Influence of oxygen partial pressure and annealing on magnetic properties of Al -doped ZnO thin films

YUNKAI QI, SHUMIN YANG, JIANJUN GU*, GUOLIANG ZHAO, HUIYUAN SUN[a]
Department of Physics, Hebei Normal University for Nationalities, Chengde 067000, China
[a]*College of Physics Science & Information Engineering, Hebei Normal University, Shijiazhuang 050024, China*

Al doped ZnO films have been prepared using different $Ar:O_2$ ratios and annealing conditions on glass substrates by dc reactive magnetron co-sputtering. The results of magnetic measurements show that different oxygen partial pressures and annealing temperatures have great influence on the magnetism of doped ZnO thin films. The fact that only the films prepared at an $Ar:O_2$ ratio of 1:1 and annealed at 200 ^oC in vacuum show clear room temperature ferromagnetism which disappears after annealed at 500 ^oC in vacuum indicates that the ferromagnetism may be related to internal lattice stress. These ferromagnetic films have been annealed at 200 ^oC in air subsequently and show lower coercivity and enhanced saturation magnetization, which may be attributed to the annealing in air causing more interstitial Al atoms to convert into substitutional Al ions, and consequently increasing the charge transfer between the Al and the ZnO matrix, leading to increased magnetism.

(Received May 6, 2012; accepted June 12, 2013)

Keywords: Diluted magnetic semiconductor, Oxygen partial pressure, Anneal, Ferromagnetism

1. Introduction

ZnO is a typical wide band gap semiconductor with useful piezoelectric and photoelectric properties. It has been widely used in photoluminescence (PL), transparent electric conduction, piezoelectricity and sensitivity to air. Recently, however, the focus of research on ZnO has shifted toward magnetic semiconductors which would be beneficial for developing devices integrating electric and magnetic properties with sensitivity to light [1-3].

According to a theoretical prediction provided by Dietl [4-5] et al., diluted magnetic semiconductors (DMSs) possessing room temperature ferromagnetism (RTFM) may be prepared based on oxide semiconductors with a wide energy gap (such as, ZnO, TiO_2 and GaN) doped with magnetic ions. Recently, there have been studies of ZnO and TiO_2 thin films for producing diluted magnetic semiconductors. Different experimental methods, such as molecular beam epitaxy, pulse laser deposition, reactive sputtering, and the sol-gel method have been used by different research groups, and thin films of oxide DMSs with RTFM have been prepared using transition magnetic ions, such as Co and Mn, doped into ZnO and TiO_2 [6-11].

There have been many controversies about the origin and the mechanism of the magnetism in DMSs. So far, there have been two main kinds of theories regarding this research. First, the origin of RTFM is induced by carrier exchange, represented by Ruderman-Kittel-Kasuya-Yosida (RKKY) theory, Mean Field theory, and Double Exchange theory. Second, in the light of bound magnetic polaron (BMP) theory, the origin of the RTFM is induced by defects.

Recently, there have been reports concerning semiconductor oxide thin films doped with non-magnetic elements. Some notable examples include Ma [12] et al. who studied Al doped ZnO films deposited on a silica substrate by PLD. The RTFM of Al doped ZnO films annealed in vacuum were observed, but the RTFM disappeared when annealed in air. Qi et al. [13] prepared Al/ZnO/Al nanoscale compound films using dc reactive magnetron sputtering, and RTFM was observed when the films were first annealed in vacuum and subsequently annealed in air. Hou et al. [14] have grown Cu doped ZnO films using dc magnetron sputtering which also showed RTFM when annealed in vacuum. Significant attention has been paid to the effects of structure and to the magnetism produced by different methods, different conditions and annealing protocols. However, much less attention has been paid to the effects of the $Ar:O_2$ ratio used during preparation of doped ZnO films and the different temperatures and ambient atmospheres used during annealing of the doped ZnO films.

In the present work, Al doped ZnO films were prepared on glass substrates at different $Ar:O_2$ ratios by dc reactive magnetron co-sputtering, and the samples were annealed under different temperature and environmental conditions. The influences of oxygen partial pressure and annealing conditions on the structure and magnetic properties of Al-doped ZnO thin films were studied.

