AJSTD Vol. 24 Issues 1&2 pp. 125-130 (2007)

CVD PREPARED Mn-DOPED ZnO NANOWIRES

T.L. Phan*, R. Vincent, D. Cherns,

Microstructures Group, Department of Physics, University of Bristol,
Bristol BS8 1TL, United Kingdom

N.X. Nghia

Institute of Materials Science,
Academy of Science and Technology (VAST), Hanoi, Vietnam

Received 27 November 2006

ABSTRACT

Mn-doped ZnO nanowires prepared by chemical vapor deposition (CVD) were obtained in the temperature range of 450 - 500^{o}C. X-ray diffraction patterns, SEM and TEM images indicate that crystals with a hexagonal structure grow along the *c* axis. At low Mn-doped concentrations, photoluminescence (PL) and Raman scattering (RS) spectra are almost independent of the Mn doping. However, the increase in concentration of Mn above 1.6 at% weakens significantly the PL signal and the RS-lines intensity in the low wavenumber range of 300 - 480 cm^{-1}, and concurrently increases the RS-lines intensity in the higher wavenumber range of 480 - 700 cm^{-1}. Magnetic measurements determined the Curie temperature of Mn-doped ZnO nanowire to be about 37 K.

Keywords: Mn-doped ZnO, spintronics materials

1. INTRODUCTION

ZnO is a wide-band gap compound semiconductor with E_g = 3.37 eV, which is transparent to visible light and has a direct-electronic transition as well as a high exciton binding energy of 60 meV. These ensure high-efficient excitonic emission above room temperature [1]. Recently, ZnO with nanostructures has attracted much interest from research groups, because of prospects in photonic applications such as LEDs (light emission displays), ultra-violet laser, field emission devices, *etc*. In particular, ZnO nanostructures doped with 3*d*-transition metals of Mn, Co, Cr, Ni, V, *etc*., the so-called dilute magnetic semiconductors (DMSs), have been of great interest, because such the integration of electronic transport (electron) and magnetic (spin) properties in the same ZnO host lattice opens a new prospective for spintronic technology. Herein, it is worthy of note that the synthesis of 3*d*-transition-metal-doped ZnO materials with nanostructures can not only improve a high-efficient emission but also limit the presence of additional metal-oxide phases, since they are low-dimensional systems.

In this work, we present preparation of Mn-doped ZnO nanowires using the chemical vapor deposition (CVD) method. The structural characterization, optical and magnetic properties of the samples are investigated to study the presence of Mn in ZnO nanowires.

* Corresponding author e-mail: phtlp@bristol.ac.uk

2. EXPERIMENT

Mn-doped ZnO nanowires were prepared by CVD using powders of Zn and $MnCl_2.4H_2O$ as precursors. Nanowires were grown on Si substrates coated with several nanometers of Au. The growing process was performed by placing initial powders with an appropriate ratio in the middle of a quartz tube at the desired temperatures. The tube was connected with a diffusion pump to keep pressure in the chamber about 0.2 bar. Ar gas was used as the carrier gas at a flow rate of about 150 sccm.

Structural characterization of the products was checked by field-emission scanning electron microscopy (FE-SEM) using a JEOL-JSM 6330F adapted with energy dispersive x-ray spectrometry (EDS), x-ray diffraction patterns using a X'Pert Philips, and transmission electron microscopy (TEM) using a 300 kV Philips EM-430 TEM. Optical properties of nanowires at room temperature were studied by photoluminescence (PL) and Raman scattering (RS) spectroscopy using Renishaw's PL and RS spectrometers with the laser lines of 325 and 448 nm. The Curie temperature of the samples was determined by using a superconducting quantum interference device (SQUID) magnetometer.

3. RESULTS AND DISCUSSION

By mixing the powders of Zn and $MnCl_2.4H_2O$ with different weight ratios and then evaporating at temperatures ranging from 420 to 750^oC, we realized that Mn-doped ZnO nanowires were only obtained in the temperature range between 450 and 500^oC; at higher preparation temperatures, thin films were created. The average diameter of obtained nanowires is about 300 nm, and the Mn concentration in nanowires determined by EDS to be 0.12, 1.3, 1.6 and 6.5 at.%.

