

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Co-doped Y-shape ZnO nanostructures: Synthesis, structure and properties

X.M. Zhang^{a,b}, W. Mai^b, Y. Zhang^a, Y. Ding^b, Z.L. Wang^{b,*}

^a Department of Materials Physics and Chemistry, State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

^b School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

ARTICLE INFO

Article history:

Received 26 August 2008

Received in revised form

24 October 2008

Accepted 29 November 2008 by E.G. Wang

Available online 9 December 2008

PACS:

73.63.-b

75.75.+a

Keywords:

A. Nanostructures

B. Crystal growth

D. Electronic transport

ABSTRACT

A novel Co-doped Y-shape ZnO nanostructure was fabricated using vapor–solid process. In contrast to conventional ZnO nanowires that usually grow along *c*-axis, the branches of the single-crystalline Y-shaped nanostructure grew along directions that deviated significantly from the *c*-axis for 22°, 96°, and 13°, respectively. Transport measurement showed that the Y-shape nanostructure can function as a switch. Due to possible ordered substitution of Zn by Co, ferromagnetism was observed at 300 K and even 400 K, suggesting its potential application as an excellent dilute magnetic semiconductor nanomaterial.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Zinc oxide, an excellent n-type semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, has a variety of applications in optoelectronics [1], laser diodes (LDs) [2], and sensors [3]. Recent theoretical calculations [4] have predicted transition metal (TM) doped ZnO is a most promising candidate for room-temperature ferromagnetism. Moreover, owing to its outstanding optical transparency, doped ZnO has the possibility of studying magneto–optical properties, which could lead to the development of magneto–optoelectronic devices [5,6]. Although diluted magnetic semiconductors (DMSs) have been extensively studied in recent years, experimental observations of ferromagnetism DMSs still remain controversial [7–12].

Co doped ZnO nanowires and nanobelts are expected to be promising candidates for studying DMS, because they are likely to offer high quality single crystalline nanostructures that have potential for fabricating DMS nanodevices. In this paper, a novel Co-doped Y-shape ZnO nanostructure was fabricated for the first time using a vapor–solid process. In contrast to conventional ZnO nanowires that usually grow along *c*-axis, the branches of the single-crystalline Y-shaped nanostructure grew along directions

that deviated significantly from the *c*-axis for 22°, 96°, and 13°, respectively. Transport measurement showed that the Y-shape nanostructure can function as a switch. Due to possibly ordered substitution of Zn by Co, ferromagnetism was observed at 300 K and even 400 K, suggesting its potential application as an excellent diluted magnetic semiconductor nanomaterial.

2. Experimental procedure

The Co doped Y-shape ZnO nanostructures were synthesized by a vapor–solid thermal evaporation process in a tube furnace. Pure zinc powders (99.99% purity), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ powders (99.9% purity) were used as source materials. An alumina boat as a loader for the source was set in the center of the tube. Ar + 2%O₂ gas mixture was introduced as the carrier gas during the fabrication process. The tube furnace was heated to 780 °C and maintained at the temperature for 160 min. The synthesized product grew on the top of the boat, located downstream ~1.5 cm away from the source material (located in the middle of the furnace).

3. Results and discussion

Co-doped ZnO nanostructures were synthesized using a vapor–solid process. Fig. 1a shows the XRD pattern of the as-received sample. The obtained XRD is a typical ZnO wurtzite structure, with sharp diffraction peaks due to high quality crystalline structure. Scanning electron microscopy (SEM) examination of the sample

* Corresponding author. Tel.: +1 4048948008; fax: +1 4048948008.

E-mail addresses: Yuezhang@ustb.edu.cn (Y. Zhang), zlwang@gatech.edu, zhong.wang@mse.gatech.edu (Z.L. Wang).

