

Ferromagnetism in Mn and Sb co-doped ZnO films

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 425207

(<http://iopscience.iop.org/0953-8984/20/42/425207>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 15:59

Please note that [terms and conditions apply](#).

Ferromagnetism in Mn and Sb co-doped ZnO films

Gen-Hua Ji, Zheng-Bin Gu, Ming-Hui Lu, Di Wu,
Shan-Tao Zhang, Yong-Yuan Zhu, Shi-Ning Zhu and
Yan-Feng Chen

National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

E-mail: yfchen@nju.edu.cn

Received 20 June 2008

Published 16 September 2008

Online at stacks.iop.org/JPhysCM/20/425207

Abstract

Zn_{0.99}Mn_{0.01}O and Zn_{0.985}(Mn_{0.01}, Sb_{0.005})O thin films were prepared on sapphire(0001) by reactive radio-frequency (rf) magnetron sputtering. Zn_{0.99}Mn_{0.01}O showed no obvious ferromagnetic behavior while Zn_{0.985}(Mn_{0.01}, Sb_{0.005})O exhibited robust ferromagnetic signals with a saturation magnetization of 0.92 μ_B/Mn^{2+} , and Zn_{0.985}(Mn_{0.01}, Sb_{0.005})O film grown in an oxygen rich condition exhibited a larger saturation magnetization of 1.76 μ_B/Mn^{2+} . The results are most consistent with the bound magnetic polaron model, in which localized p-type defects mediate the ferromagnetic ordering.

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

1. Introduction

During the last few years, there has been much interest in diluted magnetic semiconductors (DMSs), i.e. semiconductors that have been doped slightly with a magnetic element to result in room-temperature ferromagnetism (FM), that is essential for applications [1–5]. Compounds based on ZnO were theoretically predicted to be ideal candidates for room-temperature DMSs [6]. Motivated by this prediction, numerous studies have addressed the magnetic properties of transition-metal-doped ZnO, with conflicting conclusions. For Mn-doped ZnO, theoretical work of Sato and Katayama-Yoshida, based on first-principles calculations, showed that the ferromagnetic Mn²⁺:ZnO state should be more stable in p-type samples [7], and theoretical work of other groups, which was based on the B3LYP hybrid density functional method or gradient-corrected functional density theory, also confirmed that antiferromagnetism is the ground state of Mn²⁺:ZnO [8, 9]. Kevin *et al* obtained high- T_C ferromagnetism in N-capped Mn²⁺:ZnO [10], while no obvious ferromagnetism was found in O-capped films. Their results provided experimental evidence for the theoretical predictions. However, ferromagnetism near and well above room temperature was also reported for n-type Mn²⁺:ZnO by Heo *et al* and Yang *et al*, respectively [11, 12].

The ferromagnetism of TM-doped ZnO remained poorly understood experimentally despite clear theoretical predic-

tions. Recently, Behan *et al* reported that ZnO films doped with Mn or Co could be divided into three regimes with increase of carrier density: the insulating regime, the intermediate regime and the metallic regime [13]. Ferromagnetic behavior was observed in both insulating and metallic films. Two distinct mechanisms, magnetic polarons and carrier-mediated exchange, were proposed to give rise to the ferromagnetism of these two magnetic regimes. This categorization of the samples might be helpful to explain the large scatter of the results reported in the literature.

In this paper, we undertake an investigation of Sb-doped Mn²⁺:ZnO thin films to experimentally verify the effects of Sb doping on the magnetism of this specific system. Bound magnetic polarons are proposed to account for the observed magnetic behavior. The results demonstrate that ferromagnetism of Mn²⁺:ZnO is very sensitive to defects.

2. Experimental details

The Zn_{0.99}Mn_{0.01}O (ZMO) and Zn_{0.985}(Mn_{0.01}, Sb_{0.005})O (ZMSO) targets for sputtering were prepared using the standard solid-state reaction process. Fine powders of high-purity (>99.9%) ZnO, MnCO₃ and Sb₂O₃ with prescribed molar ratio were mixed thoroughly and sintered at 1350 °C for 5 h in air. All films were deposited on (0001) sapphire (α -Al₂O₃) substrates. The sputtering chamber was evacuated