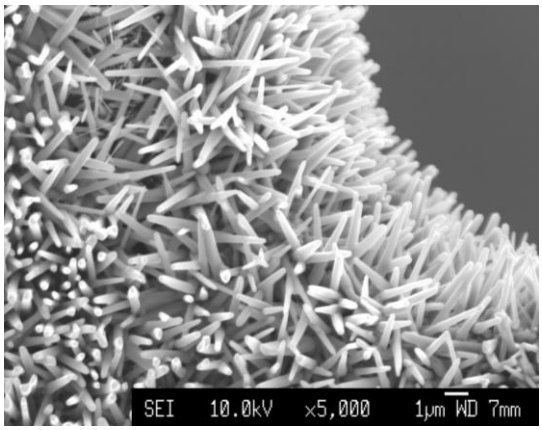

Fig. 1: *A representative FE-SEM for ZnO nanowires doped with Mn*

Figures 1 and 2 show a representative FE-SEM image and x-ray diffraction patterns of Mn-doped ZnO nanowires, respectively. We can see clearly that crystals with a hexagonal structure are uniform in morphology and grow along to the *c*-axis. The doping of Mn above 1.3 at.% leads to the shift in x-ray peaks towards lower diffraction angles, see the inset of Fig. 2, since the radius of Mn^{2+} is larger than that of Zn^{2+}[1, 4]. This reflects that Mn substituted into Zn sites of the ZnO lattice. It should be noticed that the presence of Mn in ZnO nanowires does not make appear the additional phases due to Mn metal as well as its manganese oxides [5]. These results are in good agreement with TEM images recorded.

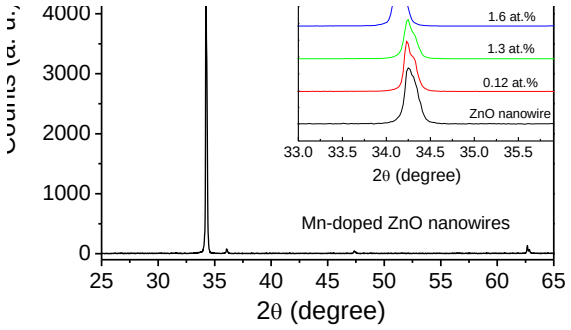

Fig. 2: *X-ray diffraction patterns for ZnO nanowires doped with Mn at different concentrations*

Photoluminescence spectra of pure ZnO nanowires and the samples with the Mn concentration of 0.12, 1.3, 1.6 and 6.5 at.% are shown in Fig. 3. As a result, PL spectra of the samples with the Mn concentration below 1.6 at.% consist of the two emission bands, which are ultra-violet (UV) and visible [1, 2, 5, 6]. The first band is centered at about 380 nm, attributed to the combination emission of free excitions near the band edge. Meanwhile, the visible band peaked at 525 nm has been believed to be intrinsic or extrinsic defects; at the moment, this is still controversial. With the Mn-doping level above 1.6 at.%, the visible emission is extinguished and the PL intensity of the UV band decreases remarkably, as can be seen in Fig. 3(a). We suppose that the presence of the Mn-doping at a concentration high enough may weakens the PL emission of ZnO nanowires.

