CHIN.PHYS.LETT. Vol. 25, No. 12 (2008) 4446

Ferromagnetism from Co-Doped ZnO Nanocantilevers above Room Temperature *

ZHOU Shao-Min(周少敏)**, WANG Peng(王鹏), LI Sheng(李盛), ZHANG Bin(张斌), GONG He-Chun(巩合春), DU Zu-Liang(杜祖亮)

Key Lab for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475004

(Received 15 June 2008)

At low temperature (400°C), chemical vapour deposition (CVD) is employed to make comb-like Co-doped ZnO nanocantilever arrays (NAs). The magnetization curves of the as-synthesized Co-doped ZnO NAs indicate the existence of above-room-temperature ferromagnetism (ARTFM) (Curie temperature, $T_c > 300\,K$) whereas undoped ZnO NAs does not. The corresponding ferromagnetic source mechanism is discussed, in which defects play an important role due to the strong green light emission.

PACS: 81.05.Dz, 81.16.Rf, 75.75.+a, 75.50.Pp

An array of hierarchical assembly of nanoscale building blocks such as nanocombs and nanocantilever arrays (NAs) is a crucial step toward realization of functional nanosystems and represents a significant challenge in the field of nanoscale science.[1−3] The search for the ARTFM in dilute magnetic semiconductors (DMSs) has been intense in recent years.[4−6] Moreover, arrays of perpendicular ferromagnetic nanowires have recently attracted considerable interest for their potential applications in many areas of advanced nanotechnology.[7,8] As far as we know, doping in semiconductors with selective elements offers an effective approach to adjust its physical properties including electrical, optical, and magnetic properties, which are crucial for practical nanodevices applications.[9−11] For nanoarrays, the ARTFM and the DMSs, NAs provide a very good opportunity to integrate new functionality into the existing semiconductor nanodevices. Previously, we have fabricated Cd-, Ni-, and Fe-doped ZnO NAs and tunable their optical properties.[2,3,12] In this Letter, the ARTFM of Co-doped ZnO NAs is reported. These results demonstrate a step toward the use of one-dimensional ZnOs as building blocks for the bottom-up construction of ARTFM DMS nanodevices.

The synthesis, compositional and structural characterizations of these samples are similar to our earlier reports.[2,3,12] Magnetism measurements were carried out using a Quantum Design SQUID magnetometer (MPMS XL5) at temperatures from 5–300 K.

The as-grown cantilever-like $Zn_{0.8}Co_{0.2}O$ nanostructures, mostly lying on the Si substrate surfaces, are depicted in a typical scanning electron microscopy (SEM) image, as shown in Fig. 1(a). The inset figure is a high resolution (HR) SEM image. The nanobelts branches are in the range of 200 nm and lengths up to 7 μm. Figure 1(b) shows the XRD patterns of the as-synthesized bulk $Zn_{0.8}Co_{0.2}O$ (dashed line), $Zn_{0.9}Co_{0.1}O$ (dot-dashed line), $Zn_{0.95}Co_{0.05}O$ (dotted line) and ZnO (solid line) NA samples. The inset plots the (103) peaks in a magnified scale. All the diffraction peaks can be indexed to a hexagonal wurtzite structured ZnO, whereas the centres of diffraction peaks (doped ZnOs, non-solid lines) have a slightly shift into low angular scale compared with undoped ZnOs (solid line). The d (103) values monotonically enlarged as the Co concentration increased, which indicates that the Co ions systematically substituted for the Zn ions in the sample without changing the wurtzite structure. The lattice parameter c calculated from the (002) peaks of the samples is 2.64 Å ($Zn_{0.8}Co_{0.2}O$), 2.63 Å ($Zn_{0.9}Co_{0.1}O$), 2.62 Å ($Zn_{0.95}Co_{0.05}O$) and 2.60 Å (ZnO). As shown in Fig. 2(a), a representative transmission electron microscopy (TEM) image of a single $Zn_{0.8}Co_{0.2}O$ NA is demonstrated, in which the NA is tooth-like arrays (the sizes are for nearly 300 × 200 nm). These hierarchically ordered nanobelt arrays are monolithically single crystalline as evidenced by the SAED patterns [the inset in Fig. 2(a)]. The high resolution TEM (HRTEM) image is indicated in Fig. 2(b), in which a perfect single-crystal structure of the NA is demonstrated. The space distance of between (001) planes corresponds to about 0.528 nm, which is very compatible with the XRD and SAED results discussed above. In addition, based on selected area electron diffraction (SAED) and HRTEM, the growth direction is for [011] as indicated with the white arrow in Fig. 2(b). The typical x-ray energy diffraction analysis (EDX) patterns, taken from the NA, are shown in Fig. 2(c) where the C and Cu peaks come from Cu grid and carbon film, as well as each of the NAs has the same composition with a small amount of Co. Further quantitative analysis of EDX finds that the atomic ratio of O:Zn:Co is about 10:8:2, indicating that the stoichiometric NA sample [(Zn+Co)/O = 1:1] is synthesized.

