Synthesis and structural, magnetic characterization of nanocrystalline $Zn_{1-x}Mn_xO$ diluted magnetic semiconductors (DMSs) synthesized by combustion reaction

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Abstract

Nanocrystalline Mn^{2+} doped $Zn_{1-x}Mn_xO$, where $x=0.1, 0.15, 0.2, 0.25, 0.3$ and 0.4 mol of Mn^{2+} diluted magnetic semiconductors (DMSs), were synthesized by the combustion reaction for spintronic applications. The effect of Mn^{2+} ion doping on the structural, morphological and magnetic properties of ZnO was investigated. The products of the reactions were characterized by X-ray diffraction (XRD), nitrogen adsorption (BET), transmission electron microscopy (TEM), and magnetic measurements (VSM). XRD spectra data revealed the formation of a ZnO phase at all the Mn^{2+} doping concentrations used, indicating that the synthesis was efficient in diluting the Mn^{2+} ions in the ZnO lattice. Increasing the Mn^{2+} ion concentrations reduced the maximum reaction and ignition temperature and contributed to reduce crystallite and particle sizes. The samples showed the typical behavior of soft magnetic materials at all the Mn^{2+} concentrations evaluated here. The Curie temperature (Tc) was higher than room temperature at all the Mn^{2+} concentrations.
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1. Introduction

Diluted magnetic semiconductors (DMSs) based on ZnO-doped transition metal have been studied extensively for the spintronic applications in order to obtain the desired magnetic properties and thereby optimize the performance of microprocessors, which are the basis of semiconductors [1]. The creation of semiconductor devices allied to suitable magnetic properties can increase the processing speed and data storage [2]. Considerable progress has been achieved in the production and development of diluted magnetic semiconductors. New materials, conditions and different synthesis techniques, types of substrate and dopants are used to engineer the semiconductors.

The semiconductor groups most commonly used for the production of DMSs are III−V type (GaAs, InAs, and SCN),

II–VI type (CdTe, ZnO, ZnS, ZnTe), IV–VI type (TiO_2 SnO_2) and/or group IV (Si, Sn, Ge) semiconductors doped with transition metals (Sc, Ti, Cr, Mn, Co, Fe, Ni, Cu) [3]. Among these groups, ZnO is known to be an excellent matrix for doping with magnetic ions, due to its wide range of applications in electronic devices and low cost processing, and its high energy discontinuity (wide band gap=3.37 eV) [4,5].

The interest in ZnO for the development of these DMSs stems from the theoretical work of Dietl et al. [6], who produced material with ferromagnetic behavior above room temperature using ZnO doped with 0.05 mol of Mn^{2+} with electron or hole concentrations (3.5×10^{20} cm^{-3}). Dietl et al.'s studies inspired numerous subsequent studies of ZnO to obtain DMSs for spintronic applications.

Several studies conducted in recent years about ZnO arrays doped with Mn^{2+} ions and some of them stand out such as: (i) the work of Dietl et al. [6], which describes the ferromagnetism model based on the Zener model of semiconductor switches

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with the crystal structure, zincblende, with a Mn^{2+} concentration of 5% mol. Based on the description of this model, the authors also used it for Group II–VI semiconductors that include ZnO. (ii) ZnO doped with 5% mol of Mn^{2+} with ferromagnetic characteristics prepared by solvothermal synthesis [7]. (iii) Mera et al. [8] demonstrated the room temperature ferromagnetism behavior of ZnO doped with 0.02–0.1 mol of Mn^{2+} thin film synthesized by pulsed-laser deposition (PLD). Lastly, (iv) Ilyas et al. [9] obtained ZnO doped with Mn by the centrifugation coating technique on Si substrate, with Mn^{2+} concentrations ranging from 0.02 to 0.05 mol, indicating the formation of single phase with ferromagnetism at room temperature.

By considering the above facts, it appears that the majority of studies report preliminary results of different chemical synthesis techniques to obtain DMSs based on ZnO doped with Mn^{2+} transition metal. However, in the present study we chose the combustion reaction technique to prepared $Zn_{1-x}Mn_xO$. The motivation of using the combustion reaction is the fact that it is a technique that produces crystalline ceramic materials, very thin and homogeneous, and thus a very promising process. Further, this method enabling the production of products for the use in advanced ceramics, such as catalysts, composites, superconductors, dielectrics, semiconductors and nanomaterials in general. The process of combustion reaction is characterized by high temperature, rapid heating rate and short reaction time. [10]. The process is based on the principle that an exothermic reaction initiated by an external source which occurs very quickly, making it self-sustaining and rapidly generating a final product (oxide) [10,11]. These characteristics make it an attractive method for the fabrication of useful materials at lower costs than those of conventional ceramic processes [11].

