Effect of annealing atmosphere on ferromagnetism in Mn doped ZnO films*

Liu Xing-Chong(刘兴翀)[a)†], Lu Zhi-Hai(陆智海)[b)], and Zhang Feng-Ming(张凤鸣)[b)]

[a)] *Institute of High Energy Electronics, School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu* 610054, *China*

[b)] *Department of Physics, Nanjing University, Nanjing* 210093, *China*

(Received 5 December 2008; revised manuscript received 1 April 2009)

This paper reports that $Zn_{0.97}Mn_{0.03}O$ thin films have been prepared by radio-frequency sputtering technology followed by rapid thermal processing in nitrogen and oxygen ambient respectively. Magnetic property investigation indicates that the films are ferromagnetic and that the Curie temperature (T_c) is over room temperature. It is observed that the saturation magnetization of the films increases after annealing in nitrogen ambience but decreases after annealing in oxygen. Room temperature photoluminescence spectra indicate that the amount of defects in the films differs after annealing in the different ambiences. This suggests that the ferromagnetism in $Zn_{0.97}Mn_{0.03}O$ films is strongly related to the defects in the films.

Keywords: magnetic semiconductor, ZnO, photoluminescence

PACC: 7550P, 7360F, 7855D

1. Introduction

In recent years, diluted magnetic semiconductors (DMS) have attracted much attention of researchers because of their potential application in spintronics.[1−5] Among the family of DMS ZnO-based DMS received special attention,[6] which had been theoretically predicted to be ferromagnetic with Curie temperature (T_c) higher than room temperature. However, in spite of much work published on Mn doped ZnO DMS, the results are inconsistent, even controversial. For instance, using the same method of solid-state reaction, Sharma *et al.*[7] observed a high temperature ferromagnetism ($T_c > 300$ K) in low-temperature-processed Mn–ZnO system, while Kolesenik *et al.*[8] found that single-phase samples only showed paramagnetic Curie–Weiss behaviour. Besides, the mechanism of ferromagnetism in Mn doped ZnO is also far from well being understood. Some researchers found that the high temperature ferromagnetism in low-temperature came from a metastable phase,[9] while others believed that a hole-mediated ferromagnetism existed in Mn-doped ZnO.[10,11] However, it is also reported that defects especially oxygen vacancies played an important role in magnetic origin in ZnO-based DMS.[12−14] More intensive and extensive work is needed for better understanding the mechanism of ferromagnetism in Mn-doped ZnO system.

In this work, $Zn_{0.97}Mn_{0.03}O$ thin films were fabricated by radio-frequency sputtering technology followed by rapid thermal process in different ambiences. Structural, magnetic and optical properties of the films were systematically investigated. Our work indicated that defects were strongly correlated with the ferromagnetism in $Zn_{0.97}Mn_{0.03}O$ thin films.

2. Experiment

The $Zn_{0.97}Mn_{0.03}O$ thin films were deposited on single crystalline Si (001) substrates by radio-frequency magnetron sputtering. The ceramic target was prepared by solid-state reaction of high purity ZnO (Alfa Aesar) and MnO_2 (Alfa Aesar) at 700 °C. With base pressure of 1×10^{-5} Pa, the operation pressure and working power were 1 Pa and 100 W, respectively. During the deposition, the temperature of substrate was kept at 500 °C. The O_2/Ar gas flow ratio during the deposition was 1:1. The thickness of the samples was fixed at 600 nm. Then the as-deposited films denoted as samples A were annealed at

*Project supported by the National Key Program for Fundamental Research Development Plan of China (973 Project).

†Corresponding author. E-mail: xcliu@uestc.edu.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

850 °C for 2 min in nitrogen and oxygen ambience respectively, correspondingly denoted as samples B (nitrogen) and C (oxygen). The concentrations of manganese in the films were detected with field-emission scanning electron microscope (EDAX). The structural properties of the films were analysed through x-ray diffraction (XRD). Superconducting quantum interference device (SQUID) system, MPMS-XL from quantum design, was employed to investigate the magnetic properties of the films. Moreover, room-temperature photoluminescence spectra of the films were measured with a continuous wave He–Cd 325-nm laser for all the samples.

3. Results and discussion

Through EDAX measurement, the Mn concentrations in the films were 3.02% and all the films were insulating. Figure 1 shows the typical XRD spectra of the samples A, B, C and pure ZnO films. Only a sharp diffraction peak corresponding to ZnO (002) orientation was observed, which gives suggestion of ordered ZnO films. It can be seen from inset that the positions of diffraction peaks (002) shift towards lower angles indicating the lattice expansion in ZnO with incorporation of Mn. Moreover, it was indicated in the figure that both the positions and relative intensity of diffraction peaks for samples A, B and C changed little which suggested that after annealing, the structure of the samples did not show any change.

