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Enhancement of thermopower of Mn doped ZnO thin film

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Abstract

We have studied the thermopower of Mn doped ZnO thin films experimentally for various Mn concentrations in the films and a theoretical attempt was taken to gain an insight into the origin of the enhancement of thermopower due to unbalancing of up spin and down spin electrons in the conduction band due to unfilled d-orbital of Mn. Also hopping contribution caused by partially filled d-orbital of Mn was taken into account.

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Keywords: ZnO; Thermoelectric power; Mn doping; Theoretical modeling

1. Introduction

ZnO is a technologically important material due to its wide range of optical and electrical properties such as wide band gap, large excitonic binding energy, controllable electrical conductivity etc. These characteristics have made ZnO films very important for a huge range of applications such as in solar cells [1], surface acoustic waves [2], gas sensors [3], pressure sensors [4], antireflecting coating [5], transducers [6], luminescent materials [7], transparent conductors [8], heat mirrors [9], etc. The quest for diluted magnetic semiconductors (DMS) has recently attracted materials scientists, as, such semiconductors are quasi-indispensable in magneto- and spin electronics. This new field of semiconductor electronics controls and hence exploits the spin degree of freedom of the electron in addition to, or in place of, its charge for several applications. Researchers have traditionally diluted mostly conventional compound semiconductors with 3d transition metals (TM) to obtain DMS as a material for magneto- and spin electronics. The presence of TM ions in these materials leads to an exchange interaction between itinerant sp-band electrons or holes and the d-electron spins localized at the magnetic ions, resulting in versatile magnetic-field induced functionalities. For this purpose, magnetic ions, such as Co^{2+}, V^{2+}, Mn^{2+}, Cr^{2+}, Fe^{2+}, etc., should be substituted for some of the metallic atoms in the semiconductor lattice to produce a semiconductor that is ferromagnetic with a Curie temperature (T_C) above room temperature. After the prediction of room temperature ferromagnetism in Mn-doped ZnO by Dietl et al. [10], magnetic properties of Mn-doped ZnO have been investigated by many authors. Experimental studies give quite controversial results regarding magnetic properties of $Zn_{1-x}Mn_xO$, like ferromagnetism [11,12], antiferromagnetic coupling [13] or paramagnetism [14]. On the other hand, the thermoelectric effects provide a mean by which thermal energy can be converted into electricity and by which electricity can be used for refrigeration. Also understanding of the physical reasons for the change in thermoelectric properties due to TM doping in ZnO thin films has fundamental importance.

ZnO thin films have been prepared by many techniques like thermal evaporation [15], chemical vapor deposition [16,17], radio-frequency (RF) magnetron sputtering [18], spray pyrolysis [19], pulsed laser deposition [20], sol–gel–dip-coating [21], electro-deposition [22], etc. We have used direct current sputtering technique for the synthesis of ZnO

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thin films because of its simplicity and cost effectiveness. In this work we have studied the thermopower of Mn doped ZnO thin films experimentally for various Mn concentration in the films and a theoretical attempt was taken to gain an insight into the origin of the enhancement of thermopower due to unbalancing of spin up and spin down electron in the conduction band due to unfilled d-orbital and hopping contribution caused by unfilled d-orbital of Mn.

2. Experiment

2.1. Target preparation

Commercially available ZnO powder (99.99%) and Mn powder (99.99%) were taken at 1:x ($x = 0.01$, 0.03, 0.05, 0.07) atomic ratios and mixed thoroughly for 1 h. The mixtures were then pressed within different grooved aluminium holder of 4.5 cm diameter with a hydrostatic pressure (100 kgf cm^{-2}). These pellets were then used as the targets for sputtering and placed into the sputtering chamber by appropriate arrangements as the upper electrode. Negative terminal of the power supply was connected to the target and the lower electrode was kept at a ground potential.

