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<tr>
<td><strong>Citation</strong></td>
<td>Applied Physics Letters, 2004, v. 84 n. 5, p. 756-758</td>
</tr>
<tr>
<td><strong>Issued Date</strong></td>
<td>2004</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10722/42394">http://hdl.handle.net/10722/42394</a></td>
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Magnetic properties of Mn doped ZnO tetrapod structures

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(Received 29 July 2003; accepted 4 December 2003)

ZnO tetrapod nanostructures were prepared by evaporating Zn metal under humid argon flow. After the fabrication, Mn diffusion doping was performed at two different temperatures (600 and 800 °C). The samples were characterized by scanning electron microscopy, transmission electron microscopy, x-ray fluorescence, x-ray diffraction (XRD), superconducting quantum interference device magnetometer, and photoluminescence. Diffusion doping resulted in the increase of the size of tetrapods, but no new peaks were found in XRD spectrum. Mn doped ZnO tetrapod structures were found to be ferromagnetic with Curie temperature ~50 K, and showed large coercive field (~3500 Oe for 800 °C sample, ~5500 Oe for 600 °C sample). © 2004 American Institute of Physics. [DOI: 10.1063/1.1645312]

Due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV), ZnO is of great interest for photonic applications and its optical properties have been studied in detail. In recent years, due to prediction of possible ferromagnetic properties in transition metal doped ZnO with Curie temperature ($T_C$) above room temperature, studies of transition metal doped ZnO have been attracting lots of attention. Theoretical calculations predict that Mn doped p-type ZnO should be ferromagnetic at room temperature. In the absence of p-type doping, theoretical calculations predict that Mn doped ZnO would exhibit antiferromagnetic properties. There have been several experimental works on transition metal doping of ZnO thin films. The obtained results have been contradictory. Paramagnetic properties were reported for Zn$_{0.93}$Mn$_{0.07}$O films prepared by magnetron sputtering. Antiferromagnetic behavior was observed in Zn$_{0.64}$Mn$_{0.36}$O films prepared by pulsed laser deposition and polycrystalline ZnO:Mn powder samples. However, ferromagnetism was reported in Mn-implanted ZnO:Sn single crystals ($T_C$ ~ 250 K) and Zn$_{1-x}$Mn$_x$O ($x = 0.1$ and $x = 0.3$) films prepared by laser molecular beam epitaxy. Most likely the differences in the reported results are due to different preparation methods, since the properties of ZnO are sensitive to the preparation conditions. The previously reported studies focus on magnetic properties of Mn doped thin films, powders and single crystals. Different shapes of ZnO nanostructures, such as nanoribbons, nanowires and tetrapod nanorods were reported. In our recent work, we reported synthesis of ZnO tetrapod nanorods and nanowires under different gas flow. The fabrication of ZnO nanostructures was performed in humid argon flow as reported previously. Diffusion doping was performed by placing 0.654 g of ZnO nanostructures and 0.054 g of Mn in the tube furnace at the desired temperature (600 or 800 °C). The quartz process tube was then connected to a vacuum pump and diffusion was performed for 30 min. The structure of the obtained material was investigated by x-ray diffraction (XRD) using a Siemens D5000 x-ray diffractometer, scanning electron microscopy (SEM) using Cambridge-440 SEM, and transmission electron microscopy (TEM) using Philips Tecnai 20 TEM. Magnetic properties were studied using a superconducting quantum interference device (SQUID) magnetometer (MPMS-5s). The Mn content was determined using x-ray fluorescence (XRF) spectrometer JEOL JSX-3201Z. The room temperature photoluminescence was measured using a HeCd laser excitation source (325 nm).