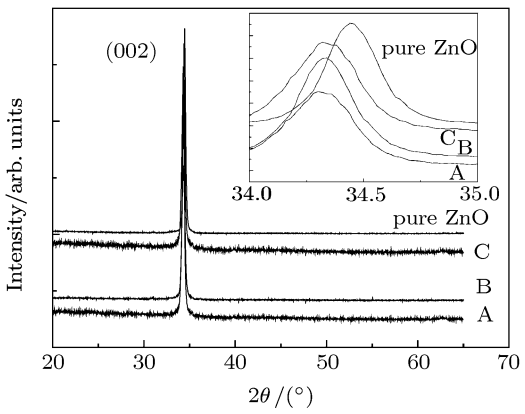


Fig. 1. XRD spectra of samples A, B, C and pure ZnO. Inset shows the highlight for peak (200) of ZnO.

Figure 2 shows the experimental results on the magnetic properties of the sample A from SQUID measurements with applied field parallel to the film plane. All the data had subtracted the diamagnetic contribution from the substrate. Figure 2(a) shows the typical magnetic hysteresis loop of the films A and pure ZnO films (inset) at 300 K, respectively. It was observed that pure ZnO films showed no ferromagnetism while the $Zn_{0.97}Mn_{0.03}O$ films were ferromagnetic at room temperature. It was well known that nearly all of the possible Mn-based binary and ternary oxide candidates are antiferromagnetic except Mn_3O_4 which is ferromagnetic with a Curie temperature of only 46 K in thin films.[15,16] Therefore, it is believed that ferromagnetism in the the $Zn_{0.97}Mn_{0.03}O$ films was caused by incorporation of Mn into ZnO lattice.

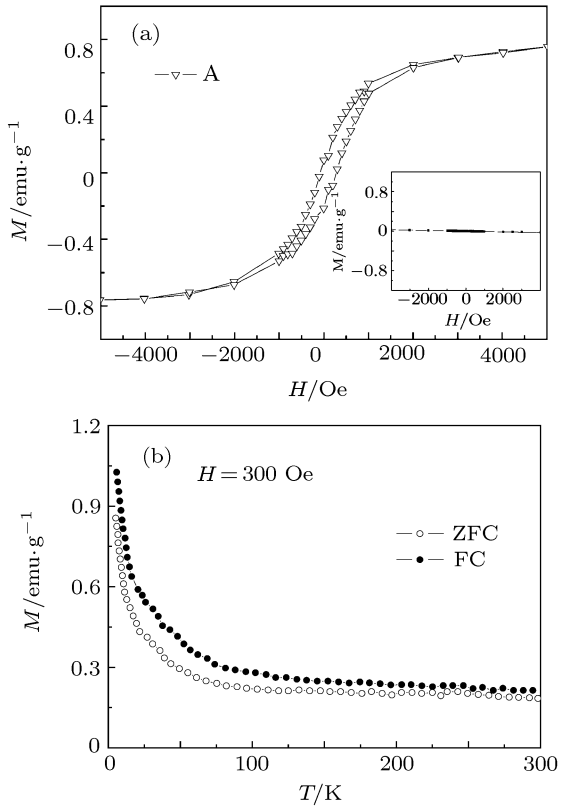


Fig. 2. (a) Typical magnetic hysteresis loops of samples A at 300 K. Inset shows the magnetic hysteresis loops of pure ZnO films. (b) Typical zero field cooled (ZFC) and field cooled (FC) M–T curves of samples A at applied field of 300 Oe.

Figure 2(b) shows the typical zero-field-cooled (ZFC) and field-cooled (FC) magnetization of the samples A as a function of temperature at applied field of 300 Oe (1 Oe=1 Gb/cm). The magnetization decreased with temperature but remained larger than zero up to 300 K, which confirmed that the hysteresis loops are attributed to the ferromagnetism in ZnMnO films.[17] It also showed a distinct splitting between the ZFC and FC curves. In the case of DMS, the FC

and ZFC curves begin to split at a temperature below the Curie temperature, then change monotonously with further decrease of temperature.[17−28] While in the magnetic nano-particle system, the FC and ZFC curves only overlap in high temperature range and in ZFC curve, a peak at a "blocking" temperature could be observed, which was caused by the competition between the thermal energy and the magnetic anisotropy energy of nano-particles.[21−23] In Fig. 2(b), no signal for the peak can be observed in the ZFC curves at high temperature range. Therefore, it was believed that any other magnetic nano-particles did not existed in all the samples and ferromagnetism at 300 K was again proved to be caused by the incorporation of Mn into ZnO. Moreover, it was also observed that the shape of the ZFC and FC curves of the samples B and C was same to samples A, which were not shown here. This gave strong evidence that rapid thermal process did not cause any extra magnetic phases or magnetic complexes in the samples, which was consistent to the results of XRD spectra.