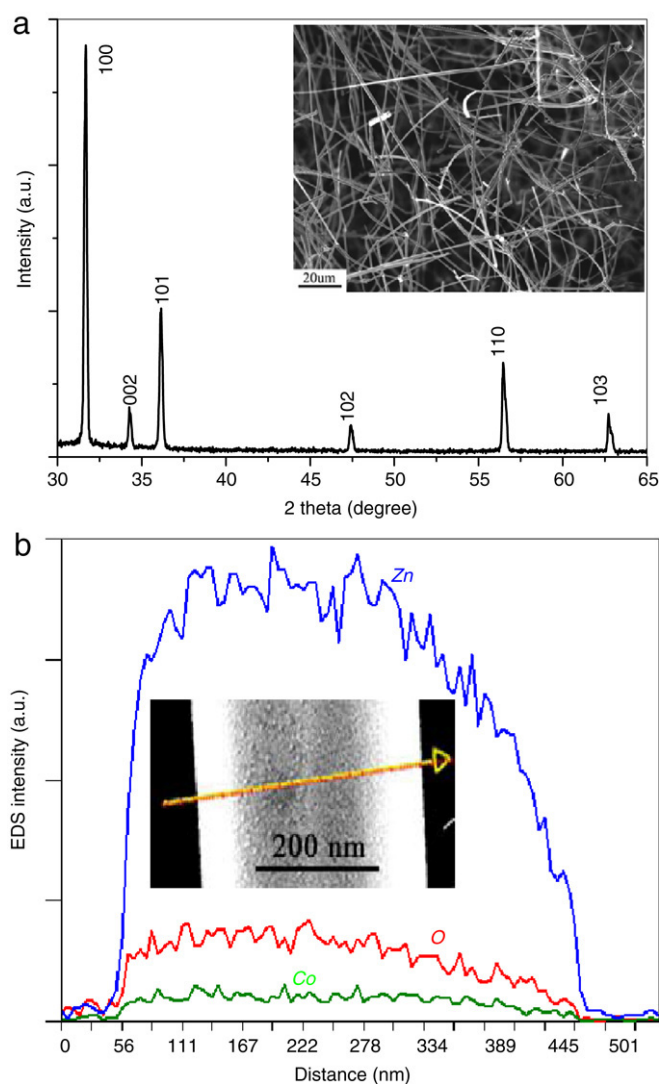


Fig. 1. (a) XRD pattern of Co doped ZnO Y-shape nanostructures, showing a typical wurtzite structure with sharp peaks. Inset is an SEM image of the Y-shaped structures with uniform size in length and width. (b) EDS line scan chemical profile reveals a homogeneous distribution of Co across the wire.

showed many branched Y shape structures, with uniform length and width. Most of them randomly tangled with each other. The concentration and homogeneity of the Co dopants were investigated by chemical mapping using energy dispersive X-ray spectroscopy (EDS) in SEM, as shown in Fig. 1b. Zinc, oxygen, and cobalt elements were uniformly distributed across the wire. From the profile of the Co signal, the Co atoms were doped into the volume without significant surface segregation. The content of the Co in ZnO was estimated to be ~ 3.6 at.%. In order to check the homogeneity of cobalt distribution within the whole Y-shaped wire, EDX spectra was also recorded at different points along the wire, and the result showed that cobalt concentration had measurable variation less than 0.2%.

Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) were used to investigate the structure and growth orientation of the Y-shaped nanostructures. Fig. 2a and b show TEM bright- and dark-field images of a typical Co doped ZnO Y-shape nanostructure. There are three branches (A, B, C marked in Fig. 2a) joining together to form a Y-shape. Uniform contrast in dark-field image (Fig. 2b) indicates that the Y-shaped nanostructure is a single crystal with dislocation free volume. Electron diffraction patterns (Fig. 2c, d, e) recorded from