*Sponsored by the National Key Basic Research Programme of China under Grant No 2007CB616911, and the Program for Science and Technology Innovation Talents in Universities of Henan Province under Grant No 2008HASTIT002.

**Email: smzhou@henu.edu.cn

© 2008 Chinese Physical Society and IOP Publishing Ltd

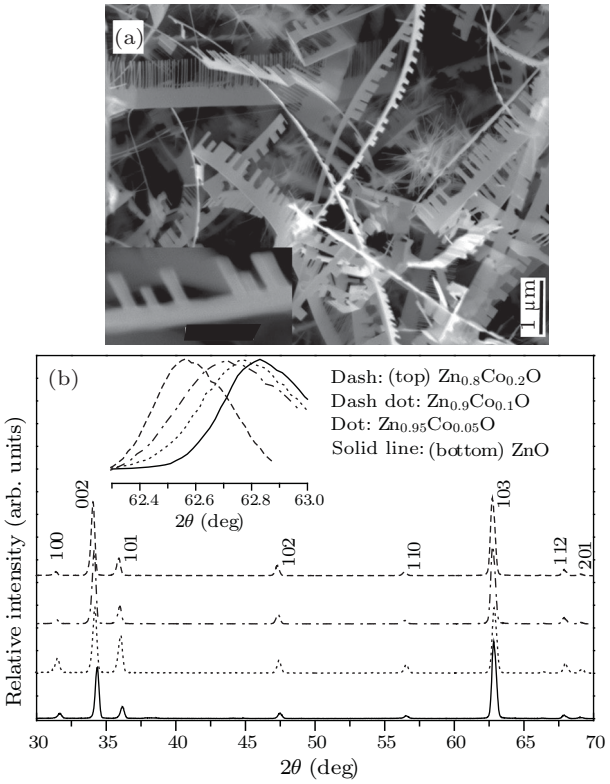


Fig. 1. (a) A representative SEM image of Co-doped NAs and inset for an high resolution SEM (the bar: 400 nm). (b) Full-range XRD patterns taken from the $Zn_{0.8}Co_{0.2}O$ (dash), $Zn_{0.9}Co_{0.1}O$ (dash dot), $Zn_{0.95}Co_{0.05}O$ (dot) and undoped ZnO NAs (solid line), as well as the inset plots the (103) peaks in a magnified scale.

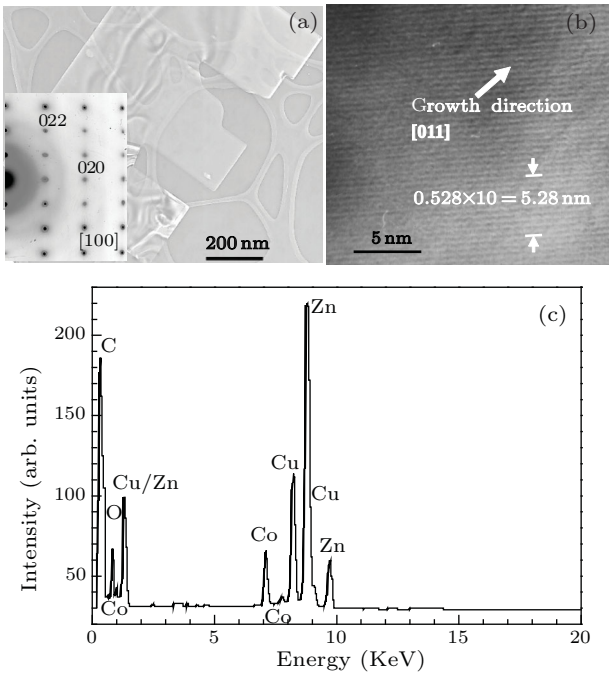


Fig. 2. (a) A typical TEM image of a single $Zn_{0.8}Co_{0.2}O$ NA (inset for the SAED patterns), (b) an HRTEM image and (c) EDX.

