Exchange bias and the origin of magnetism in Mn-doped ZnO tetrapods

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Wurtzite-type ZnO tetrapod nanostructures were prepared by evaporating Zn metal under humid argon flow. After the fabrication, Mn was doped into ZnO nanostructures by diffusion at 600 °C. The average concentration of Mn was determined to be 8.4 mol % by x-ray fluorescence. X-ray diffraction patterns obtained from the doped and undoped samples are almost the same. High-resolution transmission electron microscopy observations reveal the existence of surface layers. Magnetic measurements show that the sample has a very large coercivity $H_C=5500$ Oe at 5.5 K and a Curie temperature $T_C=43$ K, which may suggest that ferrimagnetic $(Zn,Mn)Mn_2O_4$ exists at the surface. Exchange bias is clearly observed below 22 K. Exchange bias is attributed to the exchange interaction between ferrimagnetic $(Zn,Mn)Mn_2O_4$ and spin-glass-like (or antiferromagnetic) phase in manganese oxides. © *2004 American Institute of Physics*.
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Magnetic semiconductors have been intensively studied recently due to the application in spintronics, which offers opportunities for the next generation of devices by combining standard microelectronics/nanoelectronics and spin-dependent effect.[1] In order to achieve large spin polarization in semiconductor, the Zeeman splitting of the conduction band (valence) must be greater than the Fermi energy of electrons (holes).[1] Therefore, the ferromagnetic semiconductors with Curie temperatures, T_C, above room temperature are desired. Since theoretical calculations predicted Mn-doped ZnO can be ferromagnetic even above room-temperature,[2] much effort had been done.[3–19] Theoretical calculations predict that Mn doped *p* type ZnO should be ferromagnetic at room temperature.[2,20,21] However, in the absence of *p*-type doping, Mn doped ZnO would exhibit antiferromagnetic properties.[20,21] Experimental results on Mn doped ZnO are quite contradictory to each other. Paramagnetic properties were reported for $Zn_{0.93}Mn_{0.07}O$ films prepared by magnetron sputtering.[11] Antiferromagnetic behavior was observed in $Zn_{0.64}Mn_{0.36}O$ films prepared by pulsed laser deposition[5] and polycrystalline ZnO:Mn powder samples.[12] However, ferromagnetism was reported in Mn-implanted ZnO:Sn single crystals ($T_C=250$ K),[10] $Zn_{1-x}Mn_xO$ films ($T_C=30$ and 45 K for $x=0.1$ and 0.3, respectively) prepared by laser molecular beam epitaxy,[8] and $Zn_{1-x}Mn_xO$ nanowires ($T_C=37$ K for $x=0.13$) prepared by vapor phase growth.[17]

Besides the ferromagnetic and antiferromagnetic orders due to the exchange interaction between Mn cations that substitute Zn cations, manganese oxides also have strong magnetism: MnO and MnO_2 are antiferromagnetic, Mn_3O_4 and $(Zn,Mn)Mn_2O_4$ are ferrimagnetic. It is therefore crucial to clarify where the magnetism comes from. In this letter, we report the structural and magnetic studies on the Mn doped ZnO tetrapod nanostructures. A large coercivity $H_C=9200$ Oe and an exchange bias field $H_E=300$ Oe were observed at 2 K and surface layers was found to cover on the tetrapods. We attribute exchange bias to the exchange interaction between ferrimagnetic $(Zn,Mn)Mn_2O_4$ and spin-glass-like (or antiferromagnetic) phase in manganese oxides.

ZnO tetrapod nanostructures were fabricated as follows.[22] Zn powder was evaporated in a quartz tube at 950 °C under the Ar flow of 0.7 l/min, which passed through water before being introduced into the tube furnace.[22] Diffusion doping was performed by placing 0.654 g of ZnO tetrapods and 0.054 g of Mn in the tube furnace at 600 °C. The quartz process tube was then connected to a vacuum pump and diffusion was performed for 30 min.[19] The Mn content was determined using x-ray fluorescence spectrometer (XRF). The structure of the sample was investigated by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Magnetic measurements were performed using superconducting quantum interference device (SQUID) magnetometer.