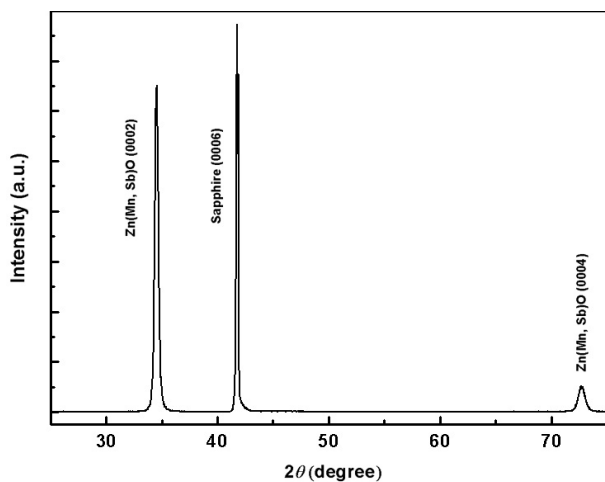


Figure 1. XRD pattern of $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ film.

Table 1. Targets and sputtering atmospheres of samples A, B and C.

Sample	Target	Working gas (sccm)
A	$\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$	Ar = 10
B	$\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$	Ar = 10
C	$\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$	Ar = 10, $\text{O}_2 = 10$

by a turbo molecular pump to a base pressure below 4.5×10^{-4} Pa. Argon and oxygen was introduced into the chamber as working gas through two mass flow controllers and the chamber pressure was fixed at 2.0 Pa during deposition. The substrate was mounted on a stage at 600°C and kept a distance of 60 mm from the target. Three samples were prepared as shown in table 1.

The thickness of the films was about 300 nm, measured by a profilometer. The crystal structures of the films were characterized by x-ray diffraction (XRD) (Cu $K\alpha$ radiation source). Chemical bonding states and chemical compositions of the films were analyzed by x-ray photoelectron spectroscopy (XPS) (ESCALAB 250) with Al $K\alpha$ x-ray source. To investigate the optical properties, the photoluminescence (PL) spectrum in the ultraviolet–visible range was taken using a He–Cd laser ($\lambda = 325$ nm) at room temperature. The absorption spectra of the films were measured at room temperature on an ultraviolet–visible (UV–VIS) spectrometer. Magnetic measurements were performed using a Quantum Design SQUID (MPMS XL-7) magnetometer with the applied magnetic field parallel to the film plane.

3. Results and discussion

All the films are light yellow and transparent with a very smooth surface. Figure 1 shows a typical XRD pattern of ZMSO film. Only diffraction peaks of wurtzite $\text{ZnO}(0002)$ planes were observed, which indicates a preferential (0001) oriented growth of the film. No manganese or antimony oxide phases were detected, suggesting that the Mn ions might be substituted into Zn sites, while it is unclear whether Sb ions substitute Zn sites or O sites.

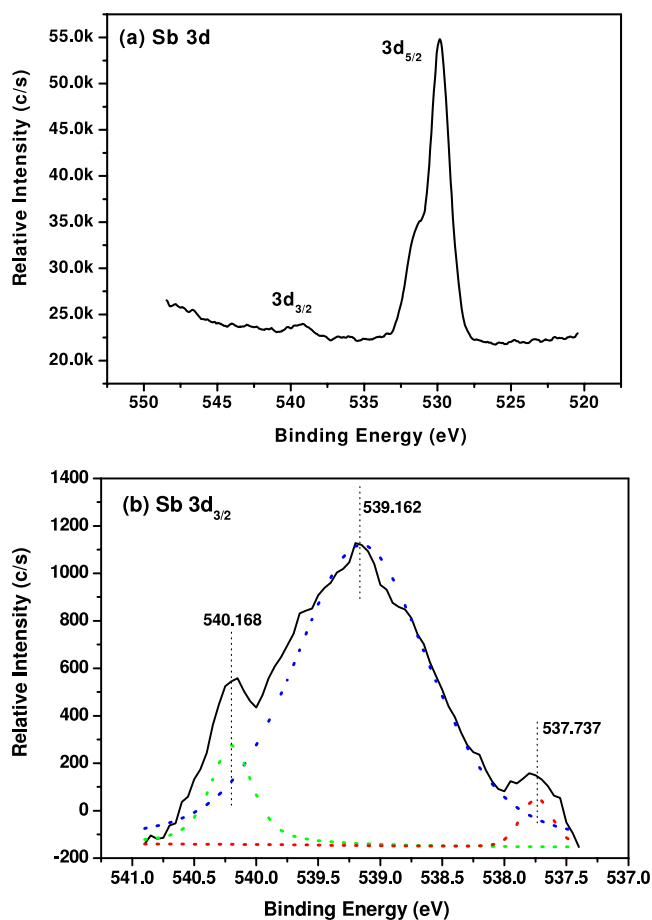


Figure 2. (a) XPS spectra for Sb $3d_{3/2}$ and $3d_{5/2}$; (b) fit for Sb $3d_{3/2}$ spectra.

