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TEM Study of Mn-Doped ZnO Thin Films Synthesized by PLD

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The prediction of high-temperature ferromagnetism (FM) in ZnO-based diluted magnetic semiconductors has stimulated considerable research [1,2]. Both the existence and absence of FM have been reported in Mn-doped ZnO thin films. The recently observed FM in Mn-Zn-O bulk materials synthesized at a low-temperature of 500 ºC has been argued to arise from the presence of modified Mn oxides, instead of intrinsically from ZnO with Mn substituting for Zn [3]. The solubility of Mn in the low-temperature synthesized bulk ZnO is very low, and Mn oxides exist with as little as only 1% Mn doping [4]. It is believed that Mn has higher solubility in ZnO thin films grown by pulsed laser deposition (PLD). In this paper, we report a TEM study of the structure of Mn-doped ZnO thin films grown by PLD, with special attention given to examining the possible existence of manganese oxides or other impurity phases.

A series of samples, $Zn_{1-x}Mn_xO$ with x=0, 0.01, 0.03 and 0.05, have been synthesized and studied. Magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL) at room temperature as a function of the applied magnetic field. Fig. 1 shows the field dependence of magnetization curves of $Zn_{1-x}Mn_xO$ thin films with x=0.01, 0.03, and 0.05 at 300 K. The magnetization curves show hysteresis, with remanences and the coercivities very similar to the previous reported result [5], suggesting existence of ferromagnetic ordering at room temperature. Details of the synthesis and magnetic properties of the Mn-doped ZnO thin films will be reported elsewhere.

The film structures were studied by using TEM (Jeol JEM-2010, 200kV). Figure 2 shows the SAED patterns. The undoped and Mn-doped ZnO films show a preferred (001) orientation. As Mn concentration increases up to 3%, the (001) orientation deteriorates in some area of the films. No manganese oxides have been detected for samples, $Zn_{1-x}Mn_xO$ with x = 0.01 and 0.03 and a weak disconnected ring of the Mn_2O_3 (211) was observed in sample $Zn_{1-x}Mn_xO$ with x=0.05. The films were also studied by X-ray diffractometer (Riguka, D/Max-B, Cu K_α, λ=0.154 nm) and the ZnO (002) and (004) peaks are observed shifting slightly to lower angle as Mn concentration increases; however, the Mn_2O_3 phase was not detected in X-ray diffraction diagrams. HREM images were taken for further study to detect if there exist Mn oxides in the $Zn_{1-x}Mn_xO$ films with x =0.01 (and x=0.0 for comparison). Figure 3 is a HREM image of a $Zn_{1-x}Mn_xO$ thin film (x=0.01) with incident beam parallel to the normal of the film, which shows clean and sharp grain boundaries. In the enlarged image of a selected area, hexagonal arrangements of spots are clearly visible throughout the entire image, consistent with the hexagonal ZnO structure. No secondary phase aggregations are found in the grains and the grain boundaries.

In summary, TEM study of $Zn_{1-x}Mn_xO$ thin films with x=0, 0.01, 0.03 and 0.05 synthesized by PLD shows that Mn oxides or other impurity phases were not present in the $Zn_{1-x}Mn_xO$ thin films for x≤0.03. Thus ferromagnetism observed at room temperature in the ZnO thin films lightly doped Mn is not related to nanometer scale manganese oxides or other impurity phases.

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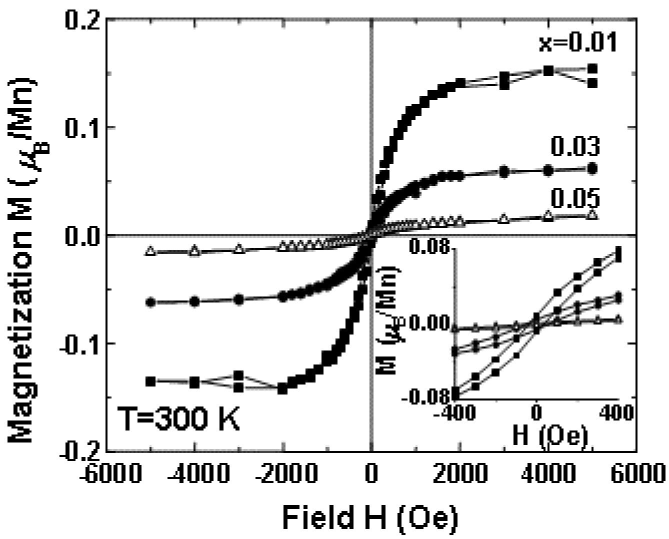

