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Influence of post-annealing on the structure and optical properties of ferromagnetic $Zn_{1-x}Mn_xO$ film prepared by PECVD technique

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ABSTRACT

Room-temperature ferromagnetic Mn-doped ZnO films have been deposited on Si(0 0 1) substrates by plasma enhanced chemical vapor deposition technique. The microstructure, structure, optical and magnetic properties were investigated systematically. X-ray diffraction and transmission electron microscopy reveal that the all samples have a wurtzite polycrystalline structure and no secondary phase is found in films. Magnetization measurements indicate that $Zn_{1-x}Mn_xO$ films show room temperature ferromagnetism. In order to elucidate the origin of the ferromagnetism, $Zn_{1-x}Mn_xO$ films were annealed under different atmosphere. The results show that photoluminescence spectra are strongly dependent on defects in films and the interface between grains.

1. Introduction

Recently, ferromagnetic semiconductors have been paid much attention both in the areas of experiment and theory due to their potential application in spintronic device [1–8]. Among those promising candidates, wide band-gap ZnO-based materials are the object of increasing interest owing to its large exciton binding energy and excellent chemical/thermal stability [9]. So far, ZnO-based magnetic semiconductors by doping various transition metal ions such as Fe, Mn, Co and Cr have been fabricated by the methods of sputtering [10], laser ablation [11], sol–gel method combined with spin-coating [12] et al. The most study of such materials has been on the investigation of the defect-induced ferromagnetism in ZnO-based materials. However, it is equally important to have as well a fundamental study of the relationship between microstructure, optical and magnetic properties, because ZnO is generally considered as a promising candidate for opto-electric applications in the visible and the ultraviolet regions. In this work, ferromagnetic Mn-doped ZnO films at low deposition temperature were deposited on Si(0 0 1) substrates at low temperature [13]. The surface morphology and grain boundaries were modified by rapid thermal treatment and plasma annealing. The effect of annealing condition on magnetic and optical properties was investigated systematically.

2. Experimental procedure

Polycrystalline $Zn_{1-x}Mn_xO$ (x=0, 0.02, 0.04) films, represented as Sample A, Sample B and Sample C, were deposited on Si(0 0 1) single crystal substrates by PECVD techniques by using zinc 2, 4-pentandionate ($C_{10}H_{14}O_4Zn\cdot H_2O$) and manganese 2,4-pentandionate ($C_{15}H_{21}O_6Mn$) as vaporization sources. The growth process has been described in detail in previous work [13]. During the deposition, the substrates were kept at a temperature of 220 °C and the total growth pressure was maintained at 12 Pa. All possible organic remnants in as-prepared films were decomposed through thermal treatment in oxygen ambient at 600 °C. Artificial defects in films were induced by the process of rapid thermal processing in nitrogen ambience at 900 °C and annealing in NH_3/Ar plasma at 400 °C, respectively. The crystal structure and the phase formation were characterized by X-ray diffractometer techniques with CuKα radiation and transmission electron microscopy (TEM) with electron diffraction (SAED). Film surface morphology was characterized using scanning electron microscope (SEM) and atomic force microscopy (AFM). The thickness of

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the films was determined by spectroskopic ellipsometer, ranging from 500 to 600 nm. Magnetization measurements were performed using a commercial superconducting quantum interference device (SQUID). Photoluminescence spectra were recorded at room temperature by using a He–Cd laser of 325 nm as an excitation source. The electric properties were determined by standard four-point method.

3. Results and discussion

Fig. 1 showed typical X-ray diffraction patterns for the $Zn_{1-x}Mn_xO$ films after removing the substrate peaks. All of the diffraction peaks could be indexed to a hexagonal wurzite structure as ZnO and no diffraction peaks of second phase were found in thin films. As highlighted in the inset, the peak (0 0 2) of ZnO was found to shift slightly towards lower angle as Mn concentration increases and the corresponding expansion of the lattice parameter could be expected, because the ionic radius of Mn^{2+} ions (0.66 Å) was larger than that of Zn^{2+} ion (0.60 Å) [14]. The shifting of (0 0 2) peak confirmed that the Mn^{2+} ions would be incorporated into ZnO lattice. Fig. 2 showed the typical SEM micrographs and TEM analysis for Sample C and Sample C subsequently annealed in nitrogen ambience, denoted as Sample CC. Analysis from SEM and TEM measurements revealed the single phase feature of our sample and the intensive boundary-diffusion among grains during the process of annealing.

