P-12-1

Hydrogenation Induced Room-Temperature Ferromagnetism in Co-doped ZnO Nanocrystals

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1. Introduction

The diluted magnetic semiconductors (DMS) have attracted much interest for the potential applications in spintronics and microelectronics [1-3]. It's very important to perform the room temperature ferromagnetism (RTFM) for the realizable applications in the microelectronics devices. Thus, the Co-doped ZnO has been introduced as the candidate for the RTFM materials. Ueda *et al*. have reported their experiment result with Curie temperature higher than room temperature for Co-doped ZnO film [1]. Lee *et al*. have also shown the ferromagnetism above 350K for Co-doped ZnO film grown by sol-gel method [2]. But some groups also failed to found ferromagnetism in ZnO based semiconductors doped with ferromagnetic transition metal [4, 5]. Martinez *et al*. proposed the relation between the microstructure of the Co-doped ZnO particle and the RTFM [6]. Recently, RTFM has been observed in the Co-doped ZnO and TiO_2 systems [7-11]. Thus, the origin of ferromagnetism in Co-doped ZnO material is still not clear [12]. In this paper, we have investigated the RTFM of the Co-doped ZnO nanocrystals samples. The samples have been hydrogenated and RTFM has been observed after the hydrogenation.

2. Experiment

In the experiment, the 0%~6% Co-doped ZnO nanocrystal samples were prepared by an aqueous solution method [13]. In the main procedure, zinc nitrate hydrate ($Zn(NO_3)_2{\cdot}6H_2O$), cobalt nitrate hydrate ($Co(NO_2)_3{\cdot}6H_2O$), hexamethylenetetramine ($C_6H_{12}N_4$) and polyethylene glycol (PEG 20000) were dissolved in deionized water and then heated to 90 ^oC to grow white Co-doped ZnO precipitates. The solution was then dried at 100 ^oC and subsequently calcined at 200 ^oC for 4h. The calcined material was ground to fine powder. The powder was then successively sintered at 400, 600 and 800 ^oC for 12 hours respectively. The specimens were then cooled in the air to the room temperature. The hydrogenations for the above samples were performed at 400, 600 and 800 ^oC for 1h and 3h respectively. The as-prepared Co-doped ZnO samples were paramagnetism, and the room temperature ferromagnetism (RTFM) was found in the Co-doped ZnO samples after the hydrogenation. The hysteresis loops of the hydrogenated samples were measured by using the vibrating sample magnetometer (VSM). The material structures of the 0%~6% Co-doped ZnO samples were investigated with X-ray diffraction (XRD) by using Cu $K\alpha$ radiation (λ=1.5405Å) and X-ray photoelectron spectroscopy (XPS) by using Al K radiation ($h\nu$=1486.6eV). The high-resolution transmission electron microscopy (HRTEM) with the energy dispersive x-ray spectroscopy (EDX) and the scanning electron microscopy (SEM) were applied for the further investigation of the microstructures of the specimens.

3. Experimental Results and Discussion

The XRD measurement results of the as-prepared $Zn_{1-x}Co_xO$ (x=0.02~0.06) samples are shown in Fig.1 (including the pure ZnO powder). For all compositions, the reflections correspond to the wurtzite structure of ZnO. The XRD patterns show that the ZnO structure is not disturbed by the substitution of small amounts of Co for Zn. These results also demonstrated the cobalt atoms were incorporated substitutionally at the Zn site without changing the original wurtzite structure.

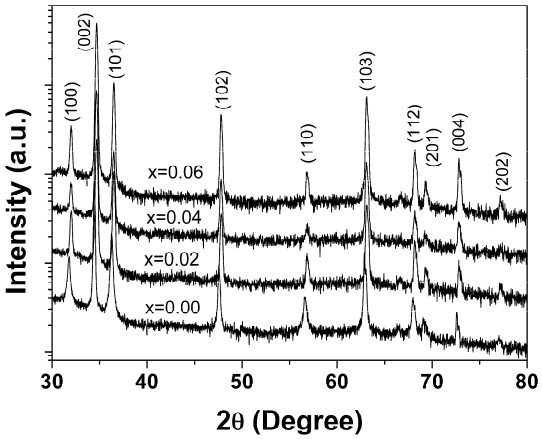

Fig.1 Powder XRD patters of $Zn_{1-x}Co_xO$ (x=0.00~0.06).