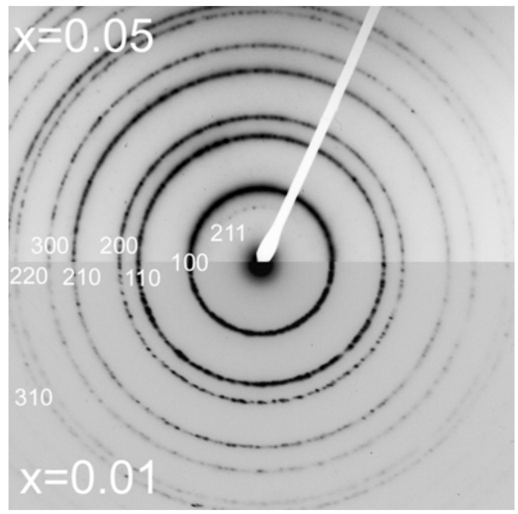

Figure 1 Magnetization curves of $Zn_{1-x}Mn_xO$ thin films at 300 K; the diamagnetic contribution from the Si substrate was subtracted. The insert shows the low-field data.

Figure 2 SAED patterns of $Zn_{1-x}Mn_xO$ thin films with x=0.01 (lower) and x=0.05 (upper).

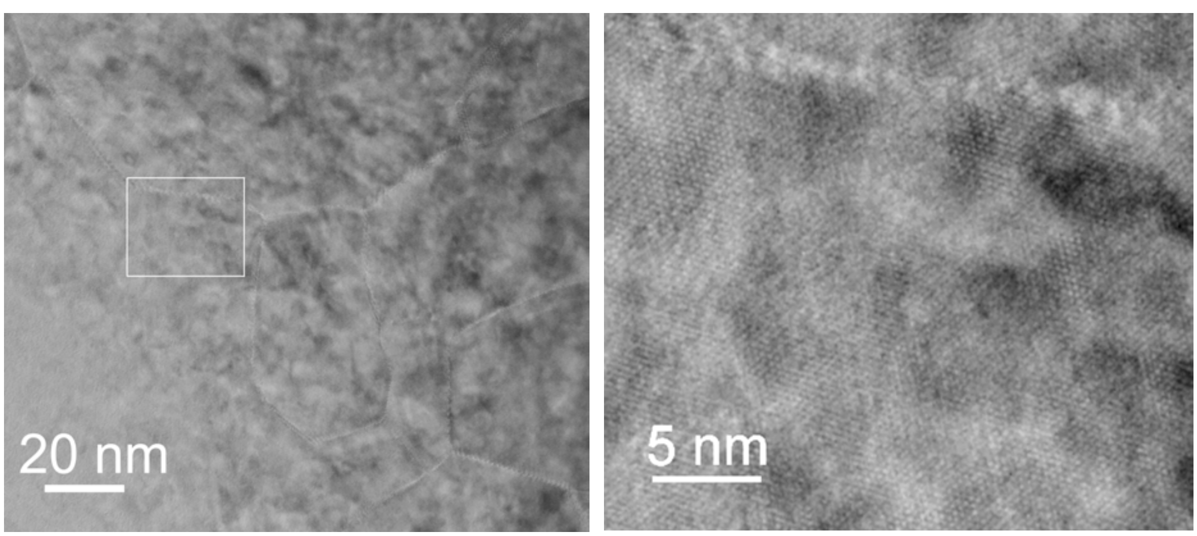

Figure 3 HREM image of a $Zn_{1-x}Mn_xO$ (x=0.01) thin film (left) and an enlarged image (right).

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