Ferromagnetism in Eu-doped ZnO films deposited by radio-frequency magnetic sputtering*

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(Received 22 December 2009; revised manuscript received 25 March 2010)

This paper reports that Eu-doped ZnO films were successfully deposited on silicon (100) by radio-frequency magnetic sputtering. The x-ray diffraction patterns indicate that Eu substitutes for Zn in the lattice. Ferromagnetic loops were obtained by using superconducting quantum interference device at 10 K and room temperature. No discontinuous change was found in both of the zero-field-cooled and field-cooled curves. The observed ferromagnetism in Eu-doped ZnO can be attributed to a single magnetic phase. The saturation magnetisation decreased remarkably for the Eu-doped ZnO prepared by introducing 5% of oxygen in the sputtering gas or by the post annealing in O_2, suggesting that the defects play key roles in the development of ferromagnetism in Eu-doped ZnO films.

Keywords: Eu-doped ZnO films, ferromagnetism, radio-frequency magnetic sputtering
PACC: 7550P, 7360F

1. Introduction

In conventional semiconductor devices, the spin of the charge carriers is usually ignored. Diluted magnetic semiconductors (DMSs) systems formed by substituting a fraction of a host semiconductor cations with magnetic ions, have been of much interest because of their potential as a new functional material, which will open a way to introduce the spin degree of freedom into semiconductor devices.[1,2]

For practical applications, DMSs should be ferromagnetic above room temperature. Theoretical works predicted that transition metal (TM) ions substitution in ZnO could produce ferromagnetism above 300 K.[3,4] The ferromagnetism measured at various temperatures was reported in Co-, Ni-, Mn-, and Fe-doped ZnO.[5−9] Rare earth atoms have partially filled f-orbitals which carry magnetic moments and may take part in magnetic coupling as in the case of TMs with partially filled d-orbitals. Recent experiments show that rare earth metals (Gd and Eu), doped GaN exhibits ferromagnetic coupling.[10−13] On the other hand, rare-earth ions are good luminescence centres due to their narrow and intense emission lines originated from 4f intrashell transitions. Many investigations on the pure optical properties of Eu, Tb, and Er doped ZnO have been carried out.[14−17] Compared with TM doped ZnO, rare earth metals doped ZnO has been much less studied with respect to ferromagnetic properties, although such a system would be very interesting for magneto-optical applications.

In this paper, we present the structural and magnetic properties of rare-earth metal Eu-doped ZnO films prepared by radio-frequency (RF) magnetic sputtering. The results showed the room temperature ferromagnetism in Eu-doped ZnO films. The influence on magnetic properties of Eu-doped ZnO film with sputtering ambience and the post annealing in O_2 is also examined.

2. Experimental

The pure and Eu-doped ZnO films were deposited on silicon (100) substrates by RF magnetic sputtering. The ceramic targets of ZnO and $Zn_{0.95}Eu_{0.05}O$ were synthesized from stoichiometric amounts of high purity ZnO and Eu_2O_3 powders. The pure argon (99.99% purity) or argon/oxygen premixed sputtering gas (oxygen content: 5%) were introduced to the chamber at a base pressure of 3×10^{-4} Pa. The substrate temperature, the working pressure and the de-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10774129 and 60425411) and the Ministry of Science and Technology of China.
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position time were 450 °C, 1 Pa and 2 h respectively. After the deposition, some of the samples were annealed in oxygen ambience at 450 °C for 2 hours. The crystalline qualities of the samples were examined by x-ray diffraction (XRD) measurements. Magnetic properties were investigated by measuring magnetisation as functions of magnetic field and temperature with superconducting quantum interference device (SQUID).

3. Results and discussion

Figure 1 shows the XRD patterns of $Zn_{0.95}Eu_{0.05}O$ and undoped ZnO films deposited on Si (100) in pure argon. The inset shows the expanded view of the XRD pattern for $Zn_{0.95}Eu_{0.05}O$ film. The patterns indicate that the films exhibit the *c*-axis orientation without any impurity phases. For the Eu-doped ZnO film, the (002) peak intensity increases with respect to ZnO film, and the (101) peak disappears. The similar results were found in Tb-doped ZnO films,[16] and these results suggest that proper quantities of Eu doping in ZnO film would stimulate the grain growth and improve the crystallinity of the film. The XRD peak corresponded to the (002) plane of $Zn_{0.95}Eu_{0.05}O$ is smaller. So the lattice constant in the c-direction is 5.2662 Å (1 Å=0.1 nm), slightly larger than that (5.2296 Å) of ZnO. As the ionic radius of Eu^{3+} (1.07 Å) is much larger than that of Zn^{2+} (0.74 Å),[14] the increase of this out-of-plane '*c*' lattice constant indicates substitution of Eu at Zn sites.