Magnetic properties of as-obtained $Zn_{0.8}Co_{0.2}O$ NAs were inspected by performing hysteresis loop measurements at 5 K, 10 K, 300 K (see Fig. 3). Clear evidence for ferromagnetism above room temperature was observed [Fig. 3(a)]. At 300 K, a saturation moment of $M_S = 0.176$ Bohr magnetons per Co^{2+} (0.0304 emu/cm^3), a coercive field of $H_C = 123$ Oe and a remanence of $M_R = 0.0292$ Bohr magnetons per Co^{2+} ($M_R/M_S = 16.6\%$) were observed. This saturation moment is similar to those reported recently for doped ZnO nanowires.[9,10,13–18]

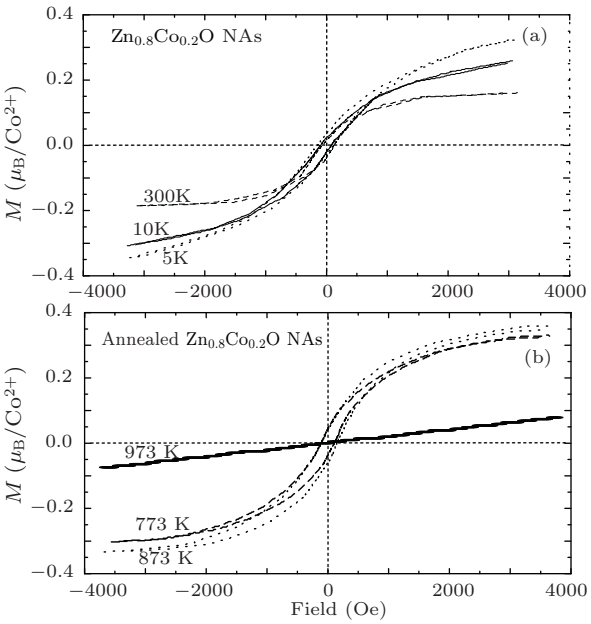


Fig. 3. (a) Magnetization hysteresis loops for bulk $Zn_{0.8}Co_{0.2}O$ NAs at 5, 10, and 300 K, and (b) RT magnetic hysteresis loops ($M - H$ curve) of bulk $Zn_{0.8}Co_{0.2}O$ NAs after being annealed at 773 K (dash), 873 K (dot) and 973 K (solid), respectively.

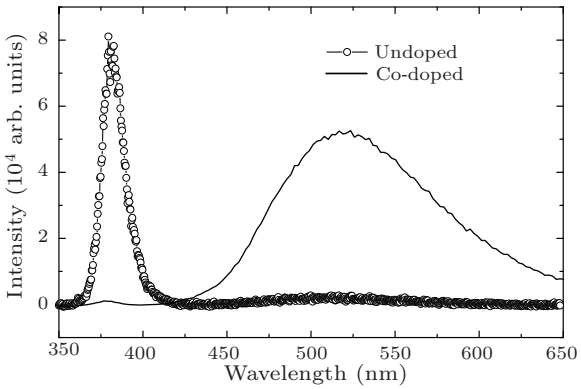


Fig. 4. PL spectra of the un- and Co-doped ZnO NAs.