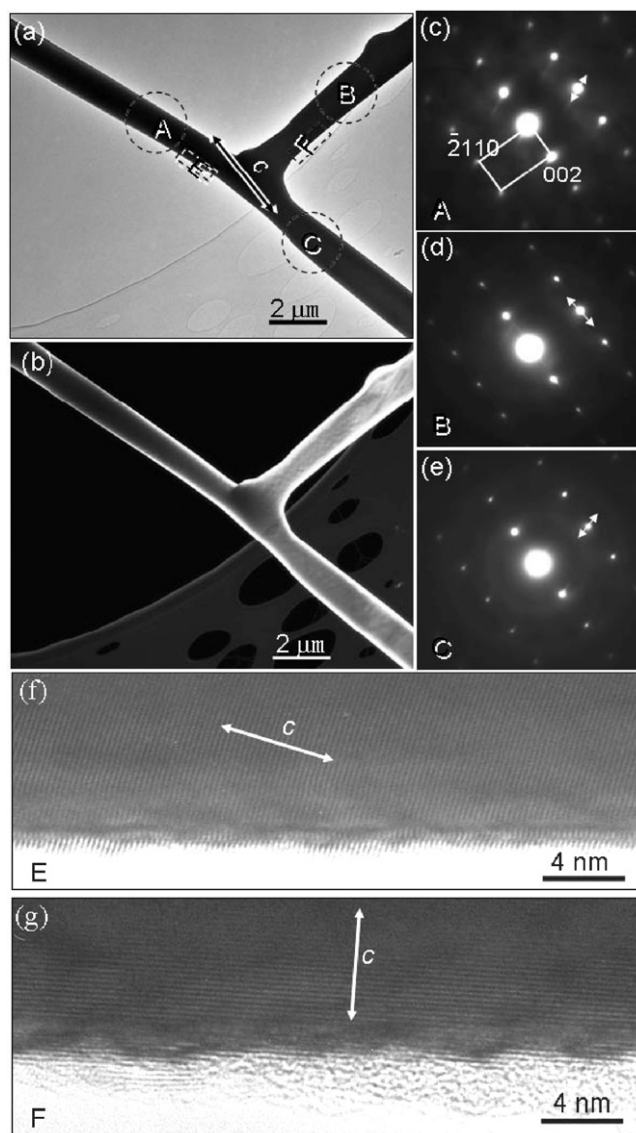


Fig. 2. (a) TEM image of a typical Co doped Y-shape ZnO nanostructure, in which the corresponding SAED of branches A, B and C were shown in (c), (d) and (e), respectively. It was confirmed that the Y-shape is a single crystal by SAED patterns, but the growth directions of the branches are not any of the main crystallographic axes for ZnO. (b) Dark field image of the Y-shape nanostructure, showing a dislocation-free volume. (f) and (g) HRTEM images taken from areas E and F, respectively, clearly indicating the direction of the local *c*-axis. Lattice images show no obvious defects or secondary phase in the structure.

the three branches is identical. It is important to point out that the *c*-axis is not parallel to any of the branches. The angles between the orientations of the branches with the *c*-axis are 22° , 96° and 13° , respectively. This is distinctly different from the ZnO nanostructures that usually grown along $[0001]$, $[10\bar{1}0]$ or $[2\bar{1}\bar{1}0]$ [13–16]. Corresponding HRTEM images taken from areas E and F showed consistent results, as shown in Fig. 2f and g, respectively. The deviation of the growth direction from the three main zone axes may be the result of Co doping.

The experimental setup for the electrical characterization of the Y-shape nanostructure was carried out using a four-probe system (Zyvox S100 nanomanipulator stage) inside an SEM, and the schematic diagram is shown in Fig. 3 inset. Three independent manipulator probes were placed in contact with three individual branches of a Y-shape nanostructure. A DC gating voltage was applied on one of the three branches of the Y-shape (gate), and a sweeping voltage was applied between the other two

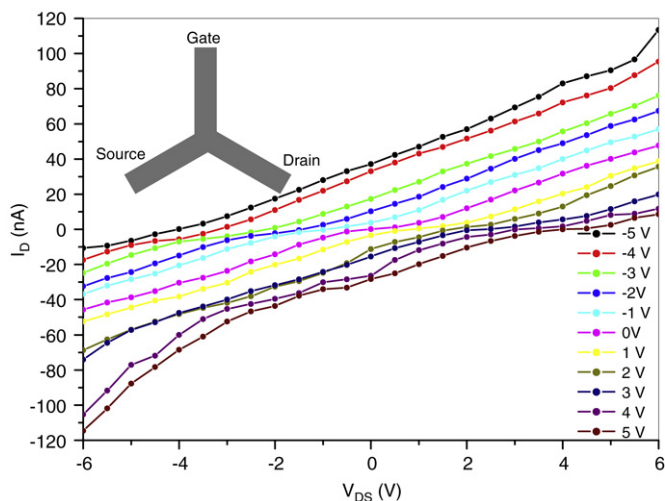


Fig. 3. Current (I_d)–Voltage (V) characteristics of a Y-shape nanostructure between the source and drain, a fixed voltage was applied at the gate. The gate voltage was varied from -5 to 5 V at an interval of 1 V.

branches (source and drain). Although ideal contacts between Y-shape nanostructure and W probes are difficult to achieve, reproducible I – V characteristics from a large number of samples would imply that the observed behavior is intrinsic to the Y-shape nanostructure. I – V curves of the Y-shaped Co doped ZnO are displayed in Fig. 3, and they show nearly linear behavior within our measured voltage ranges. When the gating voltage V_g is fixed, the drain current I_d increases linear as V_{ds} increases. The drain current I_d decreases when gating voltage V_g increases. The gating voltage V_g on the arm branch can offset the current in source and drain, so that the device can function as a current switch.