To detect the incorporation of Sb and investigate the local chemical bonding of Sb in the films, XPS measurements were performed. As is shown in figure 2, the Sb $3d_{3/2}$ spectra can be fitted into three peaks: 540.168, 539.162 and 537.737 eV. The XPS result shows that Sb ions are mainly in the form of Sb^{5+} , Sb^{3+} and Sb^0 . The $\text{Sb}^{3+}/\text{Sb}^{5+}$ ratio is found to be about 10:1 by integrating the peak intensities. The positive charge state of Sb in the film implies that Sb substitutes for Zn (Sb_{Zn}) and bonds with O. Since Sb_2O_3 or Sb_2O_5 phase separation is unlikely, as proven by the XRD pattern shown above, we suggest that the doped Sb ions should substitute for Zn ions homogeneously.

The room-temperature PL spectra of samples B and C are shown in figure 3. Both films reveal a broad band PL emission ranging from 350 to 600 nm, centered at about 520 nm. The peak at the wavelength of around 411 nm (3.02 eV) might be assigned to the near-band edge transition of free excitons [14–17]. This is in agreement with the absorption spectra shown in the inset of figure 3, which reveals a bandgap of 2.99 eV for sample B and 3.08 eV for sample C, although this bandgap difference was not clear in the PL spectrum. The typical bandgaps of pure ZnO and ZnMnO in our experimental condition are about 3.20 and 3.13 eV, respectively. The decrease in the bandgap of ZMSO compared to the pure and Mn-doped ZnO confirms the incorporation of Mn, as well as

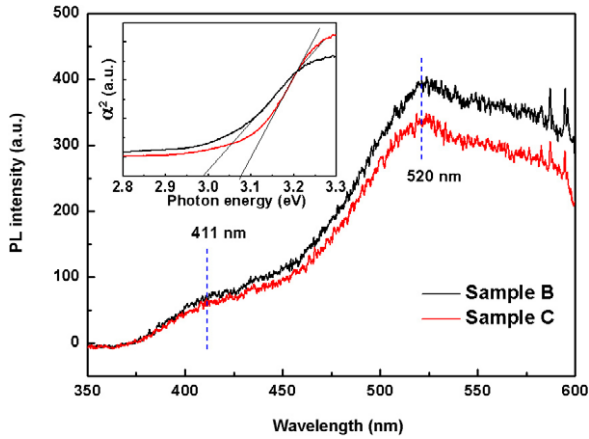


Figure 3. Room-temperature photoluminescence spectrum of $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ (sample B) and $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ grown in an oxygen rich condition (sample C). The inset shows the α^2 versus $h\nu$ plots of sample B and sample C.

the introduction of additional defects via Sb doping in the system. The green emission at around 520 nm might be ascribed to defects such as the singly ionized oxygen vacancies or incorporated Cu^{2+} ions [18–20]. Grown in an oxygen rich condition, sample C shows weaker green luminescence than sample B. This observation reveals that the oxygen vacancy might be responsible for the green luminescence in our films.

The field dependences of magnetizations of samples A, B and C measured at 300 K are shown in figure 4. It can be seen that the $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$ film (sample A) shows no ferromagnetic behavior. However, once co-doped with 0.5% Sb, samples B and C both show clearly ferromagnetic hysteresis. In figure 4, $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ film (sample B) has a saturation magnetization (M_S) of $0.92 \mu_B/\text{Mn}^{2+}$ and a coercive field (H_C) of 66 Oe, while $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ grown in an oxygen atmosphere (sample C) exhibits stronger magnetic hysteresis, with M_S as large as $1.76 \mu_B/\text{Mn}^{2+}$ and an H_C of 84 Oe. It is worth mentioning that these experiments were repeated several times and have been found to be highly reproducible. Obviously, the co-doping of Sb does indeed play a key role in tuning the ferromagnetism of the ZMO film. Furthermore, the oxygen rich atmosphere gives a great enhancement of the ferromagnetism; for example, the saturation magnetization of sample C is nearly twice that of sample B.