2. Experimental methods

Al doped ZnO thin films were grown on glass substrates by dc reactive magnetron co-sputtering in a high vacuum chamber evacuated to a base pressure of 10^{-5} Pa. Metallic targets of Al(99.99% purity) and Zn(99.99% purity) were used in this study. Argon (99.99% purity) and oxygen (99.99% purity) were used as the working and reaction gases respectively. During deposition, the

chamber pressure was fixed at 1.6 Pa while the substrate temperature was kept at 200℃. The amount of doped metal was controlled by adjusting the sputtering power, P_{Zn}=16W and P_{Al}=5W. The thickness of the films was controlled using the sputtering time, while the flows of argon and oxygen were controlled by an automatic flow meter. Pure ZnO thin films were grown on a glass substrate using an Ar:O_2 ratio of 6:1, and Al doped ZnO thin films were prepared using Ar:O_2 ratios of 6:1, 4:1 and 2:1 and 1:1. All these samples were annealed in vacuum at 200 ℃ and at 500 ℃ for 30 min. RTFM was found for Al doped ZnO thin films prepared at an Ar:O_2 ratio of 1:1 and annealed in vacuum at 200 ℃. The film showing RTFM was further annealed in air at 200 ℃ for 30 min.

The crystalline structure was investigated by x-ray diffraction (XRD) with Cu Kα radiation. The magnetic properties were determined using a Physical Properties Measurement System (PPMS-6700). For convenience, we give sample numbers corresponding to different annealing conditions in Table 1.

Table 1. The sample numbers prepared using Ar:O_2 ratio of 1:1.

Sample number	Sample 1	Sample 2	Sample 3
Annealing conditions	Annealed in vacuum at 200 ℃	Annealed in vacuum at 500 ℃	Annealed in vacuum at 200℃ and then in air at 200 ℃

3. Results and discussion

3.1 Structural characterization

Fig. 1 shows the XRD patterns and magnified XRD patterns of the (002) diffraction peaks for Al doped ZnO films annealed in vacuum at 200 ℃ and 500 ℃ for films produced using different argon oxygen ratios. From Fig. 1 (a) and (b), it can be seen that all samples have a polycrystalline wurtzite structure. Compared with pure ZnO films, the (002) diffraction peaks of doped films shift to left as the argon oxygen ratios decrease. The greatest shift can be seen in the doped films prepared at Ar:O_2 ratio of 1:1 and the annealed temperature at 200 ℃.

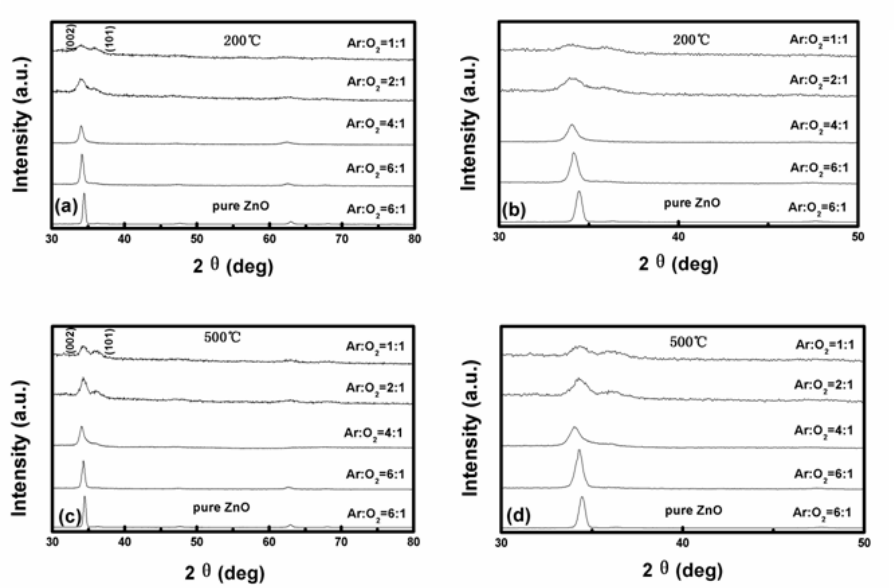

Fig. 1. The XRD patterns for ZnO films and Al doped ZnO films under different argon oxygen ratios (a) 200 ℃(c) 500 ℃ (b) and (d) magnified XRD patterns of the (002) diffraction of a and c, respectively.

