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Sample preparation and annealing effects on the ferromagnetism in Mn-doped ZnO

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Sample preparation and annealing effects on the ferromagnetism in Mn-doped ZnO

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Magnetic properties of Mn-doped ZnO strongly depend on sample preparation and annealing. While the samples sintered in air at 500 °C show ferromagnetism at room temperature, those sintered at 900 °C are paramagnetic. The samples sintered in vacuum show a ferromagnetic transition at 45 K, which is attributed to ferrimagnetic Mn_3O_4. With an increase of annealing temperature, the ferromagnetism observed at room temperature in the low-temperature-sintered samples is gradually suppressed and finally completely removed. These results can be understood by considering a metastable ferromagnetic phase and its stability under varying temperatures and atmospheres. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1845858]

ZnO-based diluted magnetic semiconductors (DMS) have recently been attracting much attention, due to the important optoelectronic properties of ZnO and their potential applications in spintronics at practical temperatures.[1] It has been theoretically predicted that, when suitably doped by transition metal ions (V, Mn, Fe, Co, or Ni), ZnO could be made to be ferromagnetic with Curie temperature (T_C) higher than room temperature.[2,3] Many efforts have been directed toward experimental realization of high-temperature ferromagnetism (FM) in ZnO-based DMS.[4–10] Although room-temperature FM has been observed in several ZnO-based materials, many controversial results also have been reported. For example, in Mn-doped ZnO, several groups have obtained various properties. Fukumura *et al.* found a spin-glass behavior;[5] Tiwari *et al.* observed paramagnetism;[6] Jung *et al.* observed FM with T_c of 45 K.[7] This suggests a strong dependence of magnetic properties on the sample preparation conditions. Recently, Sharma *et al.* found that low-temperature synthesis could favor FM in Mn-doped ZnO, and room temperature FM was obtained.[10]

In this paper we report a detailed study of the relationship between magnetic properties and sample processing in bulk Mn-doped ZnO. We found that the magnetic properties strongly depended on sample preparation and annealing. By controlling the sample preparation conditions, different and controversial magnetic properties reported before have been realized in our samples and can be understood.

Bulk $Zn_{1-x}Mn_xO$ samples ($x=0.01-0.05$, denoted as ZnMnO hereafter) were prepared by a standard solid-state reaction method. Mixed powders of ZnO (99.9995%) and MnO_2 (99.999%) were calcined at 400 °C for 8 h, and carefully mixed and pressed into pellets, which were then sintered at 500 °C and 900 °C in air or vacuum. The samples sintered at a low temperature of 500 °C in air were then annealed at temperatures between 500 °C and 900 °C in air or vacuum. The sample structural properties were characterized by x-ray diffraction (XRD) using a Rigaku diffractometer (D/Max-B, Cu K_α), and the magnetizations were measured using a SQUID magnetometer (Quantum Design, MPMS XL).

Figure 1(a) shows the XRD pattern for a ZnMnO sample with 1% Mn sintered at 500 °C. Although the Mn concentration is low, besides the diffraction peaks from the ZnO wurtzite structure, additional peaks from MnO_2 have been observed, and the peak around 33 deg labeled by a star mark indicates the possible existence of the Mn_2O_3 phase. This suggests that the solubility of Mn in ZnO is very low, and the Mn distribution is not uniform. Furthermore, sintering at higher temperature does not create a uniform distribution of Mn. As shown in Fig. 1(b), in a sample sintered at a higher temperature of 900 °C, diffraction peaks from $ZnMn_2O_4$ have been identified. Mn solubility has been reported to be higher in ZnO thin films grown under nonequilibrium condi-

