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# Hydrothermal Synthesis and Properties of Diluted Magnetic Semiconductor $Zn_{1-x}Mn_xO$ Nanowires

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## Abstract

We report the synthesis of oriented single crystalline Mn doped ZnO nanowires through a hydrothermal method. Structural characterizations using X-ray diffraction and transmission electron microscopy revealed that the Mn was doped into the lattice structure, forming solid solution. The Mn doped ZnO nanowires possess wurtzite structure with a c-axis growth orientation. The physical properties of the nanowires were investigated. Mn doped ZnO nanowires were found to be ferromagnetic with Curie temperature of about 30 K. A deep level emission band at about 566 nm was observed at room temperature.

## 1. Introduction

One-dimensional nanostructures have attracted a great deal of interest not only because of their basic scientific richness, but also of their potential utilization in optical and electronic devices [1-6]. ZnO is one of the most important semiconductors due to its wide direct band gap (3.37 eV) and large exciton binding energy (60 meV). To date, ZnO in bulk and thin film format has been widely used in field emission display, solar cell, chemical sensors, and other devices [7-9]. Recently, dilute magnetic semiconductors (DMSs) have attracted a great deal of attention in the past few years as enabling materials in the emerging field of "spintronics". DMSs are semiconductor solid solutions, where a small percentage of cations are replaced by magnetic impurities such as Mn. Unusual magnetotransport and magnetooptical phenomena like large Faraday rotations, giant negative magnetoresistances, and magnetic field induced metalinsulator transitions have been observed. Among the DMSs, Mn- doped II-VI compounds have been extensively studied. However, most of the II-VI compounds studied are chalcogenides; the corresponding oxides are comparatively less investigated. Theoretical calculations predict that ZnO should exhibit ferromagnetism above room temperature on doping with Mn [10,11]. This prediction has initiated in-

creasing efforts on Mn doping of ZnO nanostructures. Diluted magnetic semiconductor (DMS) behavior has been observed in many transition-metal doped ZnO films [12-14], and Curie temperatures above room temperature were achieved [15,16]. Although the efforts aimed at understanding the origin of the ferromagnetism resulted in hundreds of papers, substantial debate still remains. The available data cannot further advance our understanding of the mechanism since the data obtained so far on Mn doped ZnO are not quite consistent, for example, besides the ferromagnetic behavior, behavior of spin glass [17] and paramagnet [18] have also been observed. Therefore, more detailed works are essential to understand the behavior of these materials. Mn doped ZnO nanowires (or nanobelts) have been obtained by doping Mn into ZnO by using various techniques, such as ion implantation [19], thermal evaporation [20-23]. These methods generally require high temperature and expensive equipments. On the other hand, wet chemical method has been proven to be a simple and versatile approach for preparing ZnO nanowires or nanorods due to its relatively low growth temperature and good potential for mass production [24-27]. However, to the best of our knowledge, there is no report on the synthesis of Mn doped ZnO nanowires by using wet chemical method. Here, we report a simple hydrothermal method to prepare the Mn doped ZnO

nanowires. The structure and light-emitting properties are also investigated.

## 2. Experimental Section

**Materials.** Zinc sulfate hydrate ($ZnSO_4 \cdot 7H_2O$), manganese sulfate hydrate ($MnSO_4 \cdot H_2O$), carbamide ($CON_2H_4$), sodium hydroxide (NaOH), and ethanol were of analytical grade and used without further purification. Double-distilled water was employed for all experiments.

**Synthesis.** In a typical synthesis of Mn dopped ZnO nanowires, a solution of 50 ml 0.1M $ZnSO_4$, 3 ml 0.1M $MnSO_4$, 15 ml 1M carbamide ($CON_2H_4$) and 10 ml $C_2H_5OH$ was placed in a sealed Teflon autoclave with the pH of the solution adjusted to 14 by NaOH. The solution was then heated at 180℃ for 12 hours and the resulting products were obtained by washing and drying the yellowish precipitates at 60℃ for 12 hours.

**Characterization.** The microstructure and composition of the nanowires were investigated using an X-ray diffractometer (XRD, PW1140/90) with Cu K$\alpha$ radiation (25 mA and 40 kV), a scanning electron microscope (SEM, JEOL JSM-6300), transmission electron microscope (TEM, JEOL-2010), energy dispersive spectroscopy (EDS), and electron energy-loss spectroscopy (EELS). Quantitative EDS analysis shows the molar ratio of Mn is around 3%. The magnetic properties of the nanowires were studied using a Superconducting Quantum Interference Device (SQUID) magnetometer (MPMS-5S). The photoluminescence (PL) measurements were performed by using a Kimmon HeCd laser (325 nm, 55 mW) in a closed cycle Oxford cryostat. The optical signal was dispersed by a 0.25 m Oriel spectrometer and captured by an Andor CCD detector.