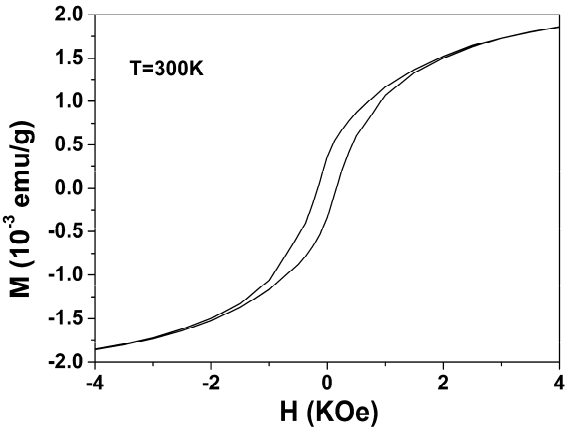

Fig. 2 Magnetic hysteretic loops of $Zn_{1-x}Co_xO$ (x=0.06) annealed at 800 ^oC and hydrogenated at 800 ^oC for 1h.

The magnetism characteristics of post hydrogenated 6% Co-doped ZnO specimens were measured with the VSM. The field dependence of the magnetization for the sample, which was annealed at 800 ^{o}C and hydrogenated at 800 ^{o}C for 1h, was shown in Fig.2. The hysteresis loop was observed at room-temperature. The coercive field was about 100 Oe for the room-temperature measurement. The others samples annealed at 400 and 600 ^{o}C respectively were also found to transform from paramagnetism to RTFM after hydrogenation. The hydrogenation processes for the above specimens were performed at 400 and 600 ^{o}C respectively.

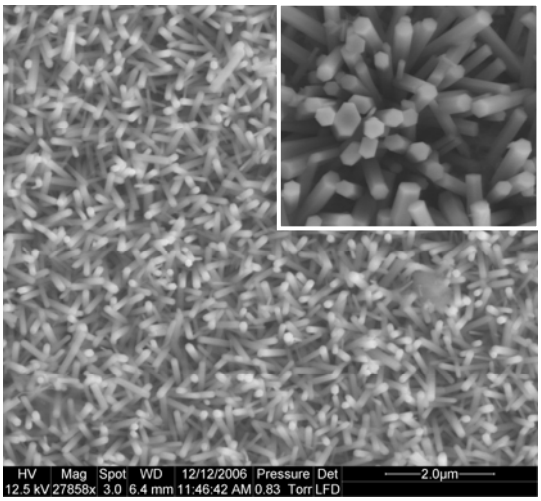

Fig. 3 Scanning electron microscopy (SEM) images of the as-prepared $Zn_{1-x}Co_xO$ (x=0.06) sample on the glass which was dipped into the reacting solution. The inset is the zoomed in photograph of the local area.

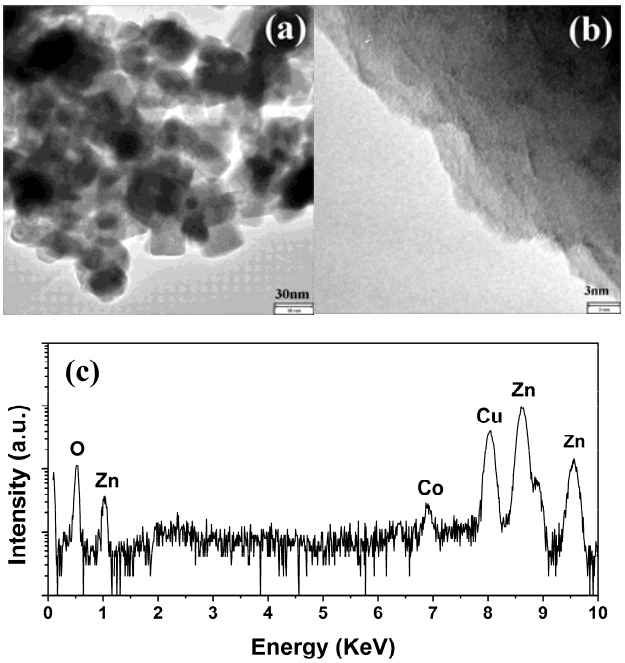

Fig. 4 Microstructure of the as-prepared $Zn_{1-x}Co_xO$ (x=0.06) powders annealed at 800 ^{o}C. (a) TEM pattern; (b) HRTEM pattern; (c) EDX pattern.