There are three possible origins of the ferromagnetism in $Zn_{1-x}Co_xO$ that we should consider. The first is the carrier-induced ferromagnetism (RKKY or double exchange mechanism) that is often reported for the Ⅲ–Ⅴ semiconductors.[4–6] The second one is the weak ferromagnetism of CoO. CoO is a well-known antiferromagnetic material with $T_N = 291$ K.[13–15] The

third possible origin is the micro Co clusters.[8] We discounted the second possibility because the magnitude of magnetization is too large to attribute to the weak ferromagnetism of cobalt oxides and because we cannot detect CoO phases in the XRD, HRTEM, SAED, and EDX. Furthermore, M_S of our samples is about 0.0304 emu/cm^3, but it would become about 0.0017 emu/cm^3 if it stems from the weak ferromagnetism of CoO. For the third possibility, no Co phase was observed in the XRD patterns, and the lattice constant (c axis) systematically increases as Co content increases. These observations indicate that the Co ions systematically substitute for Zn sites without changing the wurtzite structure. Therefore, the presence of free carriers and localized spins is a prerequisite for the appearance of FM. These defects like Zn interstitials and O vacancies usually induce n-type characteristics. In order to investigate the defects effect on magnetism, the as-grown NAs were thermally treated in a high vacuum. RT $M-H$ curves of $Zn_{0.8}Ni_{0.2}O$ NAs samples after different annealing temperature (773 K, 873 K, and 973 K) are presented in Fig. 3(b). For the NAs annealed at 773 K (dash), though a weak RTFM is still observed, Ms is less than that of NAs annealed at 873 K (dot), and H_c is very small. What is more, only paramagnetism is observed in NAs annealed at 973 K (solid). That is to say, the magnetic ordering in NAs is very sensitive to the annealing temperature. Experimentally, the enhancement of FM by defects is reported in Mn-, Co-, and Ni-doped ZnO DMSs,[4−10,13−18] respectively. In our study, considering annealed at different temperatures, it is apparent that Ms has a strong correlation with defects generated in Co-doped ZnO NAs. Further, the photoluminescence (PL) spectra of the un- and Co-doped ZnO NAs are shown in Fig. 4, and the emission in the visible emission region (about 500 nm) and the UV emission (380 nm) can be observed. In general, PL of ZnO can be attributed to near-bandedge (NBE) emission (UV) and deep-level (DL) emission (about 500 nm).[3,12] The DL emission is considered to relate to the oxygen vacancy and interface defects, and the NBE emission involves in the ultraviolet excitonic emission.[3,12] The stronger green emission (about 500 nm) of the Co-doped NAs originates from the recombination of the holes with the electrons occupying the singly ionized oxygen vacancy,[3,12] which is compatible with the defects' effect on magnetism.

In summary, un- and Co-doped ZnO NAs have been fabricated by using a simple chemical vapour-deposition method, in which ARTFM with a saturation magnetization of 0.0304 emu/cm^3 and coercivity value (123 Oe) has been observed. The process is friendly environment and such one-dimensional nanocantilever arrays may indicate a new way to assemble uniform semiconductor nanobelts into highly ordered. The simple doping technique can be applied to fabricate other semiconductors nanocantilevers or nanodevices and may be viable for large-scale applications of nanotechnologies.

References

[1] Wang Z L et al 2003 *Phys. Rev. Lett.* **91** 185502
[2] Zhou S M et al 2003 *Micron* **36** 55
[3] Zhang B et al 2003 *Phys. Lett.* A **372** 2300
[4] Dietl T et al 2000 *Science* **287** 1019
[5] Matsumoto Y et al 2000 *Science* **291** 854
[6] Ueda K et al 2001 *Appl. Phys. Lett.* **79** 988
[7] Thurn-Albrecht T et al 2000 *Science* **290** 2126
[8] Whitney T et al 1993 *Science* **261** 1316
[9] Jian W B et al 2006 *Phys. Rev.* B **73** 233308
[10] Khare N et al 2006 *Adv. Mater.* **18** 1449
[11] Zhou S M 2007 *Mater. Lett.* **61** 119
[12] Zhang B et al 2008 *Chin. Sci Bull.* **53** 390
[13] Schwartz D et al 2004 *Appl. Phys. Lett.* **85** 1395
[14] Cui Jet al 2006 *Phys. Rev. B* **74** 045416
[15] Yan H et al 2007 *Appl. Phys. Lett.* **90** 082503
[16] Cui J et al 2007 *Appl. Phys. Lett.* **87** 133108
[17] Schwartz D et al 2007 *J. Am. Chem. Soc.* **125** 13205
[18] Naeem M et al 2007 *J. Phys.: Condens. Matter* **20** 025210