The Y shape structure is a three-terminal interconnect, where the gate is not a perfect insulating gate with fixed voltage. A leakage current is diverted from one path to another when a gating voltage is applied, which results in a shift in current. A similar three-way electrical gating effect has also been observed in Y-shaped carbon nanotubes [17,18]. From the I – V curve, the conductivity of the doped nanowire is estimated to be $\sim 0.04/\Omega$ cm including the contact resistance.

The magnetization behavior of the Co doped Y-shaped wires was also investigated using SQUID. Fig. 4 shows the field-dependent magnetization curves at 300 K and 400 K for demonstrating ferromagnetism ordering. An obvious hysteresis loop is observed with a coercive field (H_c) ~ 65.8 Oe at 300 K. The saturation magnetization (M_s) of the sample is estimated to be ~ 0.2 emu/g. The hysteresis loop measured at 400 K gives a coercive field of 88.3 Oe and saturation magnetization ~ 0.04 emu/g.

A general model for describing ZnO-base DMS ferromagnetism is the strong electronic coupling between the magnetic ions and charge carriers at the Fermi level [19]. $\text{Co}^{2+} + e_{\text{donor}}^- \leftrightarrow \text{Co}^+$ is energetically favorable in Co doped ZnO. Co doping may change the perfect ZnO structure to make it possible for forming defects or holes, which could be regarded as additional charge carriers.

The photoluminescence (PL) properties of the Co-doped sample have been studied at room-temperature (Fig. 5). The excitation wavelength of photoluminescence (PL) was 325 nm using a He–Cd laser. An ultraviolet emission at ~ 383 nm with shoulder peak at 389 nm and an intensive green emission were observed. The UV emission peak with shoulder peak at 389 nm is explained by a near-band edge emission, which exhibits red shift compared with the PL emission usually received from the undoped ZnO nanowires [20] and ZnO films [21]. The energy gap narrowing down in Co-doped ZnO may account for the small red shift of the near-band-edge emission. It has been reported that UV emission is closely related to

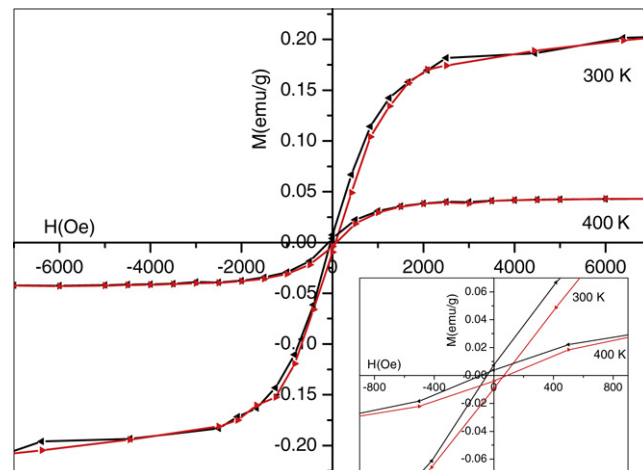


Fig. 4. Magnetization loops of the Co doped Y-shape ZnO nanostructures at 300 K and 400 K, respectively. Ferromagnetism ordering was observed at both temperatures.

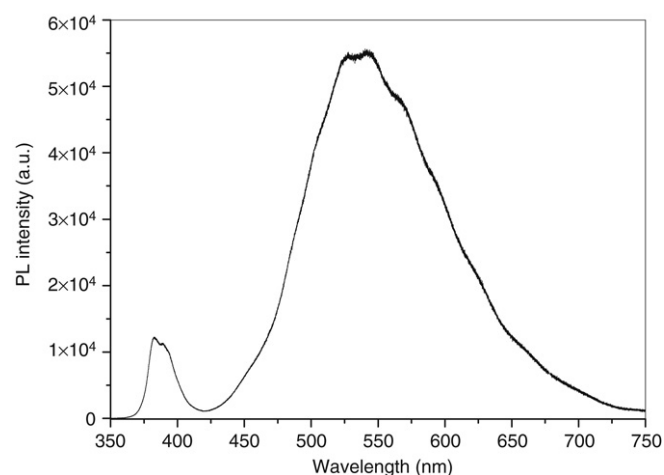


Fig. 5. Room-temperature photoluminescence spectrum taken from the Co doped ZnO nanowire sample.

the radiative annihilation of excitons [22], and the green emission to the defects. The stronger green band emission for the Co-doped product could be explained in terms of the increased amount of doping created defects in the sample. This is more evidence showing that the Co was doped into the volume of the nanowires.