Much attention should be paid to the origin of the ferromagnetism in ZMSO films. First we should consider the influence of substrates or the secondary phase such as Mn_3O_4 . The Mn concentration of 1% is much lower than the equilibrium solubility of Mn in ZnO of 13% [21], and no evidence for secondary phase was found in XRD or XPS tests. Furthermore, using the same substrates and with the same Mn concentration of 1%, samples A, B and C exhibited obvious differences of ferromagnetism intensity shown in M – H curves. We therefore come to the conclusion that, compared with the intrinsic magnetism, signals from substrates or the secondary phase can be neglected.

Ferromagnetic ordering in ZnO-based DMS is widely believed to be carrier mediated [6, 22, 23]. The large M_S

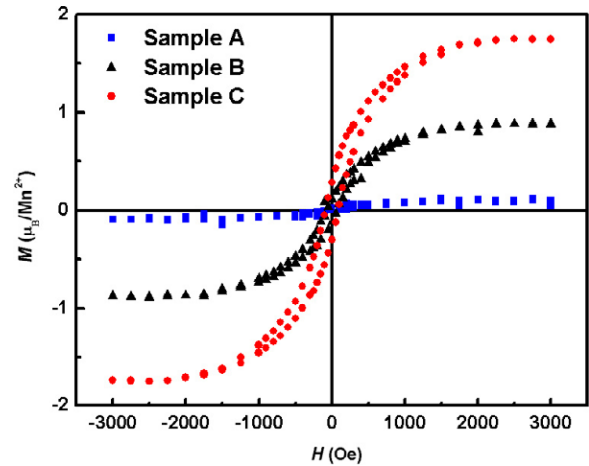


Figure 4. Hysteresis loops for $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$ (sample A), $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ (sample B) and $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ grown in an oxygen rich condition (sample C) measured at 300 K.

of ZMSO films might come from the Mn–Mn ferromagnetic interaction mediated by Sb-induced defects. As a promising p-type dopant in group V, Sb has attracted considerable research interest recently. For instance, Aoki *et al* reported on Sb-doped p-type ZnO film grown by excimer laser doping [24]. Xiu *et al* also reported on Sb-doped p-type ZnO film prepared by molecular beam epitaxy [25]. First-principles calculations attribute p-type conductivity in Sb-doped ZnO films to an acceptor complex ($\text{Sb}_{\text{Zn}}-2\text{V}_{\text{Zn}}$) [26]. In ZMSO films, the nearby Mn ions might be aligned together via localized holes introduced by the acceptor complex ($\text{Sb}_{\text{Zn}}-2\text{V}_{\text{Zn}}$), and form the so-called bound magnetic polarons (BMPs) [27]. The bound magnetic polaron model assumes an exchange interaction between localized holes and the transition-metal ion. An oxygen rich condition was thought to be beneficial to get p-type Sb-doped ZnO [26, 28]. As shown in figure 4, sample C, grown in an oxygen rich condition, shows stronger ferromagnetic signals than sample B. The above results confirm that the ferromagnetism is more likely to be mediated by the holes. Although n-type defects such as oxygen vacancies, Zn interstitials or $\text{Sb}^{3+}/\text{Sb}^{5+}$ substituted for Zn^{2+} do exist, some localized p-type defects still work to induce the ferromagnetic coupling of nearby Mn ions [10, 29, 30]. Unfortunately, attempts to measure the Hall effects have failed because of the high resistivities of the films.

4. Conclusion

In conclusion, magnetism of $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$ and $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ thin films prepared on sapphire(0001) by reactive rf magnetron sputtering was investigated. $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$ showed no obvious ferromagnetic behavior. However, $\text{Zn}_{0.985}(\text{Mn}_{0.01}, \text{Sb}_{0.005})\text{O}$ films exhibited strong ferromagnetic signals. In our experimental conditions, doping with Mn alone induced no obvious ferromagnetism in the ZnO system itself. The co-doping of Sb plays a key role in the formation of ferromagnetic ordering, while an oxygen rich condition can

enhance the magnetic moment drastically. The formation of bound magnetic polarons, which consist of localized holes and surrounding clouds of Mn spins, is thought to be responsible for the ferromagnetism. Further studies are in progress to more clearly elucidate the ferromagnetic mechanisms.

Acknowledgments

This work was jointly supported by the National Basic Research Program of China and the National Nature Science Foundation of China (grant Nos 50428202 and 10674057). We also acknowledge the support from the Changjiang Scholars and Innovative Research Team in the University (PCSIRT).

