Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2011, Article ID 464538, 5 pages
doi:10.1155/2011/464538

Research Article

The Dilute Magnetic and Optical Properties of Mn-Doped ZnO Nanowires

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Received 14 March 2011; Revised 4 July 2011; Accepted 13 July 2011

Academic Editor: Edward Andrew Payzant

We present a study of the dilute magnetic and optical properties of Mn-doped ZnO nanowires (Nws) fabricated by means of a liquid phase evaporation deposition process. The samples were grown using a mixed Zn/Mn liquid source with a mol ratio of Mn 10% in a constant O_2/Ar gas at 580°C. The nanowires show a strong UV emission at 405 nm and a blue emission at 433 nm in the photoluminescence spectrum. In addition, they present a strong reversible smooth ferromagnetic hysteresis loop at room temperature, and the corresponding saturation magnetization M_s is up to 0.015 emu/g Oe, showing that the nanowires are of a ferromagnetism semiconductor (DMS). With the strong magnetic and photoluminescence properties, ZnO : Mn Nws will be used in fields of making electromagnetic devices and magneto-optical storage devices.

1. Introduction

Zinc-oxide-(ZnO-) based dilute magnetic semiconductors (DMSs) have attracted great research interest for having a great potential of making various room temperature electromagnetic devices [1, 2]. Now, theoreticians have identified ZnO as an excellent candidate host semiconductor for supporting high-Curie-temperature (T_C) ferromagnetism when doped with a variety of 3d transition metal ions, particularly Mn [3–7]. Experimentalists have verified these predictions for Mn-doped ZnO with room-temperature ferromagnetism [8–10]. In fact, Mn-doped ZnO will be a multifunctional material with coexisting magnetic, semiconducting, and optical properties [3], which would allow tuning the band gap for making UV detector and light emitters. So far, most of the investigations on ZnO : Mn have focused on their thin films [11, 12] and revealed the ferromagnetism with a T_C ranging from 37 K to 250 K [13, 14]. There are few reports on the magnetic properties of Mn-doped ZnO nanowires [15, 16]. With the aim of investigation of the magnetism optical properties of Mn-doped ZnO nanowires, we synthesized ZnO : Mn nanowires with ferromagnetic properties at room temperature using a simple liquid phase evaporation deposition process. Our study indicates that the observed ferromagnetism in ZnO : Mn nanowires at room temperature can be attributed to the incorporation of transition metal Mn ions into ZnO lattice. At the same time, we investigated the optical properties of ZnO : Mn nanowires. The surface morphology of the products was investigated by scanning electron microscopy (SEM), and the optical characteristics were determined by photoluminescence (PL) spectra at room temperature.

2. Experiment

Mn-doped ZnO nanowires (Nws) samples were fabricated by a liquid phase evaporation deposition process. The growth system is composed of a large horizontal quartz tube furnace, a vacuum system, a gas meter, and a temperature controller. Si (111) substrates were cleaned ultrasonically with a sequence of acetone, ethanol, and deionized water. Then moved the native SiO_2 layer with diluted HF solution and dried by blowing N_2. For uniform growth, cleaned Si (111) substrates were placed at the center of the furnace. Prior to the fabrication, the furnace was pumped to high vacuum of 10^{-4} Pa and heated to 100°C and kept at this temperature for 2 hours to remove any water moisture from