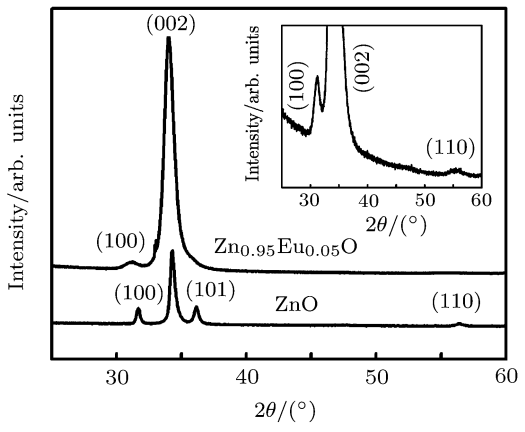


Fig. 1. XRD patterns of $Zn_{0.95}Eu_{0.05}O$ and undoped ZnO films deposited on Si (100) with pure argon. The inset shows the expanded view of the XRD pattern of $Zn_{0.95}Eu_{0.05}O$ film.

Figure 2 exhibits the curves of magnetisation versus applied field for $Zn_{0.95}Eu_{0.05}O$ film at 10 K and 300 K. The magnetic field was applied perpendicularly to the sample surface. The pure ZnO shows diamagnetic even at low temperature.[18] For the $Zn_{0.95}Eu_{0.05}O$ film, clear hysteresis loops, observed in the *M*–*H* curves both at room temperature and at low temperature down to 10 K, show that the sample is ferromagnetic. The origin for the ferromagnetism in the Eu doped ZnO, even at room temperature, can be attributed to Eu^{3+} ions substituted for Zn^{2+} ions in the lattice, since EuO is ferromagnetism with a T_C of 69 K,[19] metallic Eu is helimagnetism with a Θ_N about 92 K, and Eu_2O_3 shows paramagnetic at 300 K. Some experiments on magnetic element doped ZnO suggested that the ferromagnetism might be caused by a secondary phase such as doping elements or their oxides.[20,21] However, in the present case, the magnetism in the Eu-doped ZnO derived from impurity phase can be excluded because of no impurity phase found in $Zn_{0.95}Eu_{0.05}O$ film with XRD measurements.

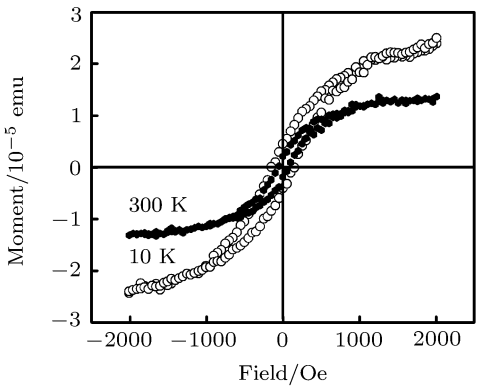


Fig. 2. Magnetisation versus applied field curves of $Zn_{0.95}Eu_{0.05}O$ film measured at 10 K and 300 K.

In order to better understand the magnetic properties of $Zn_{0.95}Eu_{0.05}O$ film, the magnetisations as functions of temperature were also carried out. Figure 3 shows the zero-field-cooled (ZFC) and field-cooled (FC) curves for the $Zn_{0.95}Eu_{0.05}O$ film. In FC measurement, a magnetic field of 200 Oe (1 Oe=79.5775 A/m) was applied perpendicularly to the sample surface, and for the ZFC measurement, the sample was first cooling down to 10 K under zero applied field, and then the net magnetisation was measured with a magnetic field of 200 Oe during heating. The ZFC and FC curves keep separate in the whole temperature range from 10 K to 300 K, suggesting that the film is ferromagnetic, and apparently, the Curie temperature of the film is much higher than 300 K, since the magnetisation in the FC curve remains almost constant up to 300 K. It is also clear that no discontinuous change in both of the FC and ZFC curves confirms that in the XRD measurement,

the observed ferromagnetism can be attributed to the single magnetic phase without any phase-separation.