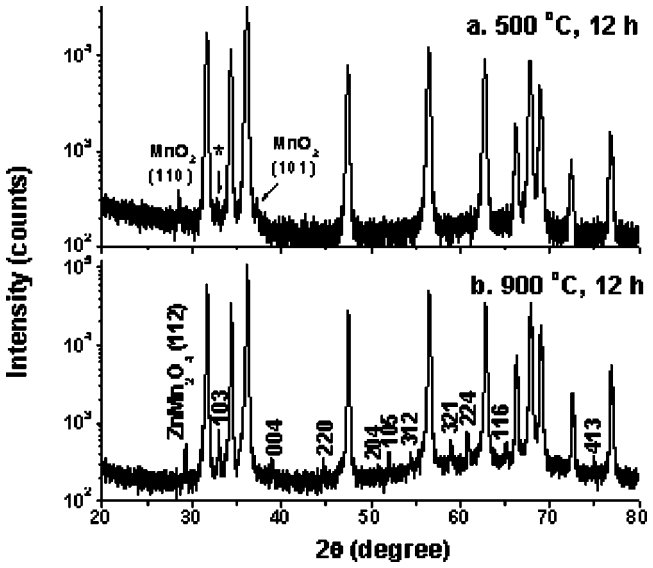

FIG. 1. XRD patterns of ZnMnO samples with 1% Mn sintered in air at 500 °C (a), and 900 °C (b), respectively. The peak labeled by a star mark in (a) is probably from Mn_2O_3, and all the labeled peaks in (b) are from $ZnMn_2O_4$. All the unlabeled peaks are from ZnO wurtzite structure.

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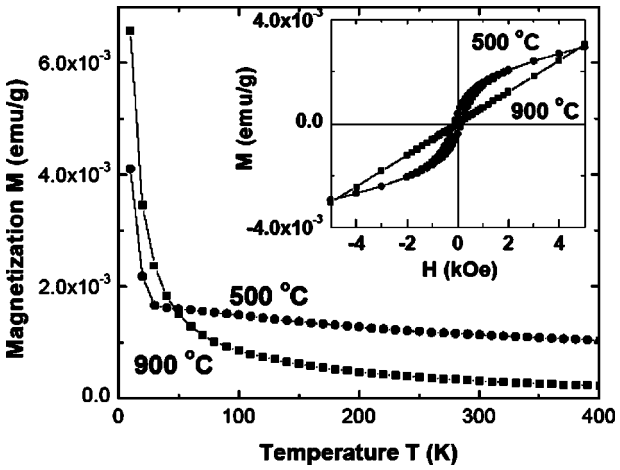

FIG. 2. Temperature-dependent magnetization curves at $H=500$ Oe for ZnMnO with 1% Mn sintered in air at 500 °C and 900 °C, respectively. Inset: Field-dependent magnetization curves at 300 K for the same samples.

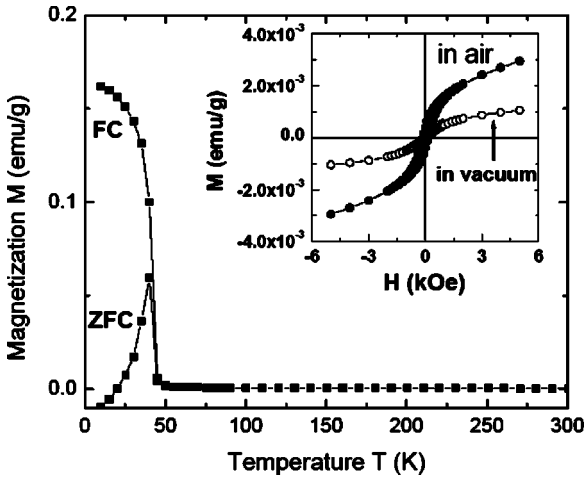

FIG. 3. Temperature-dependent magnetization curves (ZFC and FC) measured at 500 Oe for the ZnMnO sample with 1% Mn sintered at 500 °C in vacuum. Inset: Field-dependent magnetization curves for the samples with 1% Mn sintered at 500 °C in air and vacuum, respectively.

tions such as a pulsed laser deposition. However, it is obviously much lower in the low-temperature sintered samples studied here.

Magnetization was measured as functions of field and temperature. Shown in the inset of Fig. 2 are field-dependent magnetization curves at 300 K for the samples with 1% Mn sintered in air at 500 °C (low temperature) and 900 °C (high temperature), respectively. Room-temperature FM was realized in the samples sintered at low temperature, in which a well-defined hysteresis loop is observed, with considerable remanence and coercive field. But, the sample sintered at high temperature shows a linear response, indicating a paramagnetic behavior. The difference in magnetic properties was also revealed by the temperature dependence of magnetization plotted in Fig. 2. The high-temperature sintered sample follows a pure Curie–Weiss paramagnetic behavior, but the low-temperature sintered sample exhibits more complex properties. For the latter, at low temperatures, rapid decreasing of magnetization with increasing of temperature indicates a paramagnetic component. At high temperatures, the magnetization curve becomes flat and the magnetization is higher than that of the high-temperature sintered sample. These results indicate that the low-temperature sintered sample contains ferromagnetic and paramagnetic components, while the high-temperature sintered sample contains only a paramagnetic phase. Similar results were found in the samples with higher Mn concentration. Very recently, Kundaliya *et al.*[11] demonstrated that the ferromagnetic phase in low-temperature-processed Mn-ZnO is metastable and transforms to nonmagnetic phases at high temperatures.