It is generally believed that the change of the c-axis of the wurzite structure may be attributed to the substitution of Zn^{2+} by Al^{3+}, residual stress in the films and to the presence of interstitial Al atoms. If ionic substitution is dominant in the doped films, this would lead to compression of the c-axis of the ZnO wurzite structure and the diffraction peak shifting to the right, since the ionic radius of Al^{3+}(0.053 nm) is smaller than that of Zn^{2+} (0.072 nm). However, this is contrary to what we observe. ZnO, with a preferred growth direction along the c-axis and an open hexagonal wurtzite crystal structure, is inverse nested by the hexagonal-close-packed structure of oxygen and zinc. Consequently, it is easier for the Al to become an interstitial atom, resulting in lattice expansion, c-axis elongation and the diffraction peak shifting to the left as observed. In addition, it can also be seen from the XRD

patterns that as the Ar:O_2 ratio decreases, the diffraction peaks become wide which suggests the quality of the crystallization becomes poorer. The intensity of the (002) peak gradually decreases and the intensity of the (101) peak gradually increases, which implies that the preferred orientation of the (002) peak becomes more random.

3.2 Magnetic characterization

An improved magnetic correction method discussed previously [15] is used to correct measurements for the samples. For our substrate, the maximum fitting error is about 3.0×10^{-6} emu. The corrected magnetic measurement shows that the sample 1 and sample 3 revealed RTFM. The magnetic moment of other samples is less than 3.0×10^{-6} emu, implying that there is no identifiable RTFM. Table 2 and Fig. 2 show the values of the magnetic moment, the saturation magnetizations, the coercivity and the *M-H* patterns for the sample1 and sample3, respectively. The coercivity of samples 1 is 108 Oe and the saturation magnetization is 7.8 emu/cm^3. For samples 3, the coercivity decreases to 62 Oe and the saturation magnetization increased to 8.9 emu/cm^3. From the above results, it can be seen that RTFM of samples is associated with prepared and annealed conditions. Higher oxygen partial pressure and lower annealing temperatures is conductive to the presence of RTFM [16,17,18].

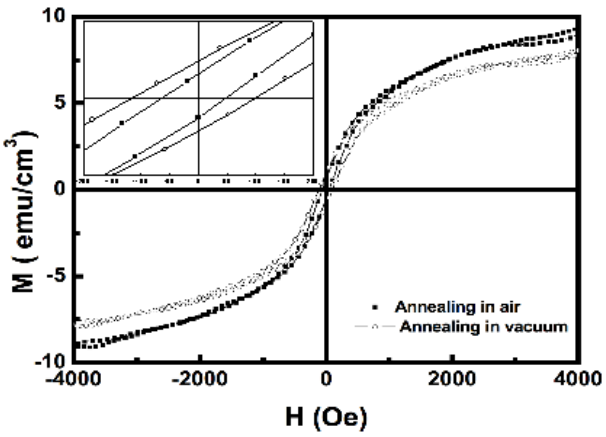

Fig. 2. Magnetization loops for Al doped ZnO films annealed in vacuum and then in air, the inset shows enlarged plots of the coercivity.

In order to further investigate the effects on samples during of the different annealing temperatures and ambient atmospheres, in a first experiment, sample 1 is annealed in vacuum at 500 ℃. In this case, shown as sample 2, the RTFM disappeared. In a second experiment, sample 3 is produced by sample 1 annealed in air at a temperature of 200 ℃. In this case, the coercivity decreases but the saturation magnetization increases. Combining with the XRD and magnetic results, we can conjecture that the origin of the magnetism is related to both the internal stress and the oxygen content in samples.

Table 2. The values of the magnetic moment, the saturation magnetizations and the coercivity of the samples.

Number	*M* (emu)	M_s (emu/cm^3)	*Hc* (Oe)
Sample 1	1.4×10^{-5}	7.8	108
Sample 3	1.6×10^{-5}	8.9	62

In order to better analyze the influence of internal stress on the magnetic properties, we calculated the internal stress for three samples. Table 3 shows the parameters of the samples. When the particle size is smaller than 100 nm, its average dimension D can be related to the FWHM of the XRD diffraction peaks, showed in the following Scherrer equation:

$$D = 0.89\lambda/(B\cos\theta) \quad (1)$$

Here, λ=0.15406 nm is the wave length of the x-rays, B is the FWHM of the (002) peaks, and θ is the corresponding angle of diffraction.

The lattice constant c can be calculated on the basis of the XRD patterns. ZnO has a polycrystalline wurtzite structure. The relation between interplanar distance d and lattice constants c can be calculated in the following equation:

$$1/d^2=4(h^2+hk+k^2)/3a^2+l^2/c^2 \quad (2)$$

Here, d is the interplanar distance, a and c are the lattice constants, and h, k, and l are the indices of the crystallographic plane. For the (002) peaks of ZnO, h=k=0, l=2. According to equation (2), c=2d, the interplanar distance d can be calculated in the following equation:

$$2d\sin\theta=n\lambda \quad (3)$$

The value of c can then be calculated. The internal stresses σ of the samples can be estimated by equation [19]:

$$\sigma= - 453.6\times10^9((c -c_0)/ c_0) \quad (4)$$

Here, c_0=0.5205 nm is the lattice constant of the standard powder for ZnO. From Table 3, it can be seen that the values of the internal stress σ for sample 2 and sample 3 decreases compared with sample 1.