The typical XRD spectra for undoped ZnO nanostructures are shown in Fig. 1, which indicates only a wurtzite-type structure with the lattice parameters, $a=0.325$ and $c=0.521$ nm. Although the XRF results reveal that the Mn content of the doped sample is 8.4 mol %, the peaks of the XRD spectrum of the doped sample are at the same positions as the corresponding ones of the undoped and no additional peaks can be clearly seen, as shown in Fig. 1. If significant Zn cations were substituted with larger Mn cations, the peaks should shift to lower angle due to the enlargement of lattice parameters according to the previous results.[4,8,14,17] For diffusion doping method, the Mn concentration should decrease gradually from surfaces to insides of the ZnO nanostructures. The Mn cations may therefore exist mainly near the surfaces,

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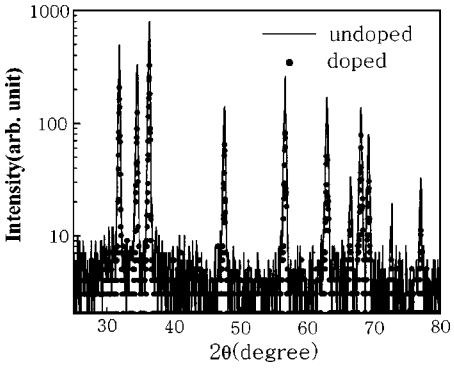

FIG. 1. XRD spectra show that both the undoped and Mn doped ZnO tetrapod nanostructures are wurtzite type. The XRD peaks of the doped sample are identical to those of the undoped.

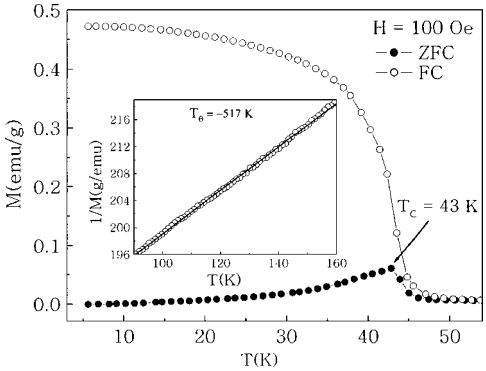

FIG. 3. ZFC-FC curves measured in 100 Oe indicate $T_C=43$ K. $T_\theta=-517$ K can be obtained by extrapolating the $1/M$ vs T curve, as shown in the inset.

and the inside ZnO remain nearly unchanged. If the XRD patterns are dominated by the inside ZnO, the peaks may be at the same positions as those of the undoped sample.

If the Mn cations mainly exist near the surfaces for a dopant up to 8.4 mol %, manganese oxides could form, which may dominate the magnetic behaviors of the doped samples. To verify this point, HRTEM studies were performed.

Figure 2 is a HRTEM image of a Mn doped ZnO tetrapod. The existence of a surface layer is evident. The fast Fourier transform (FFT) diffractogram is depicted in the left inset. This FFT diffractogram is indexed to be [100] oriented wurtzite-type ZnO, which is consistent to the XRD results. This FFT diffractogram also reveals that the pod grows along [001] direction.

Zero-field cooled (ZFC) and field cooled (FC) magnetizations of the Mn doped ZnO nanostructures were measured in a 100 Oe field. As shown in Fig. 3, $T_C=43$ K can be clearly seen, which is consistent with Curie temperature of ferrimagnetic Mn_3O_4.[23,24] Above 1443 K, Mn_3O_4 is cubic spinel, whereas it becomes tetragonal distorted spinel below 1443 K in which Mn^{2+} ions occupy the tetragonal A sites and Mn^{3+} ions occupy the octagonal B sites.[24] The paramagnetic Curie temperature, T_Θ, of the sample is about $\sim$517 K, which is in accordance with the previously reported values.[24] Since secondary ion mass spectrometer (SIMS) measurement indicates the existence of Zn^{2+} at the surface and $(Zn,Mn)Mn_2O_4$ has the similar properties to Mn_3O_4, $(Zn,Mn)Mn_2O_4$ should be responsible to the magnetism of the Mn doped ZnO nanostructures.

