Journal of Alloys and Compounds 691 (2017) 739–749

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Tailoring of room temperature ferromagnetism and electrical properties in ZnO by Co (3d) and Gd (4f) element co-doping

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ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form
30 June 2016
Accepted 27 August 2016
Available online 30 August 2016

Keywords:
Burstein-Moss effect
Space charge polarization
Dipolar orientation polarization
Magnetic properties
Bound magnetic polaron

ABSTRACT

Nanoparticles of Co^{2+} and Gd^{3+} ions co-doped Zinc oxide were prepared by co-precipitation process followed by hydrothermal method. To obtain the desired crystallographic phase and also, to enhance the Oxygen vacancy, the as prepared sample was sintered at 400 °C in vaccum atmosphere. The presence of intrinsic defects and internal stress in the lattice structure of co-doped ZnO has been substantiated by the detail analysis of X-ray diffractograms. Different optical characterizations like Raman spectroscopy and photoluminescence (PL) spectra have been measured. The presence of defects/Oxygen vacancies are also critically analyzed by Raman and PL spectra of co-doped ZnO sample. Magnetic measurement such as magnetization as a function of magnetic field at different low temperatures (300-10 K) and magnetization as a function of temperature (field cooled and zero-field cooled) are measured by SQUID magnetometer. Interestingly, a very strong magnetic interaction and a large value of coercivity even at room temperature have been observed in the co-doped ZnO nanoparticles compared to the mono-doped ZnO nanoparticles. The presence of ferromagnetic ordering and large coercivity were successfully explained by the vacancy assisted bound-magnetic-polaron model and domain wall blowing theory. Negative exchange biased has been observed in our sample implies the formation and exchange interaction at the interface of FM/AFM bilayers. Dielectric measurement suggest that for both 5% Co^{2+} and Gd^{3+} ions co-doped ZnO system, the enhanced dielectric data is the contribution of large amount of space charge polarization and the intrinsic defects in the sample. Enhancement of the ac conductivity with the increase of temperature reveals the semiconducting nature of the co-doped ZnO systems.

1. Introduction

ZnO with a wide band gap (3.37 eV) and large excitonic binding energy (60 meV) at room temperature has drawn a great deal of interest in the field of optical and electronic applications due to its attractive properties such as, tunable band gap, high transmittance in visible region, thermal and chemical stability etc. It is one of the most promising semiconducting host material for DMS system in which electronic charge and spin degrees of freedom are controlled to fabricate spintronic devices such as spin-valve transistor, spin light emitting diode, non-volatile memory, optical isolator, ultrafast optical switches etc. But for innovative magneto-optical applications, room temperature diamagnetic and paramagnetic behaviors are the main drawbacks for pure ZnO system. In recent times some vacancy mediated room temperature ferromagnetism (RTFM) has been reported in different articles [1–3] though the magnetization value is too low from application point of view. So this pressing needs for improving RTFM in ZnO has opened up a new area of research in which host Zn atom from wurtzite structure is replaced intentionally by transition metal (TM) and rare earth element (REE) magnetic atoms. Most of the authors have predicted that the cause behind the RTFM in TM doped ZnO is d-d exchange coupling amongst non-localized and exterior 3d electron of TM atom [4–6]. But due to non-localization of 3d electron in TM ions, orbital momentum is often zero. It has been reported that simultaneous doping of two TMs can fairly increase the saturation magnetization in ZnO system [7]. But compare to TM ions the rare earth (RE) ions doping may offer even stronger magnetism, since localized 4f electron execute indirect exchange interaction via 5d or 6s conduction electrons and that results in high value of magnetic

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http://dx.doi.org/10.1016/j.jallcom.2016.08.287
0925-8388/

moments per atom [8]. The REE ions such as Gd, Er and Nd doped DMS systems have invoked great research interest as Gd ion doped GaN exhibits a colossal magnetic moment [9–11]. Recently J. Das et al. [12] has reported the paramagnetic behavior of rare earth co-doping (Gd/Sm) over Mn^{2+} ions doped ZnO system and they concluded that inspite of their high magnetic moment per atom, additional doping of rare earth atom along with transition metal does not contribute towards the enhancement of the RTFM ordering in ZnO bulk ceramics. This negative results mainly due to the antiferromagnetic contribution of secondary phase of REE oxide as well as TM oxide. Origin of FM in Gd:ZnO may be due to the formation of Oxygen vacancy that has been reported by many research groups [13]. This kind of defects enhance s-f coupling by shifting Fermi level towards conduction band to form spin split state which may be considered as the strong reason for the presence of ferromagnetism in the system. Ferromagnetic response with high T_c has already been reported by Kittilstved et al. [14] in Co:ZnO due to donor bound carrier formation by shallow donor interstitial Zinc (Zn_i). This impurity band hybridized with unoccupied d-level of magnetic impurity ions. Many research groups predicted that this shallow donor and native double donor Oxygen vacancy causes FM coupling among Co-cations. Controlled aggregation of Co magnetic ion when co-doped with Eu ion in ZnO structure has been experimentally demonstrated by J. J. Lee et al. [15] and they have shown its validation by first-principle calculation based on DFT which has been encouraged many researchers in field of TM and REE ions co-doped ZnO based DMS system. But there are some limitations such as RE element atoms having large ionic radii (0.86–1.01 Å) compared to Zn, it has a restriction to the solubility limit on to ZnO wurtzite lattice structure. Therefore synthesis process and stoichiometric ratio of TM and REE ions co-doped nanocomposite is very sensitive to avoid the secondary phase of dopant magnetic element atom. In the present work we have investigate the effect of Gd^{3+} (4f) and Co^{2+} (3d) ions on the microstructure, optical, magnetic and electrical properties of ZnO nanoparticles.

