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Magnetic properties of Mn doped ZnO tetrapod structures

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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,[1,2] 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.[1,2] In the absence of *p*-type doping, theoretical calculations predict that Mn doped ZnO would exhibit antiferromagnetic properties.[2] There have been several experimental works on transition metal doping of ZnO thin films.[3–7] The obtained results have been contradictory. Paramagnetic properties were reported for $Zn_{0.93}Mn_{0.07}O$ films prepared by magnetron sputtering.[4] Antiferromagnetic behavior was observed in $Zn_{0.64}Mn_{0.36}O$ films prepared by pulsed laser deposition[7] and polycrystalline ZnO:Mn powder samples.[5] However, ferromagnetism was reported in Mn-implanted ZnO:Sn single crystals (T_c~250 K)[6] and $Zn_{1-x}Mn_xO$ ($x=0.1$ and $x=0.3$) films prepared by laser molecular beam epitaxy.[3] 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,[7] nanowires,[8,9] and tetrapod nanorods,[10–13] were reported. In our recent work, we reported synthesis of ZnO tetrapod nanorods and nanowires under different gas flow.[13] The fabrication of ZnO nanostructures was performed in humid argon flow as reported previously.[13] 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
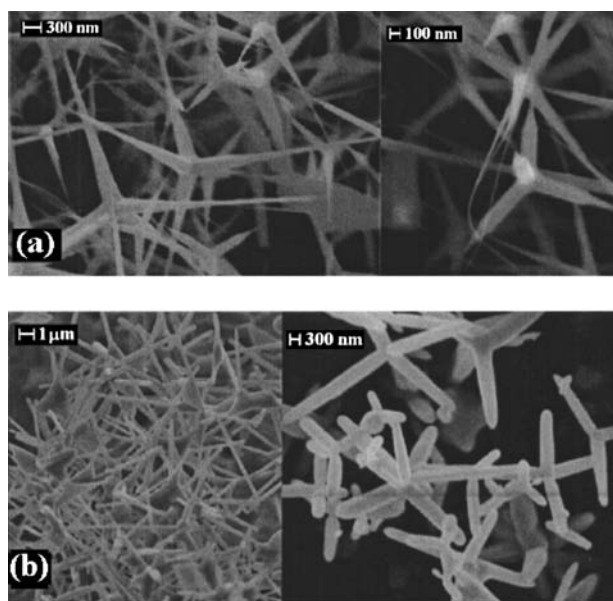

FIG. 1. Representative SEM images of (a) undoped ZnO, (b) Mn diffusion doped ZnO.

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.[3] 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.[3] Similar
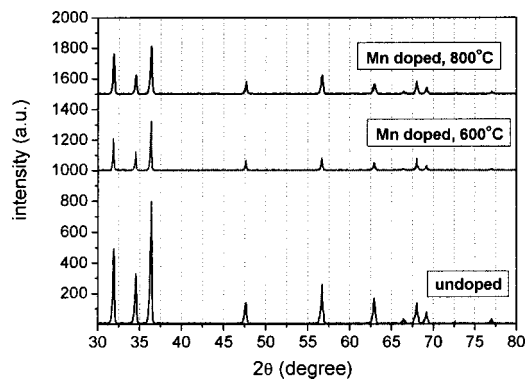

FIG. 2. XRD of undoped and Mn doped ZnO tetrapod structures. The curves have been vertically shifted to improve clarity.
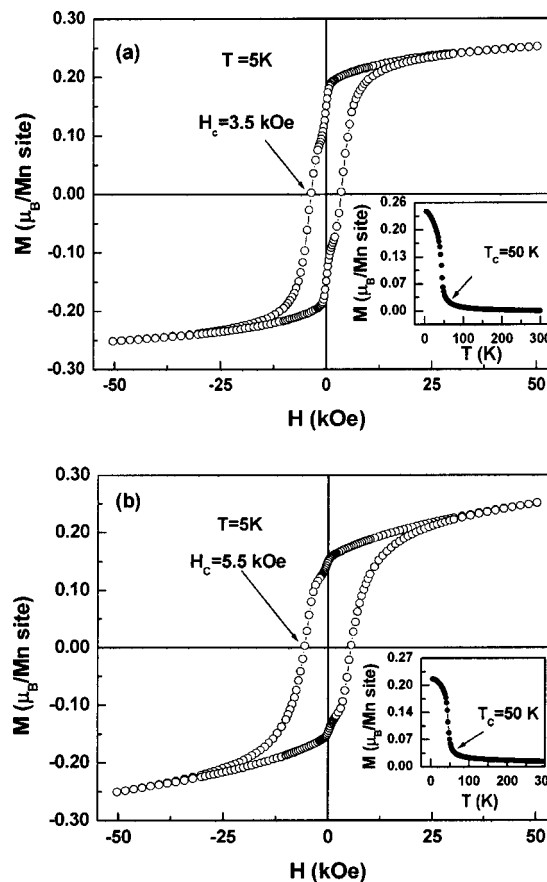