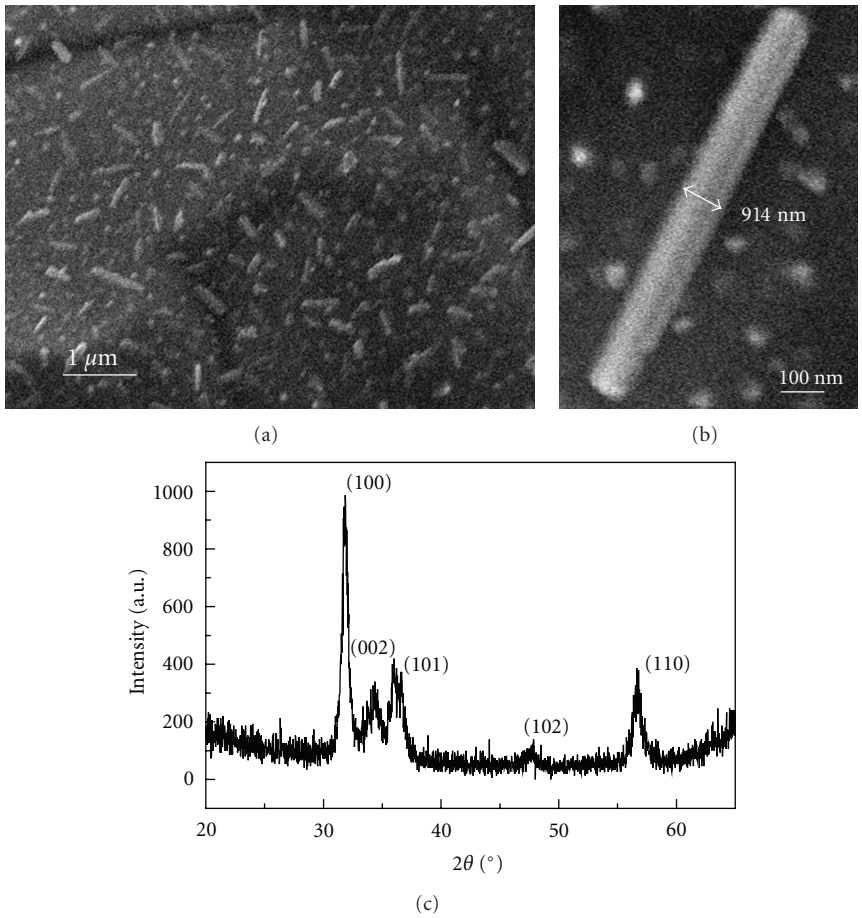

Figure 1: (a) The surface SEM image of the as-grown Mn-doped ZnO Nws with a Mn mol ratio 10% on Si substrate; (b) a magnification picture of a single ZnO : Mn nanowire with a diameter of 91.4 nm; (c) the X-ray diffraction patterns of ZnO : Mn Nws on Si substrate.

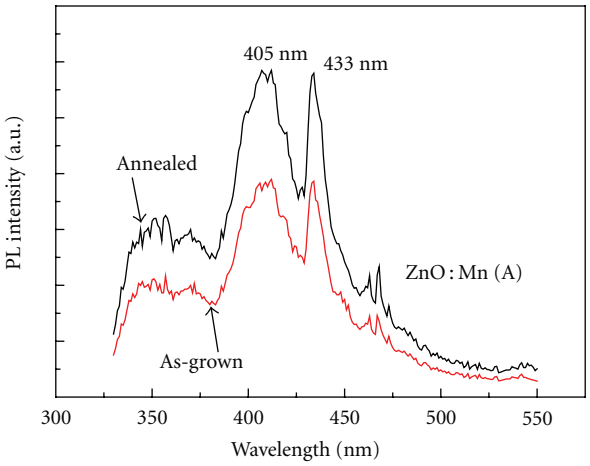

Figure 2: The PL spectra of the as-grown and the annealed ZnO : Mn Nws at room temperature, exhibiting strong UV emissions at 405 nm and a blue emission at 433 nm.

the mixture. Then the furnace was heated to the growing temperature of 580°C. Zinc acetate dihydrate and manganese acetate tetrahydrate were mixed with a Mn/Zn mol ratio of 10%, then hydrolyzed into liquid phase by ethanol and bathed in water at 95°C for 30 mins. The compounds took a chemical reaction as follow:

$$\begin{aligned} &C_4H_6O_4Mn \cdot 2H_2O + C_4H_6O_4Zn \cdot 2H_2O \\ &\quad \longrightarrow ZnO : Mn + 2C_2H_5O + 5H_2O + 4CO_2. \end{aligned} \tag{1}$$

ZnO molecules and Mn^{2+} ions were carried into the tube by a mixture gas of O_2 and Ar and flowed through the furnace with a constant velocity. They took a chemical reaction and condensed on the substrates. The growth process was carried out for 1 hour and then annealed in situ at 800°C for 1 h. Finally, the samples were removed from the furnace when the system was cooled down to room temperature.