The magnetic properties depend not only on the sample sintering temperature, but also on the sintering atmosphere. The field-dependent magnetization curves of the sample with 1% Mn sintered in air and vacuum at 500 °C are shown in the inset of Fig. 3. Comparing with the sample sintered in air, the sample sintered in vacuum shows weaker FM at room temperature. Besides the room-temperature FM, another magnetic transition at low temperature was observed in the vacuum-sintered sample. Figure 3 shows the temperature dependence of magnetization for the sample sintered in vacuum. Both the zero-field cooling (ZFC) and field cooling (FC) curves show sharp transitions around 45 K, below which there is large difference between ZFC and FC data, indicating a cluster behavior. Jung *et al.*[7] attributed a similar transition at 45 K to (Zn, Mn)O phase; however, in our vacuum-sintered sample, the transition around 45 K is more likely from Mn_3O_4, which is ferrimagnetic with T_C of 43 K. Although no Mn_3O_4 phase has been detected by XRD, Mn_3O_4 clusters may exist in the vacuum-sintered sample.

The effect of postsintering annealing on the magnetic properties has also been studied. The samples sintered in air at 500 °C were annealed in air for 12 h at 600 °C, 700 °C, and 900 °C, respectively. Figure 4 shows the field-dependent magnetization curves at 300 K for the as-sintered and annealed samples with 1% Mn. Obviously, with an increase of annealing temperature, the hysteresis loops became smaller and smaller, and the room-temperature FM was gradually suppressed and finally completely removed. The sample annealed at 900 °C is paramagnetic at 300 K, just like the samples sintered at the same temperature. Similar annealing

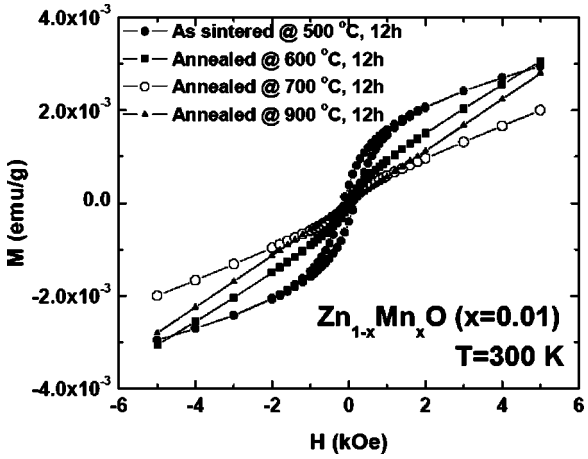

FIG. 4. Field-dependent magnetization curves measured at 300 K for the ZnMnO samples with 1% Mn as sintered at 500 °C and annealed at various temperatures.

effects also have been observed in ZnMnO samples with higher Mn concentrations.

Kundaliya *et al.*[11] suggested that the high-temperature ferromagnetism in low-temperature-processed Mn–ZnO comes from an oxygen-vacancy-stabilized metastable phase, probably in the form of $Mn_{2-x}Zn_xO_{3-\delta}$. The XRD result of our low-temperature sintered sample [Fig. 1(a)] indicates the possibility of an Mn_2O_3-like phase. So, the metastable phase may be responsible for the observed ferromagnetism in our low-temperature sintered samples. After processing at high temperatures, the metastable phase transforms to a nonmagnetic phase, and the ferromagnetism is suppressed and finally disappears. The effect of the sintering atmosphere suggests a dependence of the stability of the metastable phase on oxygen concentration. Sintering in vacuum at low temperature favors formation of Mn_3O_4 phase coexisting with $Mn_{2-x}Zn_xO_{3-\delta}$ phase. Further, vacuum annealing would change the oxygen concentration in $Mn_{2-x}Zn_xO_{3-\delta}$ phase and hence weaken room-temperature ferromagnetism.

In summary, we have studied the dependence of magnetic properties in Mn-doped ZnO on sample processing conditions. The magnetic properties strongly depend on sample preparation and annealing. Room-temperature FM observed in low-temperature-sintered samples can be eliminated by high-temperature processing. Different magnetic properties reported earlier have been realized in our samples by carefully controlling the sample processing conditions. Our results help in understanding the controversies in the magnetic properties of Mn-doped ZnO reported earlier, and can be understood by considering a metastable ferromagnetic phase and its stability under varying temperatures and atmospheres.

ACKNOWLEDGMENT

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