In view of the above, this paper reports on the combustion reaction synthesis of nanocrystalline Mn^{2+} doped $Zn_{1-x}Mn_xO$, where $x = 0.1$, 0.15, 0.2, 0.25, 0.3 and 0.4 mol of Mn^{2+} for diluted magnetic semiconductors for potential spintronic applications. The effect of Mn^{2+} ion doping on the structural, morphological and magnetic properties of ZnO were investigated in the present study.

2. Experimental

Precursors with 98% p.a. purity of manganese nitrate hexahydrate – $Mn(NO_3)_2.6\,H_2O$, zinc nitrate hexahydrate – $Zn(NO_3)_2.6\,H_2O$ and urea – $CO(NH_2)_2$ were used as a staring materials for preparing the samples of the $Zn_{1-x}Mn_xO$ systems by combustion reaction. For the synthesis, the mixtures' stoichiometry was defined based on the total valence of oxidizing (nitrates) and reducing (urea) reagents, according to the theory of propellants and explosives [12]. The redox mixture was placed in a vitreous silica crucible with a capacity of 200 mL, which was placed directly on a ceramic heater plate with electrical resistance (resistance temperature of approximately 873 K) and heated until it reached self-ignition (combustion). The product of the reaction (porous flakes) was then oven-dried at a temperature of 773 K/ 5 min, after which it was deagglomerated by sifting through a 325 mesh sieve (45 μm) and the finally characterized.

The combustion reaction temperature was determined online using an infrared pyrometer (Raytek 3i series ± 2 °C). The reaction temperature was determined at 5-s intervals between each online measurement. The pyrometer has a temperature reading accuracy of 523 K to 1973 K and automatically records the maximum temperature reached. The flame time was determined using a TECHNOS digital timer.

The samples were characterized by X-ray diffraction using a Shimadzu 6000 diffractometer, with 2θ scanning in the range of 20–80° with CuKα radiation ($\lambda = 1.5418$ Å). The Shimadzu PMgr software program and JCPDS database were used to identify the phases. The average crystallite size (t) was estimated from the X-ray diffraction (d_{311}) data using Scherrer's equation while considering the full width at half maximum (FWHM) of the diffraction peaks [13]. The gas adsorption method developed by Brunauer, Emmett and Teller (BET) was used to determine the specific surface area of the systems, using a NOVA 3200 surface area analyzer. The particle size (equivalent spherical diameter) was also determined by this technique, while particle sphericity was determined through the following equation:

$$D_{BET} = 6/S_{BET}.\rho \qquad (1)$$

where D_{BET} is the equivalent average diameter (nm), S_{BET} is the surface area determined by BET (m²/g), and ρ is the theoretical density (g/cm³) of ZnO given by the JCPDS Card No. 89–1397 ($\rho = 5.657$ g/cm³).

The size and morphology of the particles and/or clusters were analyzed by transmission electron microscopy (TEM, Philips EM420, operating at 120 kV). Samples of the different systems were dispersed in isopropyl alcohol and deagglomerated by ultrasound. One drop of suspension was diluted and deposited on a copper screen coated with a polymeric film (FORMVAR), which was dried at room temperature for 24 h, followed by carbon deposition. Bright field images were recorded, and structural information was obtained from the diffraction patterns and compared with the X-ray diffractions.

Magnetic measurements were taken with an EG & G model 4500 vibrating sample magnetometer (VSM). The hysteresis loop was obtained at room temperature (300 K) with the maximum magnetic field of 7 kOe and a scanning magnetic field of 5 Oe/s. The Curie temperature was measured by the Laoria technique, which is versatile and simple for measuring the Curie temperature of magnetic materials through electromagnets, and a thermocouple.

3. Results and discussion

Fig. 1 shows the variation in temperature as a function of reaction time for the nanocrystalline Mn^{2+} doped $Zn_{1-x}Mn_xO$, where $x = 0.1$, 0.15, 0.2, 0.25, 0.3 and 0.4 mol of Mn^{2+}. In the experiments, the formation of yellow flame was observed during the reactions. However, this happened within few seconds that it was impossible to measure the flame time with a digital timer. The temperature graphs as a function of reaction time indicate that the temperatures in all the reactions varied very slightly. It is observed that, Mn^{2+} concentrations of $x = 0.1$ and 0.4 mol