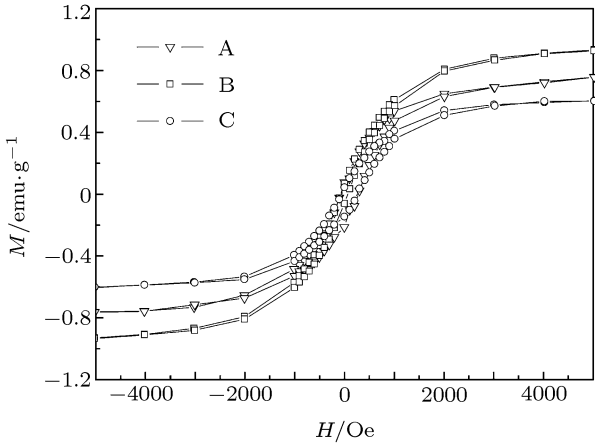


Fig. 3. Typical hysteresis loops of the samples A, B and C at 300 K.

Figure 3 shows the typical hysteresis loops of the samples A, B and C at 300 K. It was observed that after annealing at 850 °C, the saturation magnetization of the films changed obviously. The saturation magnetization of the films increased after annealing in nitrogen but decreased after annealing in oxygen. Room-temperature photoluminescence spectra of the samples A, B and C were shown in Fig. 4. It was observed that two peaks existed in room-temperature photoluminescence spectra, one near band edge (NBE) emission at around 3.26 eV and the other at around 2.4 eV, corresponding to defect-related emission,[24−26] such as oxygen vacancy and zinc interstitial. On the comparison of photoluminescence with the samples, defect-related emission was enhanced after annealing in nitrogen but decreased after annealing in oxygen. It is reasonable because annealing in oxygen could decrease the oxygen vacancy in the films, while annealing in nitrogen, the oxygen vacancy could increase due to the evaporation of some Zn atoms although the time of annealing is short.

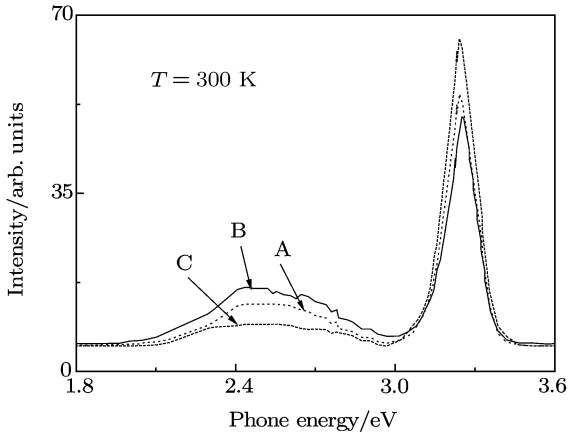


Fig. 4. Room-temperature photoluminescence spectra of the samples A, B and C.

Based on the XRD spectra and the curves of ZFC and FC as mentioned before, the structure of the films did not change after rapid thermal process. Therefore it can be easily believed that the change of saturation magnetization was related to the oxygen vacancy in the films. In the bound magnetic polarons (BMPs) model,[27] electrons are locally trapped by donor defects (such as oxygen vacancies). The donors tend to form bound magnetic polarons, coupling the local magnetic moments of the sparsely distributed transition metal within their orbits. The coupling between two transition impurities in the same bound magnetic polaron is ferromagnetic. Therefore, the ferromagnetism arises when the overlapping of the bound magnetic polarons occurs. This model has been proposed to explain the origin of room temperature ferromagnetism for some insulating oxide DMSs (such as Mn doped ZnO).[27] In our work, it was found that the room temperature ferromagnetism in $Zn_{0.97}Mn_{0.03}O$ thin films was intrinsic and the saturation magnetization of the samples was proportional to the defects in the films. The detailed amount of defects is difficult to measure. However, because defects in our films such as oxygen vacancy and zinc interstitial are donors and

the films in our work are insulating, it is reasonable to believe that the concentration of the defects in our films is much lower than the Mn concentration.