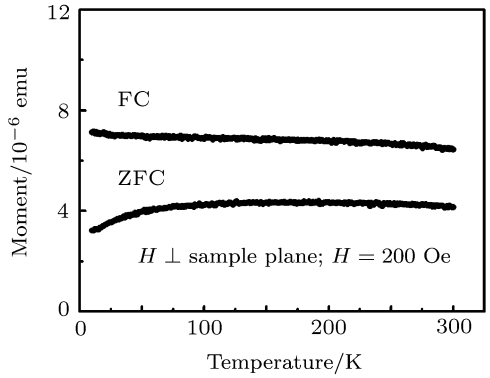


Fig. 3. The FC and ZFC curves for the $Zn_{0.95}Eu_{0.05}O$ film deposited Si (100) with pure argon. The magnetic field of 200 Oe was applied perpendicularly to the sample surface.

Figure 4 shows the room temperature M–H curves of Eu-doped ZnO films prepared by sputtering in 5% of oxygen content, and by sputtering in pure Ar ambience followed annealing in O_2 at 450 °C for 2 hours. The M–H curves of $Zn_{0.95}Eu_{0.05}O$ at room temperature (as shown in Fig. 2) were also included. Although all the films show ferromagnetism at 300 K, but the saturated magnetisation decreases remarkably for both the sample prepared by introducing 5% oxygen content into the sputtering gas and the sample prepared by sputtering followed by annealing in O_2. The sputtering and post annealing ambience have great influence on the ferromagnetism of $Zn_{0.95}Eu_{0.05}O$ film.

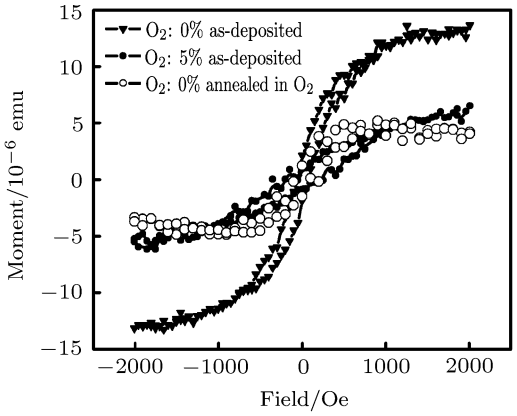


Fig. 4. The M–H curves of Eu-doped ZnO films prepared with 5% oxygen content in the sputtering gas and prepared by sputtering in pure Ar ambience followed annealing in O_2.

A large number of defects such as Zn interstitials and O vacancies can be introduced due to the lack of oxygen when the films were sputtered with pure argon. The concentration of defects, e.g., oxygen vacancies, should be decreased if the sample sputtered with 5% oxygen content in argon gas or the sample sputtered followed by annealed in O_2. As a result, the saturated magnetisation was decreased (as shown in Fig. 4). These results show clearly that the defects play key roles in the development of ferromagnetism in Eu-doped films. The ferromagnetism in Eu-doped ZnO film could be explained by the bounded magnetic polaron (BMP) model,[8] in which, the effective carriers in the films could be localised by defects. Whenever magnetic dopants sit inside the radius of localised carriers and couple with them, a BMP is formed. Once the overlapping of BMPs crosses over the sample, bulk ferromagnetism is created.[3,22,23] Recent results from other groups also suggested that room temperature ferromagnetism could be caused by defects in the TM-doped ZnO.[7,24–27]

4. Conclusions

In summary, Eu-doped ZnO films with a c-axis orientation have been grown on Si (100) substrates by RF magnetic sputtering. The (002) XRD peak of $Zn_{0.95}Eu_{0.05}O$ film is found to be smaller than that of ZnO, indicating Eu substitution for Zn. The ferromagnetic loops were obtained with the SQUID at room temperature and 10 K. No discontinuous change was found in both the ZFC and FC curves, confirming that the observed ferromagnetism can be attributed to the single magnetic phase without any phase-separation. The saturated magnetisation decreased for the Eu-doped ZnO prepared by introducing 5% oxygen in the sputtering gas as well as the post annealing in O_2, which shows that the defects play a key role in the development of ferromagnetism in the Eu-doped ZnO films. More importantly, the present result, the ferromagnetism of Eu-doped ZnO above room temperature, also shows that Eu-doped ZnO can be practically used as a DMS.