Compared the results from the samples prepared at different Ar:O_2 ratios and annealed in vacuum at 200℃, the quality of crystallization in sample 1 is worse, which may be due to the increasing internal stress resulting in the lattice distortion increasing. The increased oxygen content in the process of preparation also causes more interstitial Al atoms to become substitution Al^{3+} ions as may be seen from the right shift of the (002) diffraction peak in Fig. 1. These cause an increase in the charge transfer between Al and ZnO matrix. Thereby, RTFM is observed. The Al doped ZnO films, produced with Ar:O_2 ratios of 6:1, 4:1 and 2:1 and annealed in vacuum, contain fewer substitution ions, because the oxygen content is relatively small and the Al exists mainly as interstitial atoms. Consequently, the charge transfer between the Al and the ZnO matrix is weak. In addition, it can be seen from the XRD patterns that the quality of crystallization is better, defects within the lattice are relatively few and internal stress is less. No RTFM is observed in those samples.

For sample 2, annealed in vacuum at 500 ℃, the RTFM disappears. It is expected that the internal stress in the ZnO lattice will be released under higher annealing temperatures, as may be seen from Table 3. In the case of sample 2, oxygen is not present during the annealing, and the Al exists mainly as interstitial atoms in the ZnO lattice. The charge transfer between the Al and the ZnO matrix is therefore weak. This allows us to infer that the magnetism in sample 1 came mainly from the internal stress.

Table 3. The parameters of the samples.

samples	sample 1	sample 2	sample 3
Angle of diffraction 2θ (°)	33.97	34.47	34.35
FWHM B (°)	0.76	0.76	0.69
The intensity of (002) peaks (a.u.)	142.90	504.20	403.18
Particle size D (nm)	10.84	10.86	11.94
Internal stress σ （$\times 10^9 N/m^2$）	-5.94	-0.55	-0.96

For sample 3, annealed in air at 200 ℃, the saturation magnetization increased. Fig. 3 shows the XRD pattern for the pure ZnO films annealed in vacuum and for samples 1 and 3. Compared with the (002) diffraction peaks of sample 1, the (002) peaks of the sample 3 shift back to right. Under the oxygen-rich conditions for films annealed in air, more interstitial Al atoms convert into substitution Al^{3+} ions. Since the ionic radius of Al^{3+} (0.053 nm) is smaller than that of Zn^{2+} (0.072 nm), the (002) peaks shift to the right. Since Al has a lower electronegativity than Zn, electrons will be transferred from Al to Zn^{2+} to form Al^{3+}, and concurrently, some Zn^{2+} ions valence will be reduced to Zn^{1+} or Zn^0 [12]. Hence, charge transfer taking place between Al and ZnO may result in an electronic structural change and the appearance of RTFM [12].

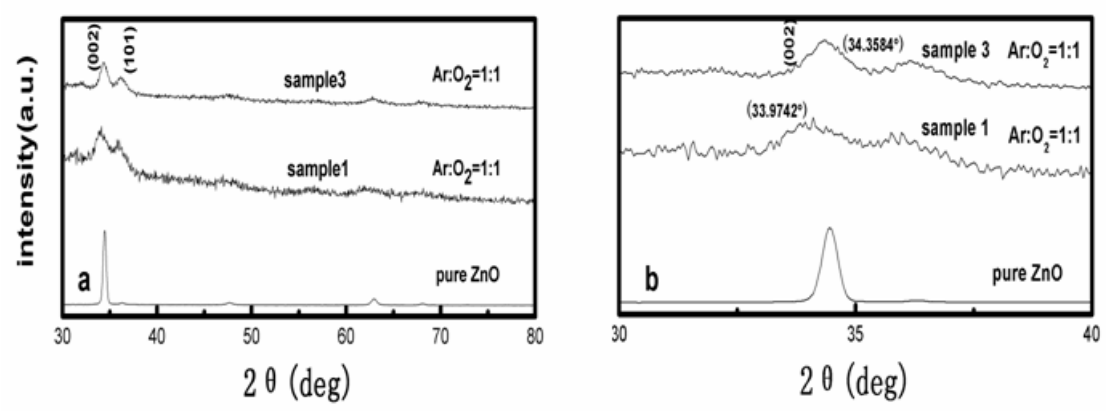

Fig. 3. (a) The XRD pattern for the pure ZnO films annealed in vacuum and Al doped ZnO films annealed in air. (b) Magnified XRD patterns of the (002) diffraction for the samples.