Therefore, it is reasonable to understand that although a lot of Mn atoms have incorporated into ZnO lattice, still many Mn atoms are isolated because of lacking defects, whose case is like that in Ref. [18]. The higher concentration of defects, the more amounts of Mn impurities were coupled to form the bound magnetic polarons, corresponding to higher magnetization. Therefore, the observations are consistent with the model of Coey *et al.*[27] Convincingly, it could be concluded that defects play an important role in the ferromagnetism in the $Zn_{0.97}Mn_{0.03}O$ films.

4. Conclusion

Structural, magnetic and optical properties of $Zn_{0.97}Mn_{0.03}O$ films prepared by sputtering have been investigated. The films were ferromagnetic with Curie temperature over 300 K which was caused by incorporation of Mn into ZnO lattice. After rapid thermal process, both the amount of defects and the saturation magnetization of the films changed. It is found that the saturation magnetization of the samples is sensitive to the defects in the films, suggesting that defect-related ferromagnetism exists in the $Zn_{0.97}Mn_{0.03}O$ films.

References

[1] Ohno H 1998 *Science* **281** 951
[2] Prinz G A 1998 *Science* **282** 1660
[3] Park J H, Vescovo E, Kim H J, Kwon C, Ramesh R and Venkatesan T 1998 *Nature* **392** 794
[4] Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnar S, Roukes M L, Chtchelkanova A Y and Treger D M 2001 *Science* **294** 1488
[5] Ball P 2002 *Nature* (London) **404** 918
[6] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 *Science* **287** 1019
[7] Sharma P, Gupta A, Rao K V, Owens F J, Sharma R, Ahuja R, Guillen J M O, Johansson B and Gehring G A 2003 *Nature Mater.* **2** 673
[8] Kolesnik S and Dabrowski B 2004 *J. Appl. Phys.* **96** 5379
[9] Kundaliya D C, Ogale S B, Lofland S E and Dhar S 2004 *Nature Mater.* **3** 709
[10] Ivill M, Pearton S J, Heo Y W, Kelly J, Hebard A F and Norton D P 2007 *J. Appl. Phys.* **101** 123909
[11] Souza T M, Lima I C, Da C H and Boselli M A 2008 *Appl. Phys. Lett.* **92** 152511
[12] Ramachandran S, Narayan S and Prater J T 2006 *Appl. Phys. Lett.* **88** 242503
[13] Hus H S, Huang J C A, Liao Y F, Lin M Z and Lee C H 2006 *Appl. Phys. Lett.* **88** 242507
[14] Weng H M, Yang X P, Dong J M, Mizuseki H, Kawasaki M and KawaZoe Y 2004 *Phys. Rev.* B **69** 125219
[15] Guo L W, Peng D L, Makino H, Inaba K, Ko H J, Sumiyama K and Yao T 2000 *J. Magn. Magn. Mater.* **213** 321
[16] Yan H L, Wang J B, Zhong X L and Zhou Y C 2008 *Appl. Phys. Lett.* **93** 142502
[17] Nroton D P, Pearton S J, Hebard A F, Theodoropoulou N, Boatner L A and Wilson R G 2003 *Appl. Phys. Lett.* **82** 239
[18] Jayakumar O D, Salunke H G, Kadam R M, Mohapatra M, Yaswant G and Kulshreshtha S K 2006 *Nanotechnology* **17** 1278
[19] Theodoropoulou N, Hebard A F, Oberberg M E, Abernathy C R, Perton S J, Chu S N G and Wilson R G 2002 *Phys. Rev. Lett.* **89** 107203
[20] Liu X C, Lu Z H, Lu Z L, Lü L Y, Wu X S, Zhang F M and Du Y W 2006 *J. Appl. Phys.* **100** 073903
[21] Seo W S, Jo H H, Lee K, Kim B, Oh S J and Park J T 2004 *Angew. Chem.* **43** 1115
[22] Gao Y H, Bao Y P, Beerman M, Yasuhara A and Shindo D 2004 *Appl. Phys. Lett.* **84** 3361
[23] Lee Y H, Han T C and Huang J C A 2003 *J. Appl. Phys.* **93** 8462
[24] Huang M H, Wu Y Y, Feick H, Tran N, Weber E and Yang P 2001 *Adv. Mater.* **13** 113
[25] Chen Y, Bagnall D M, Koh H J, Park K T, Hiraga K, Zhu Z and Yao T 1998 *J. Appl. Phys.* **84** 3912
[26] Joseph M, Tabata H and Kawai T 1999 *Jpn. J. Appl. Phys.* **38** 1205
[27] Coey J M D, Venkatesan M and Fitzgerald C B 2005 *Nature Mater.* **4** 173