The effect of annealing effect on magnetic properties was studied. Fig. 3 showed the magnetization of $Zn_{1-x}Mn_xO$ films as a function of magnetic field (*M–H*). The applied magnetic field was

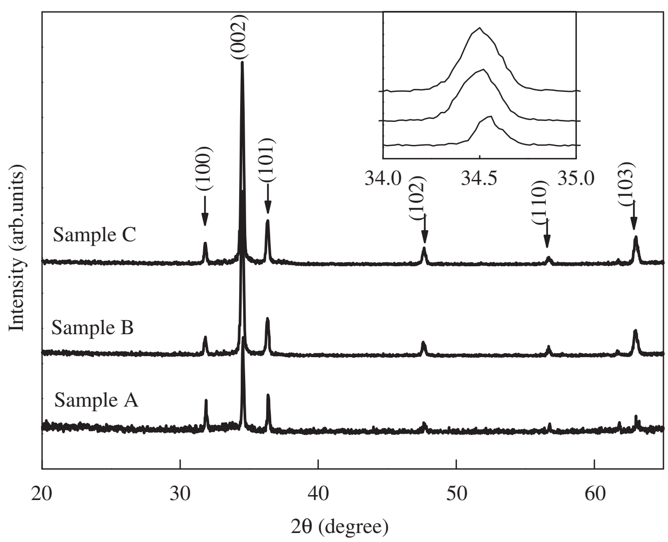

Fig. 1. Typical X-ray diffraction pattern of $Zn_{1-x}Mn_xO$ films deposited on Si(0 0 1) substrates, denoted as Samples pure, A, B and C. The inset reveals the dependence of (0 0 2) peak of ZnO shift on Mn concentration.

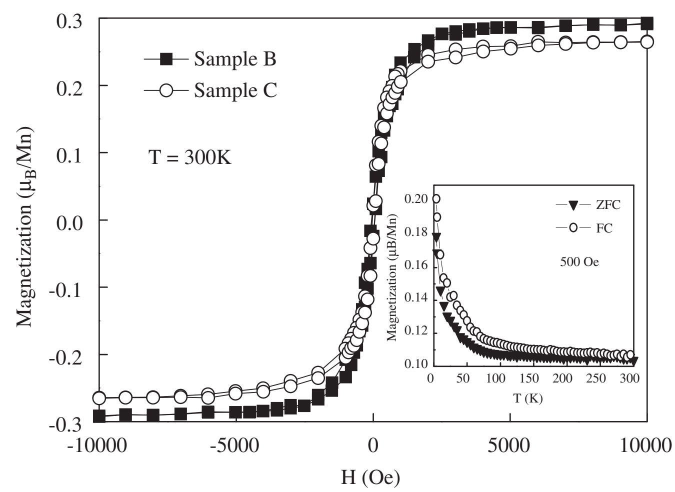

Fig. 3. An *M–H* loop at room temperature for $Zn_{1-x}Mn_xO$ films with the enlargement of hysteresis loops near the origin. Magnetic field was applied parallel to the film surface. Inset: the temperature-dependent magnetization *M*(*T*) of both zero-field cooled (ZFC) and field cooled (FC) of Sample C at 500 Oe.

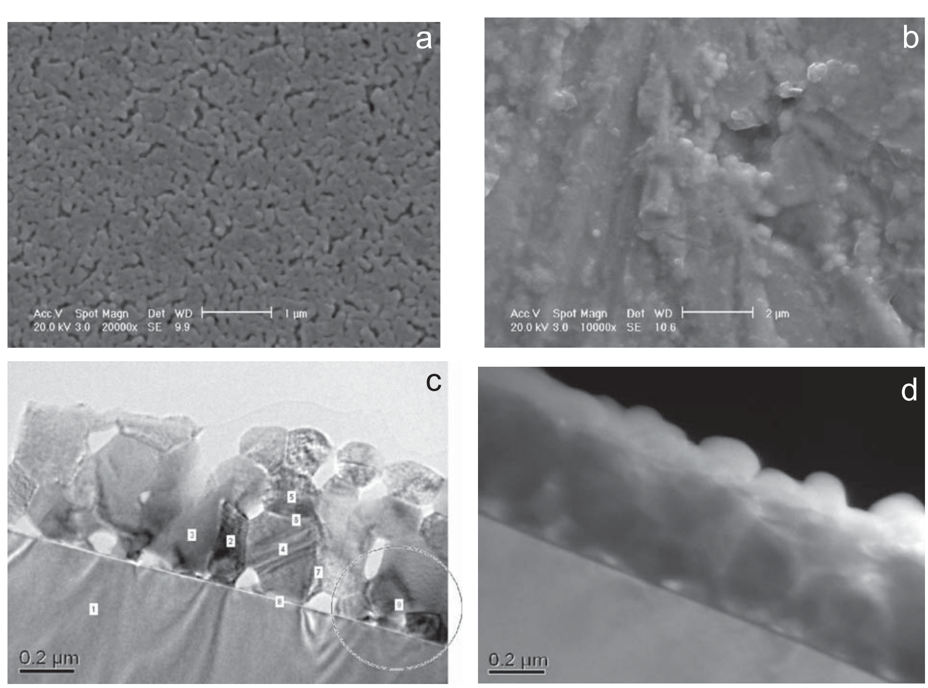

Fig. 2. (a) SEM image of Sample C; (b) SEM image of Sample CC; (c) TEM image of Sample C and (d) TEM image of Sample CC.