## 3. Results and Discussion

**Figure 1** shows the XRD spectrum of the $Zn_{1-x}Mn_xO$

nanowires, the reflection peaks of hexagonal structured ZnO are distinguishable, revealing that the doping of Mn does not change the wurtzite structure of ZnO. No Mn-related impurity phases were observed. **Figure 2 (a)** and (b) show the typical SEM and TEM images of the $Zn_{1-x}Mn_xO$ nanowires, respectively. The nanowires have uniform diameters along their entire length, the diameters and lengths are in the range of 10 to100 nm and 2 to 10 μm, respectively. **Figure 3(a)** shows TEM image of a typical long $Zn_{1-x}Mn_xO$ nanowire, the right inset shows the selected-area electron diffraction (SAED) pattern taken from a single nanowire, the analysis of the SAED reveals that the $Zn_{1-x}Mn_xO$ nanowire is single crystalline and grows along the [0001] orientation. The presence of Mn in the lattice was confirmed by the EELS measurement, the spectrum shows that Zn and Mn coexist along with O (**Figure 3(b)**). The Mn-L3/L2 intensity ratio indicates one electron in the d-orbital suggesting Mn to be in the +2 oxidation state. The nature of single-crystal structure of the $Zn_{1-x}Mn_xO$ nanowires and the growth orientation were further confirmed by high-resolution TEM (HRTEM) image as shown in **Figure 4**. The HRTEM images analysis shows that the $Zn_{1-x}Mn_xO$ nanowires are structurally uniform without any signify-
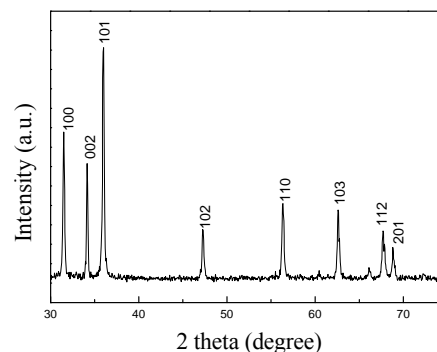


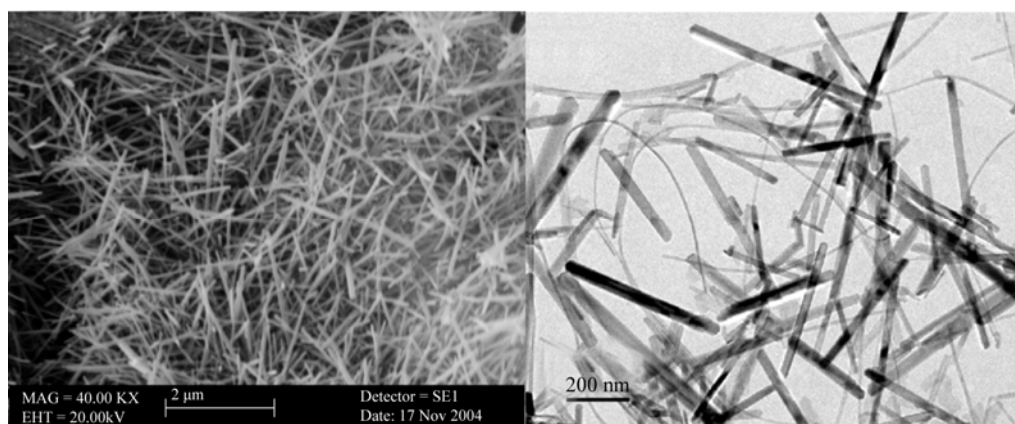**Figure 1. The XRD spectrum of the $Zn_{1-x}Mn_xO$ nanowires.**
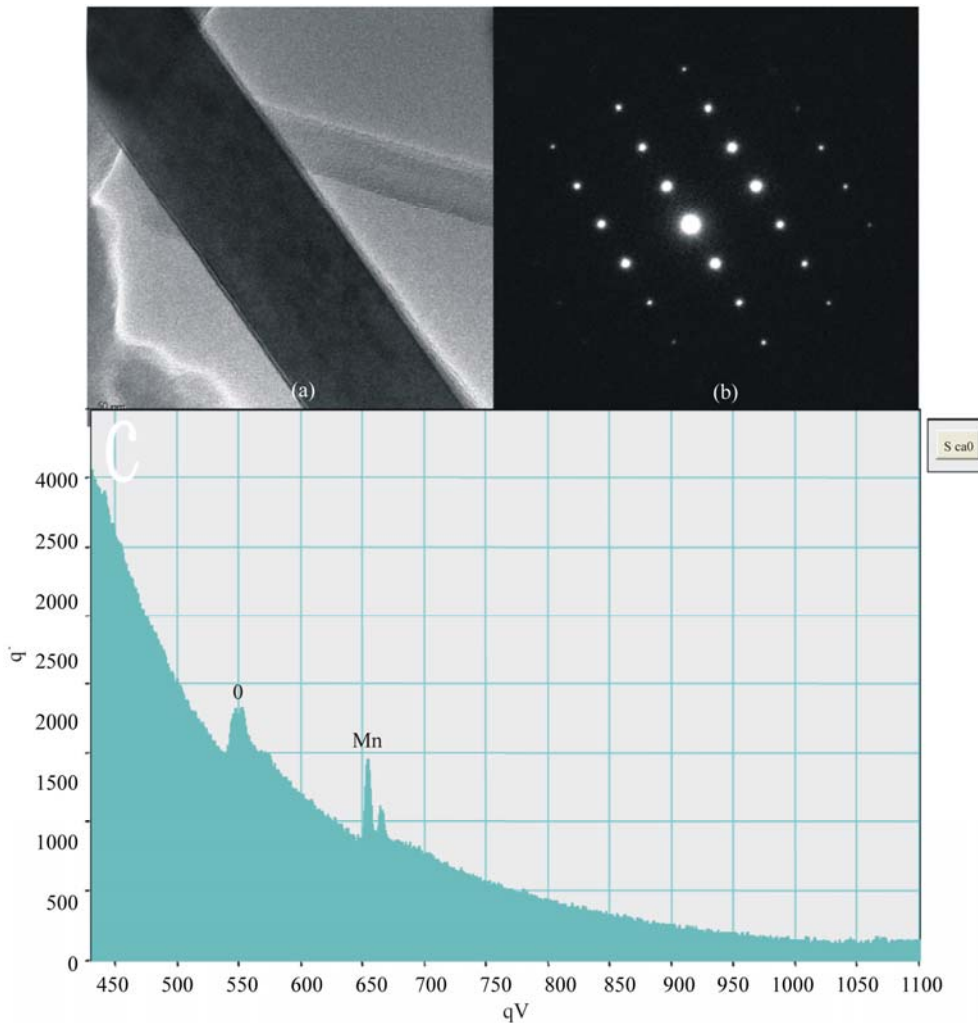