References

- [1] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and Koinuma H 2001 *Science* **291** 854
- [2] Hong N H, Sakai J, Prellier W, Hassini A, Ruyter A and Gervais F 2004 *Phys. Rev. B* **70** 195204
- [3] Prellier W, Fouchet A, Mercey B, Simon Ch and Raveau B 2003 *Appl. Phys. Lett.* **82** 3490
- [4] Ogale S B, Choudhary R J, Buban J P, Lofland S E, Shinde S R, Kale S N, Kulkarni V N, Higgins J, Lanci C, Simpson J R, Browning N D, Das Sarma S, Drew H D, Greene R L and Venkatesan T 2003 *Phys. Rev. Lett.* **91** 077205
- [5] Coey J M D, Douvalis A P, Fitzgerald C B and Venkatesan M 2004 *Appl. Phys. Lett.* **84** 1332
- [6] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 *Science* **287** 1019
- [7] Sato K and Katayama-Yoshida H 2001 *Japan. J. Appl. Phys.* **40** L334
- [8] Feng X 2004 *J. Phys.: Condens. Matter* **16** 4251
- [9] Wang Q, Sun Q, Rao B K and Sena P 2004 *Phys. Rev. B* **69** 233310
- [10] Kittilstved K R, Norberg N S and Gamelin D R 2005 *Phys. Rev. Lett.* **94** 147209
- [11] Heo Y W, Ivill M P, Ip K, Norton D P, Pearton S J, Kelly J G, Rairigh R, Hebard A F and Steiner T 2004 *Appl. Phys. Lett.* **84** 2292
- [12] Yang Z, Liu J L, Biasini M and Beyermann W P 2008 *Appl. Phys. Lett.* **92** 042111
- [13] Behan A J, Mokhtari A, Blythe H J, Score D, Xu X-H, Neal J R, Fox A M and Gehring G A 2008 *Phys. Rev. Lett.* **100** 047206
- [14] Maensiri S, Masingboon C, Promarak V and Seraphin S 2007 *Opt. Mater.* **29** 1700
- [15] Vanheusden K, Warren W L, Sesger C H, Tallant D R, Voigt J A and Gnage B E 1996 *J. Appl. Phys.* **79** 7983
- [16] Stikant V and Clarke D R 1998 *J. Appl. Phys.* **83** 5447
- [17] Bergman L, Chen X B, Morrison J L, Huso J and Purdy A P 2004 *J. Appl. Phys.* **96** 675
- [18] Studenikin S A, Golego N and Cocivera M 1998 *J. Appl. Phys.* **84** 2287
- [19] Kang H S, Kang J S, Kim J W and Lee S Y 2004 *J. Appl. Phys.* **95** 1246
- [20] Garces N Y, Wang L, Bai L, Giles N C, Halliburton L E and Cantwell G 2002 *Appl. Phys. Lett.* **81** 622
- [21] Bates C H, White W B and Roy R 1966 *J. Inorg. Nucl. Chem.* **28** 397
- [22] Norberg N S, Kittilstved K R, Amonette J E, Kukkadapu R K, Schwartz D A and Gamelin D R 2005 *J. Am. Chem. Soc.* **126** 9387
- [23] Sato K and Katayama-Yoshida H 2002 *Phys. Status Solidi b* **229** 673
- [24] Aoki T, Shimizu Y, Miyake A, Nakamura A, Nakanishi Y and Hatanaka Y 2002 *Phys. Status Solidi b* **229** 911
- [25] Xiu F X, Yang Z, Mandalapu L J, Zhao D T, Liu J L and Beyermann W P 2005 *Appl. Phys. Lett.* **87** 152101
- [26] Limpijumnong S, Zhang S B, Wei S H and Park C H 2004 *Phys. Rev. Lett.* **92** 155504
- [27] Furdyna J K and Kossut J 1988 *Diluted magnetic semiconductors Semiconductors and Semimetals* vol 25 (New York: Academic)
- [28] Xiu F X, Yang Z, Mandalapu L J, Zhao D T and Liu J L 2005 *Appl. Phys. Lett.* **87** 252102
- [29] Ivill M, Pearton S J, Norton D P, Kelly J and Hebard A F 2005 *J. Appl. Phys.* **97** 053904
- [30] Pan H, Yi J B, Shen L, Wu R Q, Yang J H, Lin J Y, Feng Y P, Ding J, Van L H and Yin J H 2007 *Phys. Rev. Lett.* **99** 127201