Figure 1 shows the representative SEM images of ZnO nanostructures before and after Mn diffusion doping. Before the diffusion doping, the sample consists of a mixture of ZnO tetrapod structures with nanowires growing out of tetrapod legs [see Fig. 1(a)]. After Mn diffusion doping, the size of the tetrapods increases as expected (but the leg diameter remains in submicron range). In some cases, structures with broadened tetrapod centers can be observed, as shown in Fig. 1(b). Obtained morphologies after Mn diffusion are very similar for 600 and 800 °C. Longer diffusion time (not...
shown) results in larger increase of the size of the tetrapod structures. The XRD spectrum is shown in Fig. 2. For both doped and undoped samples, XRD data showed peaks corresponding to wurtzite ZnO only and no peak shifts were observed. No diffraction peaks from Zn or other impurities were detected. Mn content after Mn diffusion was examined by XRF. For diffusion at 600 °C, Mn content was 8.4 mol %, while for diffusion at 800 °C, Mn content was 2.2 mol %. Mn content in samples diffused at different temperature is determined not only by the diffusion coefficient which is expected to be higher at higher temperature, but also by other factors such as loss of sublimed Mn during pumping, which will be higher at 800 °C.

Figure 3 shows magnetic hysteresis (M–H) curves obtained at 5 K for the samples doped at 600 and 800 °C. The inset shows temperature dependence of the magnetization at the applied magnetic field of 20 kOe. Obtained Curie temperature of ~50 K is significantly higher than ~25 K, observed for Zn$_{0.9}$Mn$_{0.1}$O thin films. Furthermore, the Mn doped ZnO tetrapod structures exhibit very high coercive field (~3500 Oe for sample doped at 800 °C and ~5500 Oe for sample doped at 600 °C), which is about one order of magnitude higher than that reported for thin films. Similar enhancement of the coercive field was observed in GaMnN nanowires. While GaMnN thin films typically exhibit coercive field below 100 Oe, GaMnN nanowires had coercive field in the range 620–1400 Oe. The reasons for coercivity enhancement require further investigation. Another feature in Fig. 3 that should be noticed is that the 5 T magnetization for both samples is the same, ~0.25 μ$_B$/Mn, indicating that the magnetic states of the Mn ions seem to be independent of the doping up 8.4% in our nanostructured ZnO tetrapods.

The fact that the magnetization of ~0.25 μ$_B$/Mn is much smaller than ~5 μ$_B$/Mn for a free Mn$^{2+}$ ion with S = 5/2 and g = 2, suggests that the dominant interactions between the Mn ions are antiferromagnetic, and the weak ferromagnetism could be ascribed to the nonlinear antiferromagnetic couplings (or canted ferromagnet). Actually the strong antiferromagnetic coupling has been observed in Zn$_{0.64}$Mn$_{0.36}$O epitaxial films, which resulted in a spin glass behavior and a magnetization of 0.20 μ$_B$/Mn (5 T). By comparing with ~0.17 μ$_B$/Mn obtained from the ferromagnetic epitaxial Zn$_{1-x}$Mn$_x$O epitaxial films, it is evident that it is significantly larger. It seems that data reported so far on Mn doped ZnO are not quite consistent, for example, besides the ferromagnetic behavior, behaviors of spin glass and paramagnet have also been observed. These discrepancies may be due to the different fabrication methods. Obviously, more detailed works are essential to understand the magnetic behaviors of these materials.

![FIG. 2. XRD of undoped and Mn doped ZnO tetrapod structures. The curves have been vertically shifted to improve clarity.](image)

Figure 4 shows room temperature photoluminescence...
For Mn doped ZnO nanocrystalline films, core–higher green luminescence from nanostructures with smaller concentration of defects causing the green luminescence is also expected to be higher at the surface, as concluded from results from XRD, PL and SQUID measurements suggest that ZnMnO alloy was formed, though Mn concentration is expected to be higher at the surface of tetrapod structures. Higher Mn content and/or presence of Mn oxides at the surface possibly contributed to the difference between observed magnetization and magnetization of a free Mn$^{2+}$ ion.

To summarize, we have prepared Mn doped ZnO tetrapod structures by diffusion doping at temperatures 600 and 800 °C. The obtained samples have shown clear magnetic hysteresis at 5 K. Curie temperature was determined to be ~50 K. The sample diffused at 600 °C exhibited higher Mn concentration and higher remnant magnetization at 5 K, as well as higher coercive field. Both samples exhibited very high coercive field, which is about one order of magnitude higher compared to values reported for ZnO: Mn thin films.

The authors would like to thank Amy Wong and Wing Sang Lee for SEM and TEM measurements. H.L. and X.X.Z. have been supported by the Research Grants Council of the Hong Kong Special Administration Region, People’s Republic of China (Project No. HKUST6165/01P).

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