In summary, a new Co-doped Y-shape ZnO nanostructure was fabricated for the first time using a vapor–solid process. In contrast to conventional ZnO nanowires that usually grow along c -axis, the branches of the single-crystalline Y-shaped nanostructure grew along directions that deviated significantly from the c -axis for 22° , 96° , and 13° , respectively. This unconventional growth behavior could be a unique result of Co doping. Transport measurement showed that the Y-shape nanostructure can function as a switch. Due to the nature of the three-way interconnection in the Y-shape structure, the gate voltage can linearly modulate the currents from the source to drain. Due to the possible order substitution of Zn by Co, ferromagnetism was observed at 300 K and even 400 K, suggesting its potential application as a diluted magnetic semiconductor nanomaterial.

Acknowledgements

This work was supported by the Major Project of International Cooperation and Exchanges (Nos. 50620120439, 2006DFB51000),

the National Basic Research Program of China (No. 2007CB936201) and the National Natural Science Foundation of China (No. 50772011), and USA DOE BES (DE-FG02-07ER46394) and NSF (DMS 0706436). Thanks to Prof. X.Q. Yan for assistance in PL measurements.

References

- [1] H. Hayashi, A. Ishizaka, M. Haemori, H. Koinuma, *Appl. Phys. Lett.* 82 (2003) 1365.
- [2] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* 292 (2001) 1897.
- [3] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, *Prog. Mater. Sci.* 50 (2005) 293.
- [4] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, *Science* 287 (2000) 1019.
- [5] K. Ando, H. Saito, Z. Jin, T. Fukumura, M. Kawasaki, Y. Matsumoto, H. Koinuma, *J. Appl. Phys.* 89 (11) (2001) 7284.
- [6] N. Lebedeva, P. Kuivalainen, *J. Appl. Phys.* 93 (12) (2003) 9845.
- [7] L. Liao, J.C. Li, D.F. Wang, C. Liu, M.Z. Peng, J.M. Zhou, *Nanotechnology* 17 (2006) 830.
- [8] L.B. Duan, G.H. Rao, J. Yu, Y.C. Wang, *Solid State Commun.* 145 (2008) 525.
- [9] B. Martínez, F. Sandiumenge, L1. Balcells, J. Arbiol, F. Sibiude, C. Monty, *Phys. Rev. B* 72 (2005) 165202.
- [10] D. Chu, Y.-P. Zeng, D. Jiang, *J. Phys. Chem. C* 111 (2007) 5893.
- [11] W. Li, Q. Kang, Z. Lin, W. Chu, D. Chen, Z. Wu, Y. Yan, D. Chen, F. Huang, *Appl. Phys. Lett.* 89 (2006) 112507.
- [12] A.S. Risbud, N.A. Spaldin, Z.Q. Chen, S. Stemmer, Ram Seshadri, *Phys. Rev. B* 68 (2003) 205202.
- [13] Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* 291 (2001) 1947.
- [14] X.Y. Kong, Z.L. Wang, *Nano Lett.* 3 (2003) 1625.
- [15] X.Y. Kong, Y. Ding, R. Yang, Z.L. Wang, *Science* 303 (2004) 1348.
- [16] W.L. Hughes, Z.L. Wang, *J. Am. Chem. Soc.* 126 (2004) 6703.
- [17] P.R. Bandaru, C. Daraio, S. Jin, A.M. Rao, *Nat. Mater.* 4 (2005) 663.
- [18] J. Park, C. Daraio, S. Jin, P.R. Bandaru, J. Gaillard, A.M. Rao, *Appl. Phys. Lett.* 88 (2006) 243113.
- [19] K.R. Kittilstved, W.K. Liu, D.R. Gamelin, *Nat. Mater.* 5 (2006) 291.
- [20] Y.C. Kong, D.P. Yu, B. Zhang, W. Fang, S.Q. Feng, *Appl. Phys. Lett.* 78 (2001) 407.
- [21] M.H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, P. Yang, *Adv. Mater.* 13 (2002) 113.
- [22] J.J. Wu, H.I. Wen, C.H. Tseng, S.C. Liu, *Adv. Funct. Mater.* 14 (2004) 806.