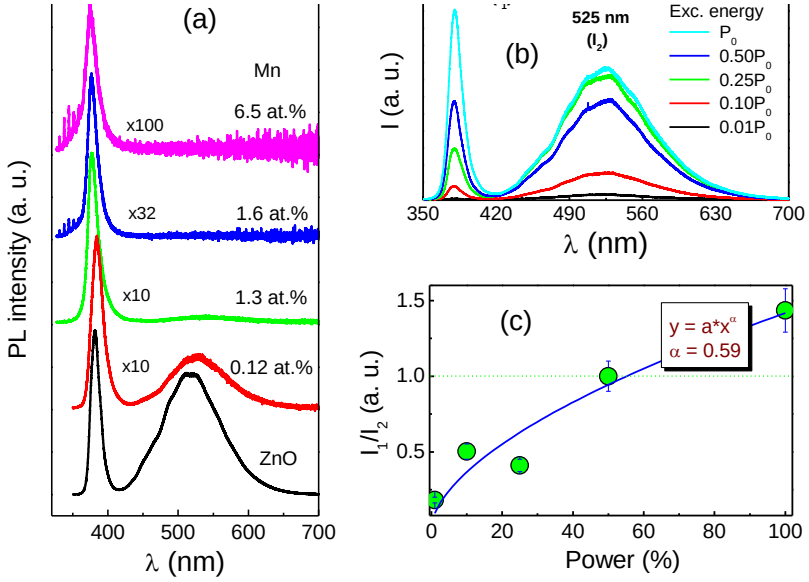

Fig. 3: *(a) PL spectra of pure and Mn-doped ZnO nanowires under an excitation line of 325 nm; (b) PL spectra of the 0.12 at.% Mn sample under different excitation powers; (c) the power dependence of the I_1/I_2 ratio fits to a function of $y = ax^{\alpha}$*

Figure 3(b) displays representatively the excitation-energy dependence of PL spectra for the samples with the Mn concentration below 1.6 at.%. We can see the increase of PL signals with increasing excitation. The intensity ratio of the UV to visible peaks increases nonlinearly according to a function of $y = ax^{\alpha}$, see Fig. 3(c), where $\alpha = 0.59$ is a factor relating to the particle size that increases for commercially available ZnO powders [1].

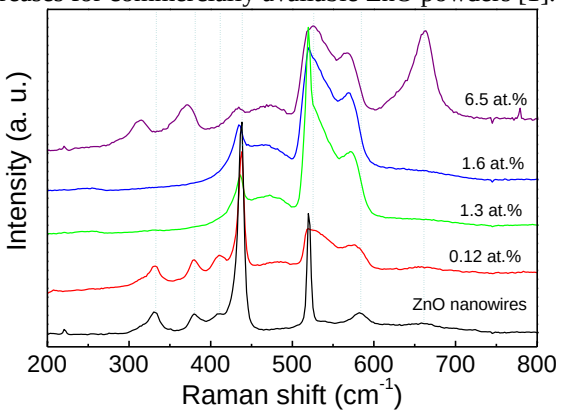

Fig. 4: *Raman scattering spectra for ZnO nanowires doped with Mn*

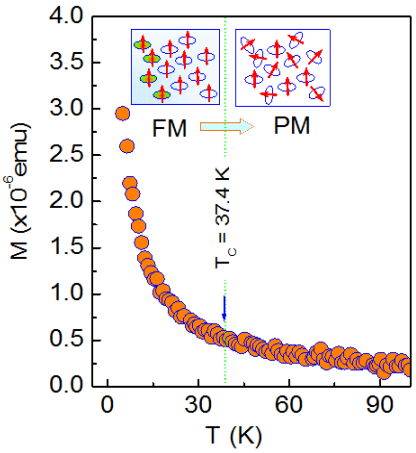

Fig. 5: *The temperature dependence of magnetization for ZnO nanowires doped with 0.12 at.% Mn*

To study further the influence of Mn doping on the optical properties of ZnO nanowires, Raman scattering (RS) spectra at room temperature were measured, as shown in Fig. 4. The well known ZnO RS lines located at frequencies of 331, 379, 409, 437, 583, and 660 cm^{-1} have been assigned to the vibration modes of $2E_2$(low), A_1(TO), E_1(TO), E_2(high), E_1(LO), and A_1(LO) + E_2(low), respectively [7 - 12]. The E_1 and A_1 modes are polar and split into transverse optical (TO) and longitudinal optical (LO) phonons, and the two E_2 modes [E_2(low) and E_2(high)] are non-polar phonon lines [11, 12]. For the nanowire samples with the Mn concentration below 1.6 at.%, the strongest and sharpest peak locating at 437 cm^{-1} belongs to E_2(high), characteristic of the wurtzite phase. However, with increasing the Mn concentration above 1.6 at.%, the lines in the wavenumber range of 480 - 700 cm^{-1} increase strongly in the intensity. Furthermore, the peaks in the range of 300 - 480 cm^{-1} shift to lower wavenumbers [7, 9], indicating that the additional presence of Mn in ZnO nanowires affects the ideal structure of ZnO and changes the parameters of the ZnO crystal field, see x-ray diffraction patterns in Fig. 2. Here, the RS line

centering at 660 cm^{-1} is probably related to a spinel phase [9], further investigation of this feature is necessary.