**Figure 2. (a) SEM; (b) TEM images of $Zn_{1-x}Mn_xO$ nanowires.**

**Figure 3. (a) TEM image of a $Zn_{1-x}Mn_xO$ nanowire; (b) the corresponding electron diffraction pattern of the $Zn_{1-x}Mn_xO$ nanowire; (c) the corresponding electron energy loss spectroscopy spectrum of the $Zn_{1-x}Mn_xO$ nanowire.**

cant defect. These characteristics of the $Zn_{1-x}Mn_xO$ nanowires are similar to those ZnO nanowires synthesized by hydrothermal methods.

The magnetic properties of the as-prepared $Zn_{1-x}Mn_xO$ nanowires were investigated using a SQUID magnetometer. **Figure 5** shows the temperature dependence of the magnetization (M-T) during cooling in a magnetic field of 5 T, the magnetization shows a slight increase from 100 to 40 K, followed by a steep increase below 30 K until 5 K. It can be seen that the FC curve shows a sharp increase at low temperature, this behavior has been considered as the effect of randomness and disorder on percolating FM clusters in most diluted magnetic semiconductor materials. So the Curie temperature of $Zn_{1-x}Mn_xO$ nanowires is about 30 K, which is higher than 25 K and lower than 50 K, observed for ZnMnO thin film and Mn doped ZnO nanotetrapods, respectively [28, 29]. It seems that data reported so far on Mn doped ZnO are not quite consistent. These discrepan-

cies may be due to the different fabrication methods. Obviously, more detailed works are essential to understand the magnetic behaviors of these materials.