According to the above results, decreasing the internal stress makes the magnetism weaker. However, the experimental results for sample 3 indicate that the contribution from charge transfer is greater than that from internal stress when the sample is annealed in air, thus resulting in the strengthened magnetism. This suggests that the change of the magnetism in sample 3 is mainly related to charge transfer between the Al and the ZnO lattice, internal stress is a secondary factor.

4. Conclusion

Al doped ZnO thin films were grown on glass substrates by dc reactive magnetron co-sputtering at different Ar:O_2 ratios. RTFM was found in Al doped ZnO thin films produced using an Ar:O_2 ratio of 1:1 and annealed in vacuum at 200℃, but the ferromagnetism disappeared after annealed at 500℃ in vacuum, which indicates that the origin of the ferromagnetism may be largely related to lattice internal stress. For samples subsequently annealed in air, the coercivity decreased but the saturation magnetization increased. This may be attributed to more Al atoms turning into Al^{3+} ions and leading to enhanced magnetism. Charge transfer between Al and the ZnO matrix is the main factor for the enhanced magnetism in thin films annealed in air.

Acknowledgments

This work is supported by the Natural Science Foundation of Hebei Province (Grant No.A2012101001, A2012205038), Science and Technology Foundation of Bureau of Finance of Chengde City (Grant No.CZ2012007), 2011 Scientific Research Project of Higher Schools in Hebei Province (Grant No.Z2011101), Hebei Normal University for Nationalities Foundation (Grant No.201108). The authors wish to thank Dr. Norm Davison for helpful discussion.

Reference

[1] V. K. Sharma, G. D. Varma, J. Appl. Phys. **105**, 07C510 (2009).
[2] H. S. Hsu, J. C. A. Huanget, Y. H. Huang, Appl. Phys. Lett. **88**, 242507 (2006).
[3] G. L. Liu, Q. Cao, J. X. Deng, Appl. Phys. Lett. **90**, 052504 (2007).
[4] T. Dietl, H. Ohno, F. Matsukura, et al, Science. **287**, 1019 (2000).
[5] T. Dietl, Semicond. Sci. Technol. **17**, 377 (2002).
[6] K. Ueda, H. Tabata, T. Kawai, Appl. Phys. Lett.**79**, 988 (2001).
[7] S. A. Wolf, D. D. Awschalom, R. A. Buhrman et al, Science. **294**, 1488 (2001).
[8] P. V. Radovanovic, D. R. Gamelin, Phys. Rev. Lett. **91,** 157202 (2003).
[9] J. H. Park, M. G. Kim, H. M. Jang et al, Appl. Phys. Lett. **84**, 1338 (2004).
[10] S. A. Chambers, T. Droubay, C. M. Wang et al, Appl. Phys. Lett. **82,** 1257 (2003).
[11] D. Karmakar, S. K. Mandal, R. M. Kadam et al, Phys. Rev. B. **75**, 144404 (2007).
[12] Y. W. Ma, J. Ding, J. B. Yi et al, J. Appl. Phys. **105**, 07C503 (2009).
[13] Y. K. Qi, J. J. Gu, L. H. Liu, H. F. Zhang, Q. Xu, H. Y. Sun Acta Phys. Sin. **60,** 057502 (2011) (in Chinese).
[14] D. L. Hou, X. J. Ye, H. J. Meng et al, Appl. Phys. Lett. **90**, 142502 (2007).
[15] J. J. Gu, L. H. Liu, Y. K. Qi et al, J. Appl. Phys. **109**, 023902 (2011).
[16] Z. Jin, T. Fukumura, M. Kawasaki et al, Appl. Phys. Lett.**78**, 3824 (2001).
[17] P. Sharma, A. Gupta, K. V. Rao et al. Nat. Mater. **2**, 673 (2003).
[18] S. W. Jung, G. Yi, C. Jung et al. Appl. Phys. Lett. **80**, 4561 (2002).
[19] W. T. Lim, C. H. Lee, Thin Solid Films. **353**, 12 (1999).

*Corresponding author: jjungu@126.com