2.2. Film deposition

The sputtering system consists of a conventional vacuum system, which was evacuated to 10^{-6} mbar by a rotary and diffusion pump arrangement. ZnO thin films were deposited on corning glass substrates. Argon was used as a sputtering gas. To remove surface contamination, if any, each target was pre-sputtered for 10 min. After that, the shutter was removed to expose the substrate in the sputtering plasma. Before placing into the sputtering chamber, the glass substrates were at first cleaned by mild soap solution, then washed thoroughly in deionized water and also in boiling water. Finally, they were ultrasonically cleaned in acetone for 15 min. The summary of deposition conditions is shown in Table 1. Therefore the films were deposited on glass substrates under the same sputtering condition with only change in Mn content in the target.

2.3. Characterization

The deposited films were characterized by X-ray diffraction (XRD, BRUKER D8 ADVANCE, by CuK_α radiation) measurements. Compositional analysis was performed by energy dispersive analysis of X-rays (EDX, JEOL JSM 6300 Oxford-7582). Electrical characterizations (thermo-electric) of the films were done by standard method from 300 to 450 K under vacuum condition (10^{-3} mbar). The thickness of the film was measured by cross-sectional scanning electron microscope (not shown here) and was found to be ~700 nm.

Table 1
Summary of deposition parameters

Electrode distance	1.8 cm
Sputtering voltage	2.6 kV
Substrate	Glass
Sputtering gas	Argon
Deposition pressure	0.2 mbar
Deposition time	2 h

3. Results and discussions

3.1. Structural property

Fig. 1 shows the XRD pattern of Mn doped ZnO thin films. All the three peaks (1 0 0), (1 0 1), (1 1 0) originate from hexagonal ZnO [23]. Similar pattern was observed by Roy et al. [24]. Also no peaks corresponding to doping materials, e.g., of Mn or its oxides were found in the pattern. This conclusively indicates that Mn^{2+} is present in the film as dopant.

EDX spectrum for a 5% Mn doped ZnO sample is shown in Fig. 2. Compositional analysis clearly confirmed that Mn was present in the film and concentrations were very close to that of the nominal composition of the target material. Mn concentrations in the target material and in the film, obtained from EDX are listed in Table 2.

Fig. 3 shows Mn^{2+} content dependence of the lattice constant of the deposited ZnO film as obtained from XRD data. Both the a- and c-axes lengths expand monotonously with Mn^{2+} content. Increments of lattice constants are due to larger ionic radius of Mn^{2+} (0.66 A) than Zn^{2+} (0.60 A) [25]. The modified lattice constant may be calculated upto a first-order approximation by Vegard's

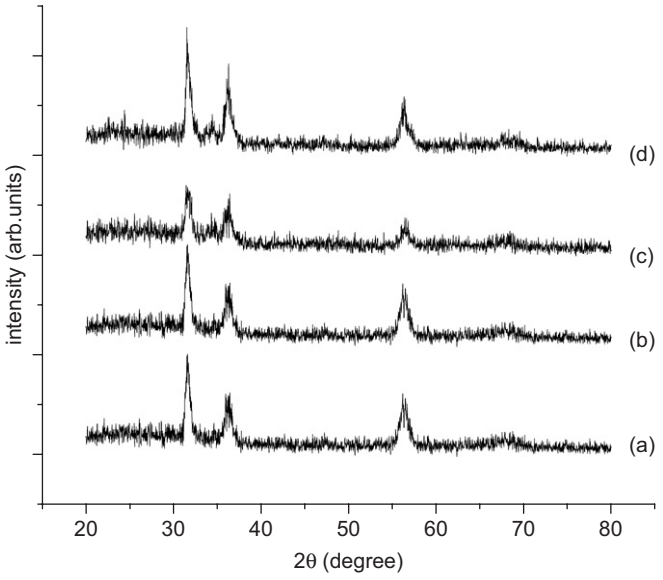

Fig. 1. XRD pattern of $Zn_{1-x}Mn_xO$ thin film deposited on glass substrate for (a) $x = 0.01$, (b) $x = 0.03$, (c) $x = 0.05$ and (d) $x = 0.07$. The curves have been vertically shifted to improve clarity.