The substitution of Mn into Zn sites in ZnO nanowires makes also changes the magnetic behavior of the samples. Figure 5 shows representatively the temperature dependence of magnetization for the sample with 0.12 at.% Mn. The ferromagnetic-to-paramagnetic phase transition temperature (or the Curie temperature - T_C) determined from this measurement is about 37 K, which is very far from applications at room temperature. The low-temperature ferromagnetism in Mn-doped ZnO nanowires may be come from the exchange coupling of Mn^{2+} ions, where spins are aligned parallel with each other, as can be seen in the inset of Fig. 5. The raising of the measurement temperature above T_C causes the random aligning of Mn^{2+} spins, consequently the paramagnetic phase in Mn-doped ZnO nanowires is observed.

4. CONCLUSION

We prepared Mn-doped ZnO nanowires with the nanowires diameter of 300 nm using the CVD method. Structural characterization, optical and magnetic properties of the samples were investigated in detail. As a result, PL and RS spectra are independent of the Mn doping as the doping concentrations below 1.6 at.%. The increase in concentration of Mn above 1.6 at.% weakens significantly the PL signals and the RS-lines intensity in the range 300 - 480 cm^{-1}, and concurrently which increases the RS-lines intensity in the frequency range of 480 - 600 cm^{-1}. The Curie temperature was determined for Mn-doped ZnO nanowire to be about 37 K. We suppose that the low-temperature ferromagnetic behavior in Mn-doped ZnO nanowires is due to the exchange couplings of Mn^{2+} ions.

ACKNOWLEDGEMENT

One of the authors (T.L. Phan) wishes to acknowledge the support from the Overseas Research Student (ORS) Award and the University of Bristol Postgraduate Research Scholarship. This work was partially supported by the National Program on Basic Research of Vietnam.

REFERENCES

1. Ozgur, U., Alivov, Ya.I., Liu, C., Teke, A., Reshchikov, M.A., Doğan, S., Avrutin, V., Cho, S.-J., and Morko, H. (2005), J. Appl. Phys., vol. 98, p. 041301.
2. Wang, Z.L. (2004), J. Phys.: Condens. Matter, vol. 16, p. R829.
3. Dietl, T., Ohno, H., Matsukura, F., Clibert, J., and Ferrand, D. (2000), Science, vol. 287, p. 1019.
4. Pong, W.-F., Mayanovic, R.A., Bunker, B.A., Furdyna, J.K., and Debska, U. (1990), Phys. Rev., vol. B 41, p. 8440.
5. Chen, Y.W., Liu, Y.C., Lu, S.X., Xu, C.S., Shao, C.L., Wang, C., Zhang, J.Y., Lu, Y.M., Shen, D.Z., and Fan, X.W. (2005), J. Chem. Phys., vol. 123, p. 134701.
6. Djurisic, A.B., Leung, Y.H., Tam, K.H., Ding, L., Ge, W.K., Chen, H.Y., and Gwo, S. (2006), Appl. Phys. Lett., vol. 88, p. 103107.
7. Wang, J.B., Zhong, H.M., Li, Z.F., and Lu, W. (2005), J. Appl. Phys., vol. 97, p. 086105.
8. Wang, J.B., Huang, G.J., Zhong, X.L., Sun, L.Z., Zhou, Y.C., and Liu, E.H. (2006), Appl. Phys. Lett., vol. 88, p. 252502.

9. Xu, H.Y., Liu, Y.C., Xu, C.S., Liu, Y.X., Shao, C.L., and Mu, R. (2006), J. Chem. Phys., vol. 124, p. 074707.
10. Cong, C.J., Liao, L., Liu, Q.Y., Li, J.C., and Zhang, K.L. (2006), Nanotech, vol. 17, p. 1520.
11. Alim, K.A., Fonoberov, V.A., Shamsa, M., and Balandin, A.A. (2005), J. Appl. Phys., vol. 97, p. 124313.
12. Cheng, H.M., Hsu, H.C., Tseng, Y.K., Lin, L.J., and Hsieh, W.F. (2005), J. Phys. Chem., vol. B 109, p. 8749.