The morphology of the products was investigated by a Shimadzu SS-550 super scanning electron microscope (SEM). The composition was analyzed by X-ray diffraction (XRD) on a RINT2000 vertical goniometer with Cu Kα radiation (λ = 0.1541 nm). The photoluminescence (PL) measurement was performed using a 310 nm excitation source at room temperature. And the magnetism properties are measured by a magnetic gauge at 77 K and room temperature.

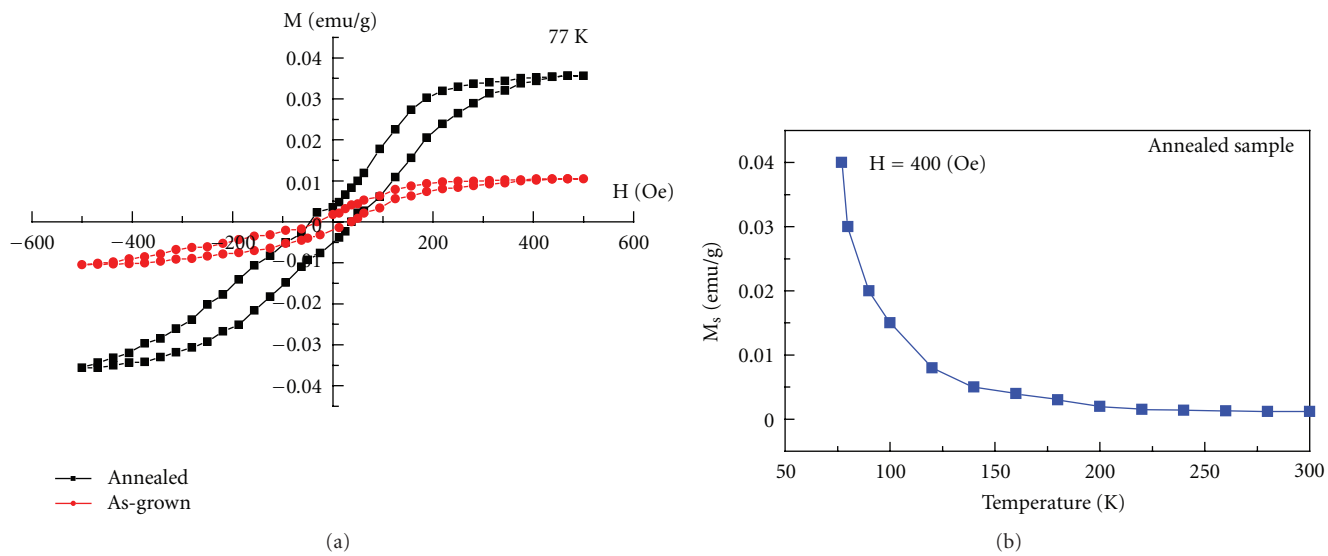

Figure 3: (a) The magnetism properties of the as-grown and the annealed ZnO : Mn Nws at 77 K with the applied magnetic field H; (b) the temperature dependence of the saturation magnetization M_s at H = 400 Oe.