Magnetic hysteresis loops were measured at various temperatures after the sample was cooled from 337 K in a field of 50 kOe. Large coercivity $H_C=9.2$ kOe was observed at 2 K, which is much larger than previous reported values in the Mn doped ZnO materials.[8] $H_C=6.1$ kOe at 5 K was reported in the Mn_3O_4 particles of 200 nm in diameter.[25] Theoretical calculations show that $H_C=4.6$ kOe at 4.2 K for bulk single crystals.[23] In fact, our sample displays $H_C=5.5$ kOe at 5.5 K, which is a reasonable value comparing with previous reports. Furthermore, the hysteresis loops of the Mn doped ZnO nanostructures have almost the same shape as those in the Mn_3O_4 particles.[25] All phenomena observed indicate that $(Zn,Mn)Mn_2O_4$ exists in the Mn doped ZnO nanostructures and dominates magnetic behaviors. The magnetization of 0.25 μ_B/Mn was found in a 50 kOe field, which is about 1/2 of previous reported value of Mn_3O_4 (e.g., 1.82 μ_B/molecule).[23] The reason for the reduction of the magnetization includes the formation of $(Zn,Mn)Mn_2O_4$,[26] the existence of antiferromagnetic manganese oxides, or (Zn,Mn)O.[5,8,14]

Exchange bias was clearly observed below 22 K in the FC hysteresis loops. The temperature dependencies of the exchange bias field (H_E) and coercivity (HC) are shown in the inset of Fig. 4. To generate exchange bias, the system must have, at least, one fixed magnetic phase (usually an antiferromagnetic phase) that does not reverse during hysteresis loop measurements.[27] There are two possible candidates for the fixed phase here: one is antiferromagnetic

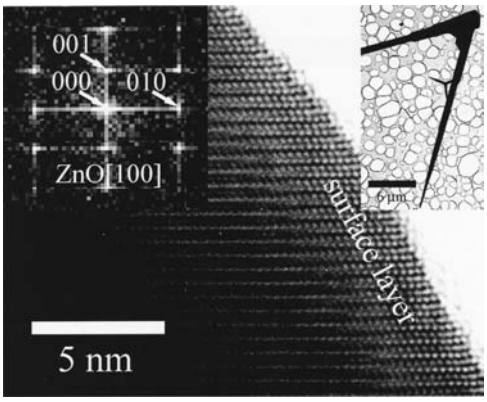

FIG. 2. HRTEM image of a Mn doped ZnO tetrapod. The left inset is the corresponding FFT diffractogram of the inner part. The right inset shows the size of a whole pod.

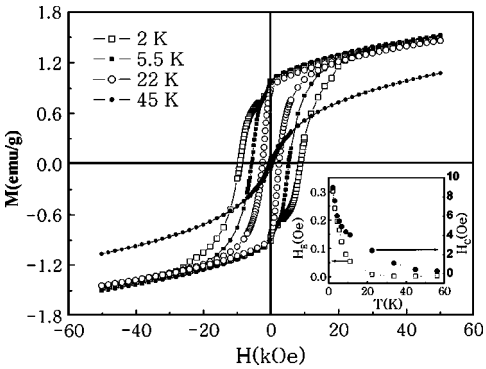

FIG. 4. Hysteresis loops measured at various temperatures after field cooling of 50 kOe. Inset shows the temperature dependencies of H_C and H_E.

(Zn,Mn)O;[5,12] the other is spin-glass-like manganese oxides[28,29] [$(Zn,Mn)Mn_2O_4$, or (Zn,Mn)O]. As shown in the inset of Fig. 4, exchange bias disappears above 22 K, which is corresponding to the phase transition temperature of the fixed phase.

To summarize, it is found that the Mn-doped wurtzite-type ZnO nanostructures by diffusion are covered by the Mn-rich layers, which might be $(Zn,Mn)Mn_2O_4$ suggested by the magnetic measurements. Exchange bias is clearly observed below 22 K. Exchange bias is attributed to the exchange interaction between ferrimagnetic $(Zn,Mn)Mn_2O_4$ and antiferromagnetic (Zn,Mn)O or spin-glass-like phase in manganese oxides [$(Zn,Mn)Mn_2O_4$ or (Zn,Mn)O].

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