FIG. 3. (a) M vs. H curve at 5 K for Mn doped sample diffused at 800 °C. The inset shows magnetization vs temperature. (b) M vs. H curve at 5 K for Mn doped sample diffused at 600 °C. The inset shows magnetization vs temperature.

enhancement of the coercive field was observed in GaMnN nanowires.[14] While GaMnN thin films typically exhibit coercive field below 100 Oe, GaMnN nanowires had coercive field in the range 620–1400 Oe.[14] 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,[7] 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 $Zn_{1-x}Mn_xO$ epitaxial films,[3] 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,[3] behaviors of spin glass[7] and paramagnet[4] 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.

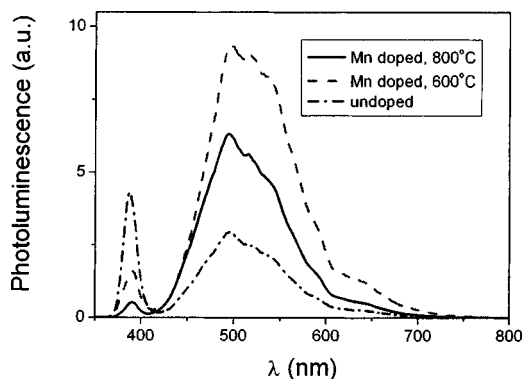Figure 4 shows room temperature photoluminescence

FIG. 4. Photoluminescence of undoped and Mn doped ZnO tetrapod structures.

(PL) of ZnO tetrapod structures with and without Mn diffusion doping. The PL spectrum of the undoped ZnO tetrapod nanorods shows characteristic UV emission and broad green emission, in agreement with previously reported results for ZnO tetrapod nanorods.[12] It can be observed from Fig. 4 that Mn doping does not change the peak positions, which is in good agreement with the results reported in the literature.[15,16] Mn doping is expected to cause reduction in the intensity of both UV[16] and green emission.[15,16] Since our samples are in the powder form of fluffy powder-like material, the ratio of UV to green emission should be compared instead of the absolute PL intensity since it is not possible to ensure that we probe the same amount of the material. It can be observed that both Mn doped samples show similar reduction in UV to green emission ratio, though UV emission is stronger in sample doped at 600 °C. The reduction in emission intensity with Mn doping was attributed to increased nonradiative recombination processes.[16] However, the relationship between the emission intensity and Mn concentration in the case of diffusion doping is likely to be complex due to the influence of annealing. The origin of green luminescence in ZnO is still not fully clear, but it is commonly believed that this emission originates from intrinsic defects in ZnO, such as oxygen vacancy,[17] donor–acceptor complexes[18,19] and antisite oxygen.[20] The intrinsic defects involved in green luminescence would be affected by annealing, so that the obtained PL spectrum after Mn doping would be affected both by annealing itself and by inclusion of Mn.

It should also be pointed out that the diffusion doping will likely result in higher Mn concentration near the surface of ZnO tetrapod structures. Higher doping in the surface region was also found in nitrogen doped GaP nanobelts.[21] The concentration of defects causing the green luminescence is also expected to be higher at the surface, as concluded from higher green luminescence from nanostructures with smaller diameter.[9,10] For Mn doped ZnO nanocrystalline films, core-shell structure of nanocrystalline (ZnO core, interfacial region and MnO_2 shell) was proposed to explain complete quenching of the green luminescence. However, in our work green luminescence can still be observed; the proposed explanation is not likely to be applicable to the tetrapod structures studied in this work. Moreover, the possible existence of Mn oxides, MnO and MnO_2, which cannot be excluded even though no secondary phases were detected by XRD, does not explain observed ferromagnetic properties. Both MnO and MnO_2 are antiferromagnetic with Néel temperatures of 116 and 84 K, respectively.[3] Therefore, obtained 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.

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