The photoluminescence (PL) of the $Zn_{1-x}Mn_xO$ nanowires and undoped ZnO nanowires was investigated at room temperature. Usually, the PL spectrum of the undoped ZnO nanowires shows characteristic UV emission and broad green emission, in agreement with previously reported results for ZnO nanowires [30]. However, the photoluminescence of the $Zn_{1-x}Mn_xO$ nanowires is apparently different from that of undoped ZnO nanowires. It can be observed from **Figure 6** that a strong green emission appears, while the violet emission completely disappears. The mechanism of green emission has been suggested to be mainly due to the existence of various points that can easily form recombination centers [31]. In the present situation, the strong green emission suggests that these $Zn_{1-x}Mn_xO$ nanowires should have many point
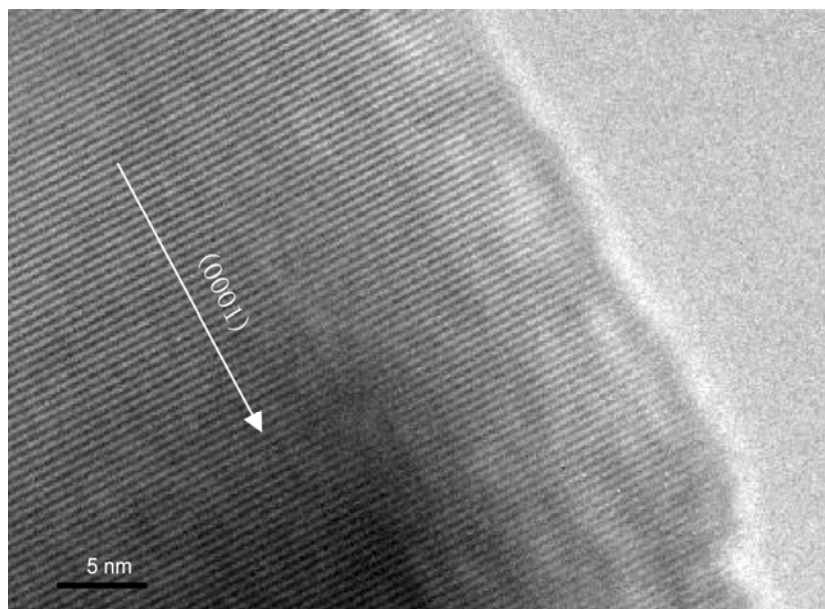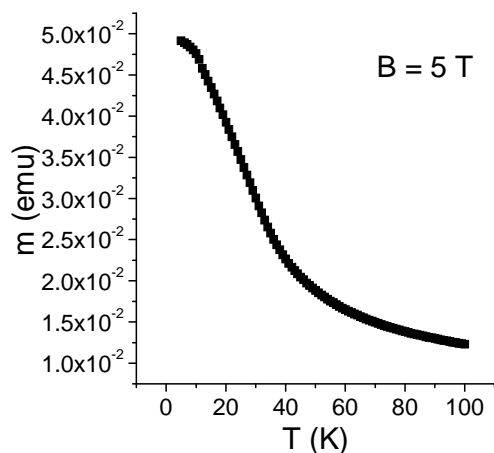
**Figure 4. HRTEM image of a Zn$_{1-x}$Mn$_x$O nanowire.**



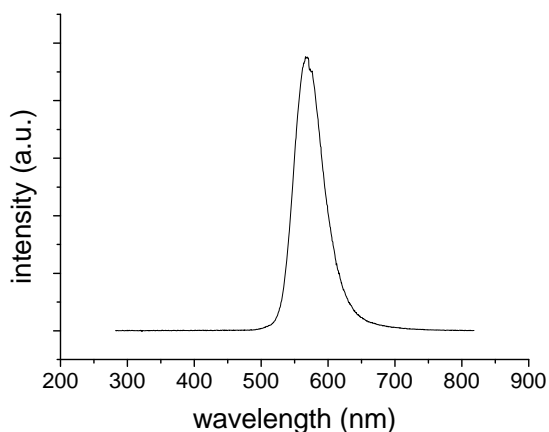**Figure 5. Temperature dependent magnification (M-T) curve of the Zn$_{1-x}$Mn$_x$O nanowires at a magnetic field B = 5T.**



**Figure 6. The photoluminescence (PL) spectrum recorded from the Zn$_{1-x}$Mn$_x$O nanowires at room temperature.**

defects, such as oxygen vacancies $V_O^+$ [32,33]. It can be inferred that the ZnO formed during the hydrothermal process features a high density of oxygen vacancies, which enhanced the green emission intensity. It has been suggested that the violet emission band could be assigned to the $V_{Zn}^-$ centers, and the violet emission intensity depends on the density of $V_{Zn}^-$. The high density of $V_O^+$ resulted during the hydrothermal process can lead to a decrease in the density of $V_{Zn}^-$ centers and a increase of nonradiative recombination processes. Furthermore, the doping of Mn in the ZnO may change the electronic structure of ZnO such as the position of the Fermi level [34]. These should be responsible for the quench of the violet emission.

## 4. Conclusions

In conclusion, large quantity and single crystalline Zn$_{1-x}$Mn$_x$O nanowires have been synthesized through a hydrothermal method. Structural characterization by x-ray diffraction and transmission electron microscopy revealed that the Zn$_{1-x}$Mn$_x$O nanowires possess wurtzite structure with c-axis growth orientation. Mn doped ZnO nanowires are ferromagnetic with Curie temperature ~30 K. The Zn$_{1-x}$Mn$_x$O nanowires exhibit a deep level emission at 566 nm. This simple approach shows promise for fabricating nanoscale sensor and other devices.

## 5. Acknowledgments

# 6. References

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