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Room temperature ferromagnetism in combustion synthesized nanocrystalline Co, Al co-doped ZnO

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ABSTRACT

Pure and Co, Al co-doped ZnO($Zn_{1-x-y}Co_xAl_yO$; $x = 0.04, 0.03, 0.02$; $y = 0.01, 0.02, 0.03$) nanoparticles were synthesized by wet chemical combustion method at 500 °C for various doping levels using zinc, cobalt and aluminium nitrates as precursors. The synthesized powders were calcined at 600 °C and sintered at 1000 °C after uni-axial compaction. Structure, morphology and the presence of magnetism in combusted and sintered materials of pure and doped ZnO were examined. At room temperature, both the calcined nanoparticles and sintered compacts of pure ZnO exhibited paramagnetism. But, ferromagnetism was observed for Co and Al co-doped ZnO (diluted magnetic semiconductor) nanoparticles calcined at 600 °C. Also, it was found that the ferromagnetism increased correspondingly for the calcined particles with Co concentration. Whereas, a strong paramagnetic behavior was observed for the sintered compacts of various concentrations of Co and Al dopants due to grain growth.

1. Introduction

Recently, there has been a considerable interest in development of room temperature ferromagnetic semiconductors so called diluted magnetic semiconductors (DMS) which are used for spintronics and magneto-electronic application due to its high Curie temperature above 300 K as predicted by theoretical calculations [1]. Diluted magnetic semiconductors provide the capability of binary control of charge and spin simultaneously, which has been considered for future semiconductor spintronics. The utilize of both carrier–spin and charge appears promising for a new class of devices such as polarized light emitters, chips that integrate memory and microprocessor functions, magnetic devices exhibiting gain and ultra-low power transistors [2–6]. Also, the carrier–spin in metallic multilayers forms the basis of hard-drives in information storage. The control of spin dependent phenomena in electronic oxides or conventional semiconductors is used in devices such as light emitting diode (LED), field effect transistor (FET) and Q-bits for quantum computers. A key requirement in realizing most devices based on spins in solids is that the host material to be ferromagnetic at room temperature. In addition, it is also necessary to have both efficient spin-polarized carrier injection and charge transport. The theoretical predictions of magnetic ordering obtained for 5 mol% of Mn doped GaN, diamond and ZnO at above room temperature, is a major breakthrough in this field [1,7]. For spintronics, it suggests that the room temperature carrier-mediated ferromagnetism should be possible in ZnO albeit a *p*-type material which has proven difficult until recently. Earlier, calculations do predict the existence of ferromagnetism in *n*-type ZnO doped with transition metal ions including Co and Cr doped ZnO [8], and several researchers have been reported the presence of ferromagnetism in transition metal-doped ZnO [9–19]. Incorporation of selective elements such as Al and Co in ZnO tenders an effective way to alter their optical, electrical and magnetic properties. The Al doping in ZnO can improve its conductivity without impairing the optical transmission, which is considered as best candidate material for optoelectronics [3,20]. In this work, the difference in magnetic properties of the combustion synthesized pure and Co, Al co-doped ZnO nanoparticles and their sintered compacts were studied and reported.

2. Experimental

Nanocrystalline pure and co-doped ZnO ($Zn_{0.95}Co_{0.04}Al_{0.01}O$, $Zn_{0.95}Co_{0.03}Al_{0.02}O$ and $Zn_{0.95}Co_{0.02}Al_{0.03}O$) were obtained by combustion method using an aqueous solution of Zn, Co, Al nitrates precursors with citric acid (fuel). The homogeneously mixed precursor solution was combusted at 500 °C in a time span of <10 min to yield a porous solid foam contains nanoparticles. The as-combusted foams were collected and converted into powders by gentle grinding. The as-prepared powders were calcined at 600 °C for 2 h (at a heating rate of 5 °C/min) in order to get complete crystalline powders. The calcined powders were uni-axially pressed into

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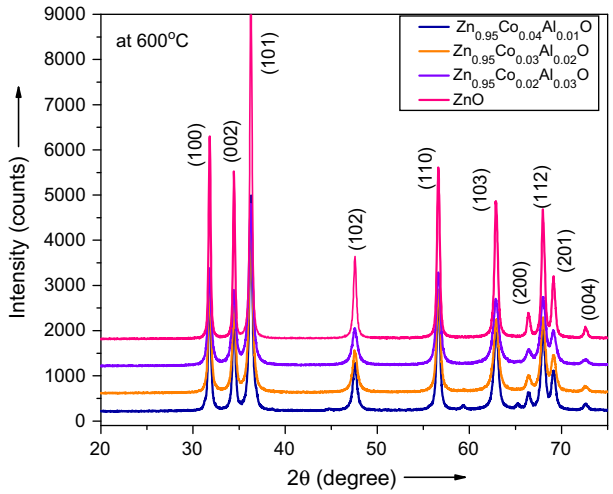

Fig. 1a. X-ray diffraction spectra of pure and doped ZnO nanoparticles calcined at 600 °C.

