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Zinc defect enhanced saturation magnetization in Mn-doped ZnO thin films

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Abstract

Effect of manganese doping on the structural, optical and magnetic properties of $Zn_{1-x}Mn_xO$ thin films have been investigated systematically in this report. All of the films are highly c-axis-oriented wurtzite structures. No manganese metal or oxides were detected using x-ray diffraction or Raman spectroscopy. Photoluminescence spectra show that there are zinc vacancies in the undoped ZnO film, wherein a distinct paramagnetic response, as well as a weak ferromagnetic signal, persisted up to room temperature. The results suggest that ferromagnetism in the Mn-doped ZnO films can be rationalized in terms of an intrinsic zinc defect.

1. Introduction

Zinc oxide (ZnO) doped with a number of transition metal (TM) elements, such as Cr[1], Mn[2] and Co[3] has been intensively investigated as a promising oxide-based dilute magnetic semiconductor (DMS), wherein a spontaneous magnetization would persist to above room temperature (RT), for spintronic device applications[4] such as spin-polarized light-emitting diodes and lasers, spin field-effect transistors, and quantum computation.

While ferromagnetism (FM) has been frequently reported for many of ZnO-based DMSs, no consensus has been reached about the coupling mechanism or even the origin of magnetic moments. Some researchers argued that magnetic moments could stem solely from the intrinsic defects, such as V_O and V_{Zn},[5],[6] residing on surfaces or in grain boundaries of undoped ZnO films.[7] Much evidence has shown that defect-induced ferromagnetism is a universal feature of inorganic materials.[5],[8] To date, the actual effect of the TM dopant on the magnetic properties of TM-doped ZnO is unconfirmed. Thus far, experimental results on magnetism in ZnO-based DMS are still conflicting and controversial. For example, some researchers observed ferromagnetic behavior,[9] while others obtained paramagnetic results in Mn-doped ZnO.[10]

In order to clarify the role of the Mn dopant and to elucidate the possible origin of ferromagnetism, we have prepared $Zn_{1-x}Mn_xO$ ($0 \le x \le 0.023$) thin films by a magnetron co-sputtering method, and examined the structural, optical and magnetic properties by utilizing comprehensive and rigorous characterization techniques.

2. Experimental details

$Zn_{1-x}Mn_xO$ ($0 \le x \le 0.023$) thin films with thickness of about 500 nm were deposited on c-plane sapphire substrates at 500℃ by sputtering ZnO ceramic (99.99%) and/or Mn metallic (99.99%) targets in an ultra-high vacuum system at a pressure of ~25 mTorr. Ultra-pure (99.999%) Ar and N_2 gases were introduced at flow rates of 50 and 20 sccm, respectively, via two independent mass flow controllers. The crystal structure was examined by an x-ray diffractometer (XRD, PANalytical X'Pert PRO) with Cu Kα radiation (λ= 1.5406 Å). Raman spectra were recorded in the back-scattering configuration, using the MicroRaman spectrometer (HORIBA HR800) with an incident 633 nm He-Ne laser. Room temperature photoluminescence (RT-PL) spectra were recorded, exciting with the 325 nm-line of a He-Cd laser. Magnetic properties were probed by a commercial MPMS / SQUID / VSM dc magnetometer (Quantum Design).

3. Results and discussion

Figure 1(a) shows the XRD θ-2θ scans of $Zn_{1-x}Mn_xO$ thin films on a logarithmic scale. All the films were highly c-axis-oriented wurtzite structures, evidenced by the prominent ZnO (002) peak. No manganese metal or oxide phases were observed within the detection limit of XRD.

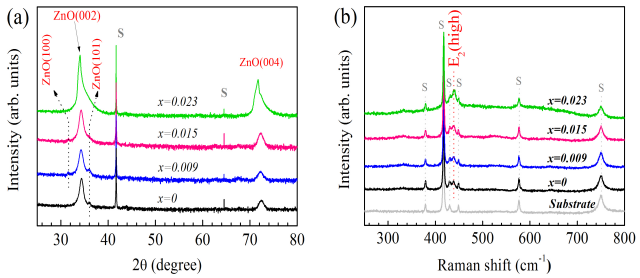

Fig. 1. (a) XRD θ-2θ scans of $Zn_{1-x}Mn_xO$ films. (b) Raman spectra of the $Zn_{1-x}Mn_xO$ films.

Figure 1(b) shows Raman spectra of the $Zn_{1-x}Mn_xO$ films. Only the E_2 (high) mode can be observed and no peaks related to manganese oxides can be detected in any of the films. In addition, the absence of the E_1 (LO) mode[11] suggests all of the films are nearly free from V_O, which is expected due to the addition of O_2 gas during film growth and in agreement with the following PL results.