3. Result and Discussion

Figure 1(a) illustrates the typical surface morphology of the as grown Mn-doped ZnO Nws as determined by SEM. Many ZnO : Mn nanowires are uniformly dispersed on the Si substrate. They have a uniform diameter about 90 nm but their length varies in a large range of 100–800 nm. In addition to ZnO Nws, there are many newly nucleated nanoparticles scatted around the nanowires. This attributes to the long growth process, leading to new particles nucleation continually. Figure 1(b) is a magnification picture of a single ZnO : Mn nanowire with a diameter of 91.4 nm. It is very straight and uniform, showing that the nanowire is of high quality. Figure 1(c) shows an in-plane X-ray diffraction pattern of the as grown ZnO : Mn Nws. The diffraction peaks are located at 31.7°, 34.7°, 36.7°, 47.9°, and 56.4°, corresponding to the (100), (002), (101), (102), and (110) crystal planes of the standard diffraction spectrum of bulk wurtzite ZnO. The intensity of the (100) peak is very strong, almost three times of that (101) and (110), indicating that the growth of ZnO nanowires predominates in (100) facet. The small diffraction peaks are attributed to the small nanocrystals scattered on the substrate. There are no extra peaks from Mn, showing that the structure of ZnO remains unchanged for low-doping concentration of Mn. The doped Mn^{2+} ions simply replace Zn ions in the structure. From the diffraction peaks, we can confirm that liquid phase synthesized ZnO : Mn nanowires have a distinct wurtzite structure.

Figure 2 shows the photoluminescence (PL) spectra of the as grown and the annealed ZnO : Mn Nws samples at room temperature. Both of them emit a strong UV emission at 405 nm and a blue emission at 433 nm. The former emission is considered to be the UV emission of ZnO band edge emission shifted to a longer wavelength [17], which caused by Mn impurities introducing an impurity level in the band gap of ZnO. The shape of PL spectra of the two samples is very similar, but the PL intensity of the annealed sample is stronger 1.5 times that of the as grown sample. The ZnO : Mn Nws samples achieve a very strong UV emission when synthesized through a liquid phase evaporation deposition, showing that the ZnO Nws are of high quality.

To investigate the dilute magnetic semiconductors (DMSs) properties of ZnO : Mn Nws, we measured the magnetization M with the applied magnetic field H at 77 K and room temperature. Figure 3(a) shows the magnetization M behaviors at 77 K of the samples. M initially increases with H linearly and then slowly arrive their saturation. The saturation value M_s is 0.01 emu/g for the as grown sample and 0.035 emu/g for the annealed sample. For a reverse magnetic field H, the changing of M is symmetrical with that of the positive H. Therefore, we observe two narrow and smooth magnetic hysteresis loops as the magnetic field H changes from −400 to 400 Oe. The coercive field strengths H_c are 0.023 emu/g and 0.0054 emu/g for the as grown and the annealed samples, respectively, showing that the ZnO : Mn Nws are characteristic of the ferromagnetic materials. Figure 3(b) shows a temperature dependence of the magnetization M at H = 400 Oe for the annealed ZnO : Mn sample. It decreases quickly from 0.035 emu/g at 77 K to 0.001 emu/g as temperature increased to 300 K. ZnO : Mn Nws present a better magnetic signal at low temperatures we can deduce that there are some isolated Mn^{2+} ions exhibit the ferromagnetism at low temperatures but no ferromagnetism contribution at RT. The results show that ZnO : Mn Nws may have some complicate magnetic behavior at low temperatures. It is reasonable to say that the spins of these isolated Mn^{2+} ions are frozen at room temperatures but give rise to the ferromagnetic component at 77 K.