References

[1] Koshihara S, Oiwa T, Hirasawa M, Katsumoto S, Iye Y, Urano C, Takagi H and Munekata H 1997 *Phys. Rev. Lett.* **78** 4617

[2] Ohno H 1998 *Science* **281** 951

[3] Dietl T, Ohno H, Matsukura F, Cubert J and Ferrand D 2000 *Science* **287** 1019

[4] Dietl T, Ohno H and Matsukura F 2001 *Phys. Rev.* B **63** 195205

[5] Venkatesan M, Fitzgerald C B, Lunney J G and Coey J M D 2004 *Phys. Rev. Lett.* **93** 177206

[6] Fitzgerald C B, Venkatesan M, Lunney J G, Dorneles L S and Coey J M D 2005 *Appl. Surf. Sci.* **247** 493

[7] Chambers S A, Droubay T C, Wang C M, Rosso K M, Heald S M, Schwartz D A, Kittilstved K R and Gamelin D R 2006 *Mater. Today* **9** 28

[8] Chou H, Lin C P, Huang J C A and Hsu H S 2008 *Phys. Rev.* B **77** 245210

[9] Lin C Y, Wang W H, Lee C S, Sun K W and Suen Y W 2009 *Appl. Phys. Lett.* **94** 151909

[10] Teraguchi N, Suzuki A, Nanishi Y, Zhou Y K, Hashimoto M and Asahi H 2002 *Solid State Commun.* **122** 651

[11] Hite J, Thaler G T, Khanna R, Abemathy C R, Pearton S J, Park J H, Steckl A J and Zavada J M 2006 *Appl. Phys. Lett.* **89** 132119

[12] Dhar S, Brandt O, Ramsteiner M, Sapega V F and Ploog K H 2005 *Phys. Rev. Lett.* **94** 037305

[13] Zhou Y K, Choi S W, Kimura S, Emura S, Hasegawa S and Asahi H J 2007 *Supercond. Nov. Magn.* **20** 429

[14] Zhang Y Z, Liu Y P, Wu L H, Xie E Q and Chen J T 2009 *J. Phys.* D: *Appl. Phys.* **42** 085106

[15] Chen P L, Ma X Y and Yang D 2007 *J. Alloys Comp.* **431** 317

[16] Fang Z B, Tan Y S, Liu X Q, Yang Y H and Yang Y Y 2004 *Chin. Phys.* **13** 1330

[17] Zhou Z, Komori T, Yoshino M, Morinaga M, Matsunami N, Koizumi A and Takeda Y 2005 *Appl. Phys. Lett.* **86** 041107

[18] Potzger K, Zhou S Q, Eichhorn F, Helm M, Skorupa W, Mucklich A, Fassbender J, Herrmannsdorfer T and Bianchi A 2006 *J. Appl. Phys.* **99** 063906

[19] Ulbricht R W, Schmehl A, Heeg T, Schubert J and Schlom D G 2008 *Appl. Phys. Lett.* **93** 102105

[20] Zhang J, Skomski R and Sellmyer D J 2005 *J. Appl. Phys.* **97** 10D303

[21] Bhatti K P, Chaudhary S, Pandya D K and Kashyap S C 2007 *J. Appl. Phys.* **101** 103919

[22] Durst A C, Bhatt R N and Wolf P A 2002 *Phys. Rev.* B **65** 235205

[23] Coey J M D, Venkatesan M and Fitzgerald C B 2005 *Nature Mater.* **4** 173

[24] Khare N, Kappers M J, Wei M, Blamire M G and MacManus-Driscoll J L 2006 *Adv. Mater.* **18** 1449

[25] Yu Z, Li X, Long X, Cheng X W, Liu Y and Cao C B 2009 *Chin. Phys.* B **18** 3040

[26] Liu X J, Zhu X Y, Song C, Zeng F and Pan F 2009 *J. Phys.* D: *Appl. Phys.* **42** 035004

[27] Liu X C, Lu Z H and Zhang F M 2010 *Chin. Phys.* B **19** 027502