Figure 2 displays the RT-PL spectra of the $Zn_{1-x}Mn_xO$ films. The undoped ZnO film exhibits a sharp near-band-edge (NBE) emission at 3.2 eV. The V_O-related emission (~ 2.4 eV)[12] is absent in all of the films. Howev-

er, there is an emission shoulder centered at 3.05 eV. Theoretical calculations have predicted that the V_{Zn} level is located 0.3 eV above the valence band.[13] This emission shoulder may be assigned to a transition from the conduction band to the V_{Zn} level. The result suggests that there is intrinsic V_{Zn} defect in the undoped ZnO film. The V_{Zn} will be demonstrated to be crucial to the observed FM. In addition, V_{Zn} has been detected by positron annihilation spectroscopy to be one of the main defects in ZnO films.[14] Theoretical calculations based on density functional theory (DFT) with generalized gradient approximation (GGA) have predicted that V_{Zn} may lead to ferromagnetism in ZnO films even without TM dopant.[15]

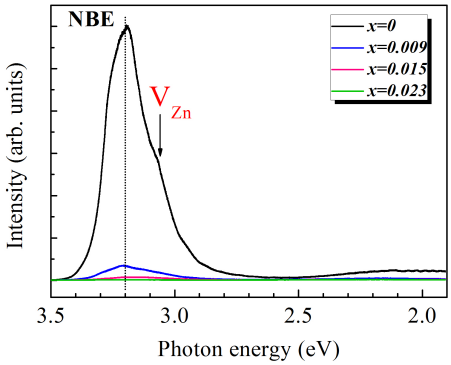

Fig. 2. RT-PL spectra of the $Zn_{1-x}Mn_xO$ films.

Figure 3(a) show M-H curves of all of the $Zn_{1-x}Mn_xO$ films at RT, where the diamagnetic contribution from sapphire substrate has been subtracted directly from the row data. Clearly, all the $Zn_{1-x}Mn_xO$ films show a dominant paramagnetic (PM) response. After subtracting the dominant PM response, we obtain weak FM signals for all of the $Zn_{1-x}Mn_xO$ films, as shown in Figure 3(b). The saturation magnetization (0.4 emu/cm^3) of the undoped ZnO film is comparable with that (0.5 emu/cm^3) of ZnO nanoparticles.[16] As already mentioned, the magnetic moments in undoped ZnO could stem from the V_O or V_{Zn}, residing on surfaces or in grain boundaries.

Using first-principles calculation, Wang *et al.*[15] have showed that ZnO with V_O is nonmagnetic but with V_{Zn} is magnetic. They also indicated that V_{Zn} prefer to cluster and reside on surfaces, and may introduce spin polarization of the top of valence band. From an energetic point of view, the magnetic moments arising from the unpaired 2*p* electrons at O sites surrounding V_{Zn} prefer to couple ferromagnetically, if neighbored. The PL results also suggest the existence of V_{Zn}, not V_O. Accordingly, the FM and PM contributions in the undoped ZnO film may stem from the clustered and isolated V_{Zn}, respectively, residing on surfaces or in grain boundaries. Since the ferromagnetic coupling is short-distance and weak, isolated V_{Zn} will display PM behavior. Noting that V_{Zn} prefer to cluster and reside on the surface region, rather than in the interior, of ZnO films, it is suggested that the Mn doping will modify the surface and grain boundaries of films, lessening the quantity of clustered V_{Zn}, and thereby lead to the much weak FM signal.

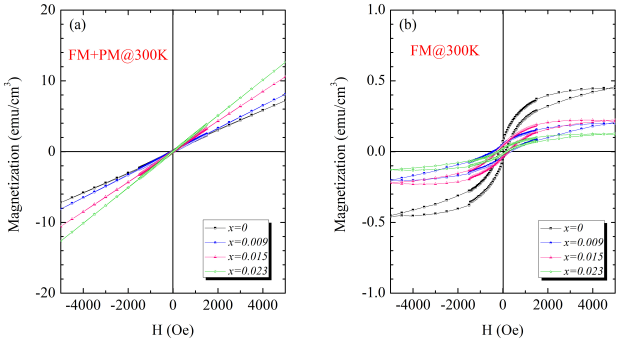

Fig. 3. (a) M-H curves of $Zn_{1-x}Mn_xO$ films at 300K. After subtracting the PM contribution for each curve, the hysteresis loops are displayed in (b).

4. Conclusions

All the films are highly c-axis oriented wurtzite structures and nearly free from V_O. No manganese oxide phases were observed within the detection limit of XRD and Raman spectra. The PL spectra show that there are zinc vacancies in the undoped ZnO film. We conclude that the ferromagnetism in $Zn_{1-x}Mn_xO$ films may be attributed to the intrinsic point defects.

Acknowledgements

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