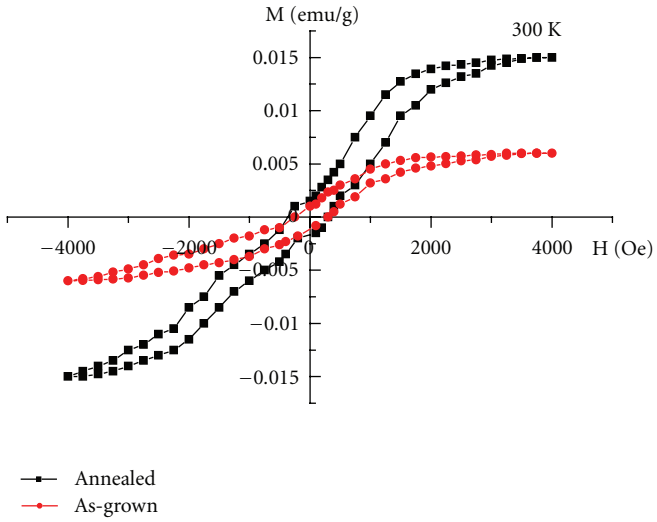

Figure 4: The magnetism properties of the as grown and the annealed ZnO : Mn Nws at room temperature with the applied magnetic field H.

Figure 4 shows the magnetic properties of the samples at room temperature. Clearly, with an applied magnetic field over 500 Oe, both of the samples show significantly ferromagnetic characters at room temperature. M increases and arrives to the saturation value M_s 0.005 emu/g and 0.015 emu/g for the as grown and the annealed samples when H is up to 4000 K, respectively. The corresponding coercive field strengths H_c are 2.5×10^{-3} emu/g and 1.0×10^{-3} emu/g. These observations consistent with those reported for other ferromagnetic ZnO and nanocrystalline DMS-quantum dots aggregates [18, 19]. Similar coexistence of ferromagnetic and paramagnetic moments has been observed in Fe-doped ZnO systems [10] and Ni : ZnO quantum dots [20]. The hysteresis loops at 300 K indicate that the presence of a ferromagnetic phase in ZnO : Mn at room temperature and the steep rise in magnetization seems to be intrinsic to diluted magnetic semiconductors [21].

Figure 5 shows the magnetic conductivity of the as grown and the annealed ZnO : Mn Nws at room temperature with the applied magnetic field H. The corresponding maximum values of the magnetic conductivity are $5\,\mu_B$ and $2.4\,\mu_B$, respectively. That further confirms that ZnO : Mn Nws have good ferromagnetism properties.

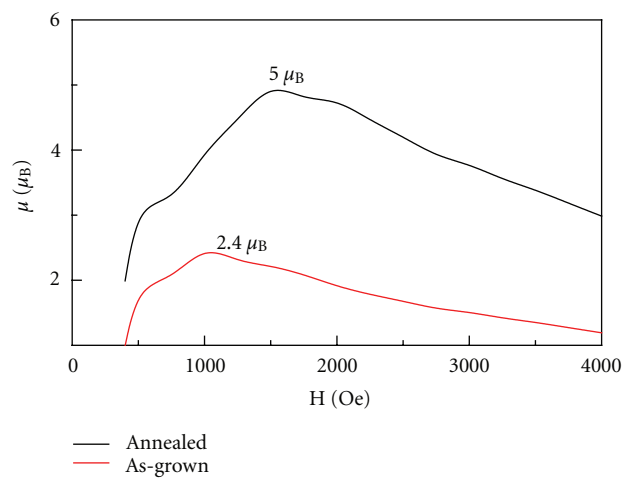

Figure 5: The magnetic conductivity of the as-grown and the annealed ZnO : Mn Nws at room temperature with the applied magnetic field H.

4. Conclusion

Mn-doped ZnO Nws with a diameter of 90 nm have been grown using a liquid phase evaporation vapor phase deposition. ZnO : Mn Nws exhibit a strong dominant UV emission at 408 nm and a blue emission at 433 nm at room temperature. Moreover, they present a strong ferromagnetic properties and a narrow and smooth ferromagnetic hysteresis loop as the magnetic field H changes from −4000 to 4000 Oe at room temperature. The results show that Zn : Mn Nws are of strong ferromagnetism and optical properties that can be used as blue light magneto-optical storage material.

Acknowledgment

This work was supported in parts by the National Natural Science Foundation of China (nos. 60776004, 60976071).

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