In order to study the microstructures of the as-prepared samples, the SEM, TEM and HRTEM measurements were performed and the results were shown in Fig.3 and Fig.4. On the glass that we dipped into the reacting solution, the nanocrystal structure of the $Zn_{1-x}Co_xO$ was observed, as shown in Fig.3. And there is no cobalt clusters observed in the TEM and HRTEM images of the as-prepared $Zn_{1-x}Co_xO$ (x=0.06) sample, as shown in Fig.4(a) and (b). And in the EDX pattern of the doped ZnO sample in Fig.4(c), the oxygen, cobalt and zinc peaks were also observed. Above results indicated that the cobalt ions were uniformly distributed in the entire $Zn_{1-x}Co_xO$ sample. Therefore, we suggested the cobalt ions existing in the hydrogenated sample were nanoparticles.

4. Conclusions

In this paper, the room-temperature ferromagnetism properties of Co-doped ZnO nanocrystals have been observed. The $Zn_{1-x}Co_xO$ ($0.0<x<0.06$) specimens were synthesized by the aqueous solution method. And the as-prepared powders were subsequently hydrogenated at 400, 600 and 800 ^{o}C for 1h respectively. In all the above hydrogenated samples, the RTFM properties were all found. According to the structure measurement results, the cobalt ions were uniformly distributed in the $Zn_{1-x}Co_xO$ powders. And the origin of the RTFM in the Co-doped ZnO was due to the hydrogenated of samples.

Acknowledgments

The authors acknowledged the support from the 973 Program (2006CB302700) and the Instrumental Analysis Fund of Peking University.

References

[1] K. Ueda, H. Tabat, T. Kawai, Appl. Phys. Lett. **79** (2001) 988.

[2] H.J. Lee, S.Y. Jeong, C.R. Cho, C.H. Park, Appl. Phys. Lett. **81** (2002) 4020.

[3] S.S. Yan, C. Ren, X. Wang, Y. Xin, Z.X. Zhou, L.M. Mei, M.J. Ren, Y.X. Chen, Y.H. Liu, Appl. Phys. Lett. **84** (2004) 2376.

[4] Z.W. Jin, T. Fukumura, M. Kawasali, K. Ando, H. Saito, T. Sekiguchi, Y.Z. Yoo, M. Murakami, Y. Matsumoto, T. Hasegawa, H. Koinuma, Appl. Phys. Lett. **78** (2001) 3824.

[5] C.N.R. Rao, F.L. Deepak, J. Mater. Chem. **15** (2005) 573.

[6] B. Martinez, F. Sandiumenge, Ll, Balcells, J. Arbiol, F. Sibieude, C. Monty, Appl. Phys. Lett. **86** (2005) 103113.

[7] Y. Wang, L. Sun, L.G. Kong, J.F. Kang, X. Zhang, and R.Q Han, J. Alloys Compd. **423** (2006) 256.

[8] Y. Wang, L. Sun, L. G. Kong, J. F. Kang, X. Zhang, and R.Q Han, J. Electroceram. **16** (2006) 389.

[9] K.P. Bhatti, S. Chaudhary, D.K. Pandya and S.C. Kashyap, J. Appl. Phys. **101** (2007) 033902.

[10] K.P. Bhatti, S. Kundu, S. Chaudhary, S.C. Kashyap, D.K. Pandya, J. Phys. D: Appl. Phys. **39** (2006) 4090.

[11] O.D. Jayakumar, I.K. Gopalakrishnan, K. Shashikala, S.K. Kulshreshtha, C. Sudakar, Appl. Phys. Lett. **89** (2006) 202507.

[12] J.C.A. Huang, H.S. Hsu, Y.M. Hu, C.H. Lee, Y.H. Huang, M.Z. Lin, Appl. Phys. Lett. **85** (2004) 3815.

[13] J.B. Cui and U.J. Gibson, Appl. Phys. Lett. **87** (2005) 133108.