to stabilize the ferromagnetic order in this system. Indeeed, Kittilstved and Gamelin [10] have reported ferromagnetism in hole-doped ZnO:Mn nano-particles and suggested the presence of bound magnetic polarons upon introduction of hole carriers, where magnetic exchange interaction between defect-bound holes and Mn^{2+} ions is proposed to align Mn^{2+} spins with respect to one another. Although there is evidence showing that Mn substitutes for Zn in a 2+ state [5] and the carrier induced ferromagnetic mechanism has been proposed to predominate [11], the origin of the ferromagnetic interaction in the ZnO:Mn system remains to be clarified. Thus, to achieve better understanding of this type of DMSs and to perform new material design, investigation of the electronic structure of the ZnO:Mn system is crucial.

In this paper, we report on soft x-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) studies of the ZnO:Mn thin films, which are hole-doped through N_2 treatment and exhibit room temperature ferromagnetism [12].

2. Experiment

400-nm-thick thin films of ZnO:Mn (Mn = 2 %) were grown on Si substrates by reactive sputtering using 99.9 % pure Zn target using the radio frequency (RF)/direct current (DC) sputtering system. In order to dope the system with holes, two ZnO-DMSs (samples A and B) were prepared under nitrogen pressure of P_N^2 = 4.0 and 1.5×10^{-5} mbr, respectively. XAS and XMCD measurements were performed at the Dragon Beamline BL11A of National Synchrotron Radiation Research Center (NSRRC) in the total-electron-yield (TEY) mode (probing depth ～2-3 nm). The monochromator resolution was $E/\Delta E > 10000$ and the circular polarization of x-rays was ～ 55 %.

3 Results and discussion

Figure 1 shows the Mn 2*p*-3*d* XAS spectra of samples A and B compared with cluster-model calculations for the Mn^{2+}, Mn^{3+} and Mn^{4+} ions coordinated tetrahedarally. The spectral line shape of the calculated Mn^{2+} spectrum agrees with the experimental results, indicating that the Mn atoms in the ZnO:Mn are mainly in the Mn^{2+} ionic state. In the Mn-doped ZnO system, the valence state of Mn is expected to be +2 if Mn simply substitutes for Zn. Although it is likely that the experimental spectra (samples A and B) are derived mainly from the Mn^{2+} ions, it may also be attributed to a small amount of the Mn^{3+} due to the hole doping.

Figure 2(a) shows the magnetization curves of samples A and B at room temperature measured with a SQUID magnetometer. The result confirms that these samples are ferromagnetic at room temperature. Figure 2(b) shows the intensities of Mn 2*p*-3*d* XMCD spectra of the ZnO:Mn thin films as functions of magnetic field. We could observe finite XMCD signals down to $H \sim 0.1$ T, indicating that the ferromagnetism is originated from the Mn 3*d* electrons. The ferromagnetism of sample B is stabilized compared to that of sample A because the remanent magnetization (XMCD signal at H = 0T) of sample B is larger than that of sample A, consistent with the SQUID results. Our XMCD and SQUID re-

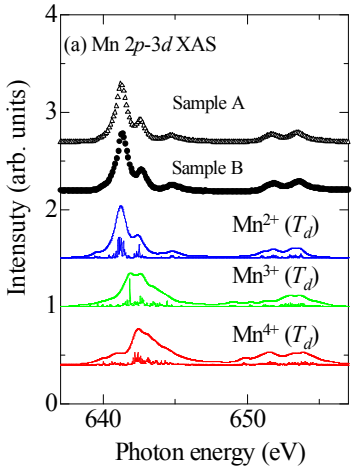

Fig.1: Mn 2*p*-3*d* XAS spectra of the ZnO:Mn thin films compared with cluster-model calculations for the Mn^{2+}, Mn^{3+} and Mn^{4+} ions coordinated tetrahedarally.

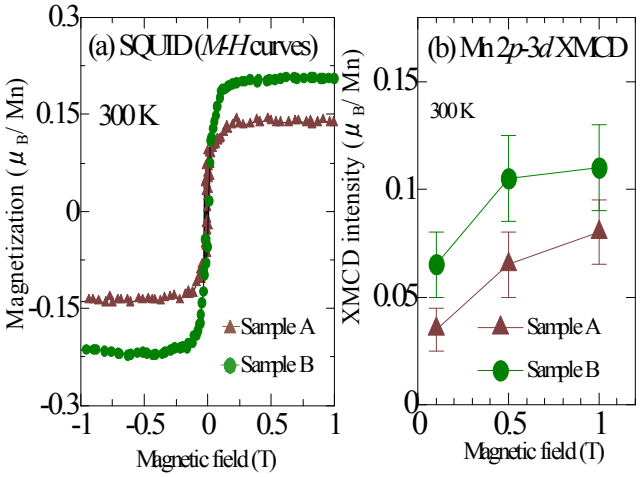

Fig.2: Magnetization curves (a) of the ZnO:Mn thin films at room temperature. (b) Intensities of Mn 2*p*-3*d* XMCD of the ZnO:Mn thin films as functions of magnetic field.

sults suggest that hole doping in the ZnO:Mn system induces the ferromagnetism, but excess hole doping may reduce the ferromagnetism in the ZnO:Mn system.

3. Conclusions

We have performed XAS and XMCD measurements on Mn-doped ZnO thin films, which exhibit ferromagnetism at room temperature. The XAS spectrum shows a multiple structure derived from the Mn^{2+} ion. We find from the XMCD measurements that the ferromagnetism of the ZnO:Mn thin films is originated from the Mn 3*d* electrons. Our XMCD and SQUID results suggest that hole doping in ZnO:Mn system produces the ferromagnetism but excess hole doping may reduce the ferromagnetism in the ZnO:Mn system.

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Appendix

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