2. Experimental details

2.1. Materials and methods

Various compositions of $Zn_{0.95-x}Co_xGd_{0.05}O$ (x = 0.03, 0.05 and 0.07) were prepared by the hydrothermal method. Zinc acetate dehydrate $Zn(O_2CCH_3)_2\cdot 2H_2O$ (Sigma Aldrich, 99%), Cobalt acetate tetrahydrate $Co(O_2CCH_3)_2\cdot 4H_2O$, Gadolinium nitrate hexahydrate $Gd(NO_3)_3\cdot 6H_2O$ (Sigma Aldrich, 99%) and Ammonium hydroxide NH_4OH (concentration ~ 25%) were used as the precursor materials and without any further purification. Co^{2+} and Gd^{3+} ions co-doped ZnO nanoparticles were first prepared by simple co-precipitation method. All the constituents were dissolved separately in milli-Q water (resistivity value 16–17 MΩ cm @ 25 °C, Heal force ASTM Type-I Easy Series model) with proper stoichiometric ratio using magnetic stirrer. Then solution of doping element was mixed with Zinc acetate solution dropwise under vigorous stirring condition to make a uniform distribution of ions. After that NH_4OH solution was added in the salt solution for co-precipitation and the final pH of the solution was kept at ~9. Stirring was continued for 3 h at room temperature for complete reaction. After the completion of stirring, the co-precipitated particles were collected properly for washing and it has been done several times by using milli-Q water and ethyl alcohol to neutralize the pH of the solution as well as to remove the extra ions. Washed precipitates were dissolved in milli-Q water and it was transferred to a Teflon linked autoclave which was placed in an oven at 160 °C for 48 h. In the hydrothermal technique the nucleation of the ZnO nanoparticles inside the Teflon jacket was performed under the effect of high pressure and temperature which favours surface growth of ZnO nanoparticles. After 48 h the solid precipitates at the bottom of the Teflon jacket were collected, washed and dried in a vaccum desiccator at room temperature. Finally, dried powders of different Co concentrations were sintered at 400 °C temperatures in vaccum atmosphere and named as CG35, CG55 and CG75 for x = 0.03, 0.05, 0.07 respectively in composition of $Zn_{0.95-x}Co_xGd_{0.05}O$. This posterior thermal treatment of all the samples at 400 °C is essentially required to eliminate unreacted precursor waste and to achieve better crystallographic phase.

2.2. Characterization techniques

The XRD of all the samples were recorded in powder X-ray diffractometer, Model D8, BRUKER AXS, using Cu K_α radiation (λ = 1.5405 Å) in the range of 2θ from 20 to 80 °C. The Energy dispersive spectroscopy was obtained using EDS attachment with INSPECT F50 (FEI, Netherland). The RT Raman spectroscopy study was employed by using Newport RS 2000TM. The photoluminescence spectroscopy study was done by using a spectroflurometer, Perkin Elmer, Germany with an excitation wavelength (λ_{ex}) of 300 nm. Magnetization vs. applied magnetic field (M-H) data of all the samples at RT and at low temperatures were recorded by using SQUID magnetometer (MPMS XL 7, Quantum Design), where the maximum applied field was 50 kOe. Electrical conduction mechanism was investigated from dielectric measurement using Agilent 4294A Precision Impedance Analyzer.

3. Result and discussion

3.1. XRD analysis

XRD patterns of different $Zn_{0.95-x}Co_xGd_{0.05}O$ (x = 0.03, 0.05, 0.07) nanostructures have been given in Fig. 1(A). It is clear from the XRD pattern that the simultaneously doping of both Co^{2+} and Gd^{3+} ions even upto 5% (CG55) does not changes ZnO wurtzite structure which consists of alternating planes of tetrahedrally coordinated O^{2-} and Zn^{2+} ions stacked along the c-axis. It is to be mentioned here that no secondary phase impurity has been developed in diffraction pattern and all the peaks of the diffraction pattern are duly assigned with the help of JCPDS (file no. 36-1451). But as we increased the concentration of the Co^{2+} ion upto 7% the diffraction pattern displays a weak undesired peak of Co_3O_4 (marked as *) in the peaks of ZnO nanocomposite. The average crystallite diameters of all the samples were calculated from the broadening of most intensed peak (101) present in the corresponding diffraction pattern by using Debye-Scherrer equation.

$$\langle D\rangle_{(101)} = \frac{0.9\lambda}{\beta_{\frac{1}{2}}\cos\theta} \quad (1)$$

here, D is the average nanocrystallite size, λ is the wavelength of the incident X-ray beam, θ is the corresponding Braggs angle, $\beta_{1/2}$ is the full width at half maximum (FWHM) of the (101) peak. The average crystallite sizes (D) for different doped samples were found within the range of 32–40 nm. The lattice parameter of hexagonal ZnO were calculated from the relation

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2+hk+k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

where 'a' and 'c' are the lattice parameters, h, k and l are the Miller indices and d is the inter planer spacing for the plane (h k l). The different values of d have been calculated from the Bragg's equation given below