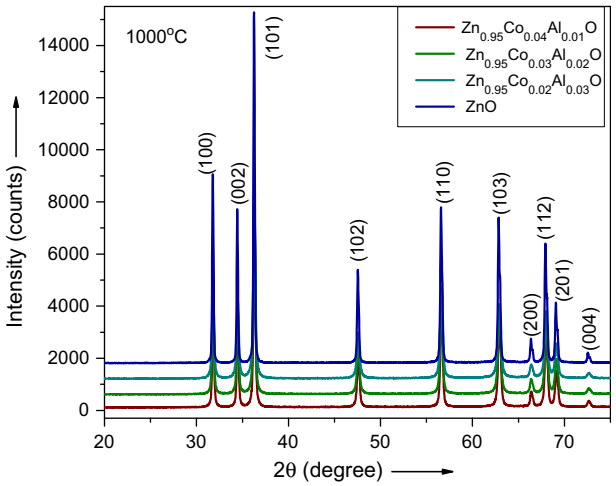

Fig. 1b. X-ray diffraction spectra of pure and doped ZnO compacts sintered at 1000 °C.

cylindrical discs of thickness $t = 2$ mm and diameter $D = 7$ mm, and subsequently sintered at 1000 °C for 2 h. The calcined nanopowders and the sintered compacts were subjected to X-ray diffraction using (Siemens D5000 diffractometer) Cu Kα radiation, operating at 40 kV, 20 mA, with graphite monochromator. The 2θ step size was 0.02° with step time of 1 s over the 2θ scan range 20–80°. The particles morphologies were examined using scanning electron microscope (SEM-JEOL 6460 LV) and transmission electron microscope (TEM-JEOL JEM 2000 EX) equipped with EDS. The room temperature magnetic behavior of the calcined powders and sintered ZnO were characterized using a physical properties measurement system (PPMS, Quantum Design) in vibrating sample magnetometer (VSM) mode.

3. Results and discussion

Figs. 1a and 1b shows the X-ray diffraction patterns of calcined and sintered Co, Al co-doped ZnO. The XRD pattern was analyzed and indexed using X'Pert highScore software. The diffraction patterns reflect the single phase wurtzite structure of ZnO. It is obvious that the calcined and sintered ZnO of all the dopant combinations have the same crystalline structure with intensity variations. There are no traces of Co and Al oxides, any binary zinc–cobalt or zinc–aluminium and ternary zinc–cobalt–aluminium phases have been observed. Therefore, it substantiates that the Co and Al doping in ZnO is substitutional impurity, which is regarded as single phase formation.

The morphologies of the as-prepared and calcined (600 °C) nanoparticles are shown by the SEM micrographs in Fig. 2a and b. Large particle aggregates composed of small crystallites with spherical shapes are observed. In order to see the insight morphology of the nanoparticles, TEM microscopic analyses were performed. The TEM micrographs in Fig. 3a and b exhibit the particle size and shape of the Co and Al co-doped ZnO. The powders calcined at 600 °C (Fig. 3b) shows the spherical particles of size about 25 nm with uniform distribution. The defects and cluster nature were minimized by calcination.

The presence of impurity element in pure and doped ZnO was confirmed by performing TEM-attached energy dispersive X-ray spectroscopy (EDS) as shown in Fig. 4. In Fig. 4a, it can be clearly seen that the peaks are corresponding to Zn and O excluding the presence of any impurity element in pure ZnO. Whereas in Fig. 4b, the peaks ascribed to Zn, Co, Al and O were detected for the Co and Al co-doped ZnO. Peaks corresponding to Cu and C were also detected from the carbon coated copper grid. It is also confirmed by SEM attached EDS in Fig. 2a and b. The selective area electron diffraction (SAED) patterns obtained on Co, Al co-doped ZnO particles clearly indicate the crystalline nature of each sample.

Magnetic hysteresis measurements of the pure and Co, Al co-doped ZnO were performed at room temperature (300 K). Since the diluted magnetic semiconducting materials exhibit weaker magnetization, the diamagnetic nature of the sample holder was tested and confirmed without samples. The M-H curves were determined for nanoparticles calcined at 600 °C and the compacts sintered at 1000 °C. It is well known that the bulk ZnO exhibits diamagnetism [21,22]. Nevertheless, ferromagnetism has been observed in ZnO nanostructures due to existence of defects which are always considered to be responsible for the magnetism [23–26]. The field dependent magnetization curves for pure ZnO powder calcined at 600 °C shows a very low paramagnetic behavior. It is observed that there is a small hysteresis behavior of ZnO at near field $H = 0$ as shown in Fig. 5. The detected value is within the sensitivity range of the measuring apparatus. Also, the sintered pure ZnO shows a diamagnetic behavior. When it is closely observed near $H = 0$, there is an anomalous diamagnetic response which may due to the point defects in ZnO. The defects such as O and Zn vacancies and interstitials are considered to be responsible for

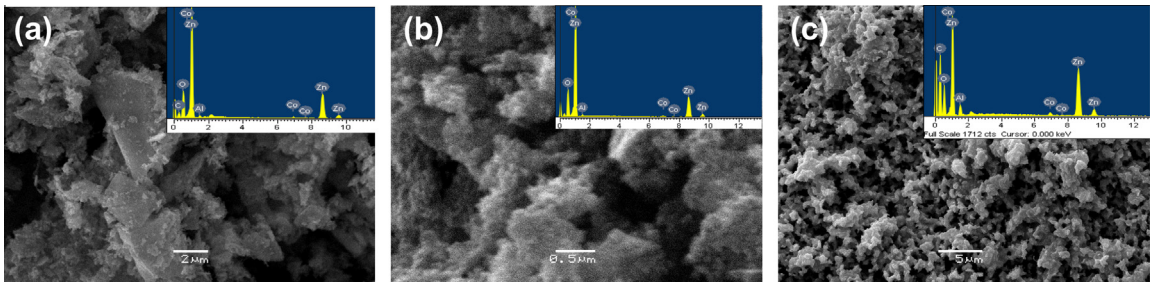

Fig. 2. SEM micrographs of (a) synthesized, (b) calcined at 600 °C and (c) sintered at 1000 °C ($Zn_{0.95}Co_{0.04}Al_{0.01}O$) nanoparticles.