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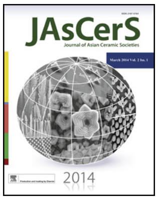

Role of cobalt doping on the electrical conductivity of ZnO nanoparticles

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ABSTRACT

Cobalt doped zinc oxide ($Zn_{1-x}Co_xO$; x = 0, 0.05, 0.10, 0.15) samples were synthesized using co-precipitation method. The Co doped ZnO nanoparticles showed the maximum solubility limit. The XRD patterns confirm the hexagonal type wurtzite structure without secondary phase in Co substituted ZnO samples. The particle size was studied using transmission electron microscope (TEM) and grain size estimated using scanning electron microscope (SEM). We report the study of temperature dependence of conductivity on ZnO and Co doped ZnO nanoparticles. It is found that at a higher temperature range (above 470 K) thermally activated type of conduction is in dominance with the lower temperature range of conduction in which donor carrier hopping mechanism is dominated. DC conductivity result shows the reduction nature for cobalt doped ZnO. The obtained results are discussed on basis of potential barrier, donor concentration, point defects and adsorption–desorption of oxygen. Cobalt substitution increases resistivity, reduces grain growth, lower particle size and increase in activation energy. Detailed mapping of two regions of electrical conductivity is done to understand the activation energy mechanisms prevailing in cobalt doped ZnO. Q2

1. Introduction

Zinc oxide (ZnO) is a II–VI group semiconductor has a wurtzite crystal structure, with a direct and wide bandgap of 3.37 eV, a large exciton binding energy (60 meV) and high optical gain at room temperature [1–3]. Numerous applications of wurtzite ZnO comprises of field-effect transistor [4], optical device [5], dye-sensitized solar cell [6], solid-state gas sensor [7,8]. The strong n-type conductivity is exhibited by zinc oxide varistor (ZnO) with the electrons to move in the conduction band as charge carriers. Primary dependence of electrical properties of ZnO is based on the composition and on microstructure characteristics such as grain size, density and morphology. The study of effect of dopants on physical and electrical properties of ZnO are related to applications in electronic components such as piezoelectric transducers and varistor.

Most of the ZnO nanomaterials have been fabricated by conventional high temperature solid state mechanisms which is energy consuming and unfavorable to control the particle properties [9]. ZnO nanoparticles can be synthesized by simple solution based methods on a large scale such as chemical precipitation, sol–gel synthesis, and solvothermal/hydrothermal reaction [10]. We synthesized ZnO nano powders using precipitation method at a sintering temperature of 400 °C. This fabrication method has been successfully employed in our work to prepare nanoscale particles being cost-effective and controlled which desires low temperatures for processing and a high degree of solubility can be acquired.

Among many research dopants in zinc oxide, cobalt doped zinc oxide shows potential in various applications [11,12]. According to reference studies [13], doping Cobalt in ZnO creates more zinc vacancies. Thus among diluted magnetic semiconductors (DMS), Cobalt doped ZnO is considered as a potential candidate among the TM because of its abundant electron states, large solubility in the ZnO matrix and also cobalt has a similar ionic radius (0.58 Å) to that of Zn (0.60 Å) [14]. Further different complex morphologies such as flowers, rods, sheets etc require too many control parameters which limit the application of the nanostructures.

The presence of secondary phases like Co^{3+} ions which may coexist with Co^{2+} ions in Co doped ZnO nanoparticles, are expected to have lattice defects [15]. Kumar and Khare, Roy et al. [16,17] and Yan et al. [18] reported increase in resistivity of Co^{2+} doped

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ZnO samples, can be attributed to the shallow acceptor nature of these impurities. Birajdar et al. [19] and Kulandaisamy et al. [20] reported an increase in resistivity due to cobalt defect scattering centre in the ZnO lattice. Substitution of any dopant can expect changes in lattice parameter (a,c) and volume (V) showing initial proof of doping effects. Creating defects or doping in zinc oxide to generate multi-valence nature in the system to tailor the level or occupancy of the fermi energy level further affects the conductivity nature [21]. Doping any element in zinc oxide could produce distortions, results variations in optical band gap [22]. Considering the Burtein-Moss effect, the band gap value increases with the number of carrier concentration in conduction band. This could be also verified using conductivity nature of the samples. Therefore, from the current study, we attempt to dope cobalt in Zinc oxide by varying weight percentages and to study the conductivity properties.

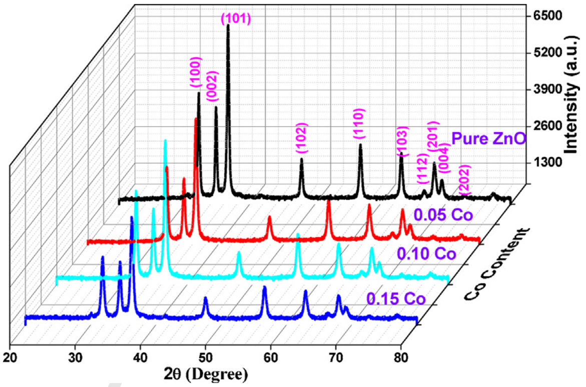

Fig. 1. X-ray diffraction patterns of $Zn_{1-x}Co_xO$ nanoparticles.

2. Experimental

2.1. Preparation of the pure and Co doped ZnO nanoparticles

The following high purity chemicals such as zinc acetate dehydrate (Zn $(CH_3COO)_2{\cdot}2H_2O$), cobalt acetate tetrahydrate (Co $(CH_3COO)_2{\cdot}4H_2O$), sodium hydroxide (NaOH), ethanol and methanol (99.998%) were used as the precursors without further purification. For the preparation of pure ZnO nanoparticles (NPs), specific amounts of zinc acetate and NaOH are dissolved in 50 ml methanol which is added drop wise and then stirred with heating at 325 K for 2 h. The precipitate is separated from the solution by filtration, washed several times with distilled water and ethanol then dried in air at 400 K to obtain ZnO nanocrystals. The samples obtained were annealed at 673 K for 8 h. For the synthesis cobalt doped ZnO, zinc acetate dehydrate and cobalt acetate dehydrate were dissolved in methanol (100 ml) and other containing of NaOH in methanol (100 ml) were prepared and added by constant magnetic stirring while heating at 325 K for 2 h. Precipitate is then separated from the solution by filtration, washed several times with distilled water and ethanol then dried in air at 400 K to obtain Co doped ZnO nanoparticles and annealing at 673 K for 8 h.

2.2. Characterization of samples

For electrical conductivity measurements, the powder samples were pressed uniaxially into a pellet of thickness 4–5 mm and of diameter 10 mm by applying pressure of 120 Mpa for 3 min. Pellets were sintered at 573 K for 3 h for thermal stabilization. Fine quality silver paint was applied on both sides of the pellets for good electrical contacts. The DC electrical conductivity measurements were carried by two probe method in the temperature range 300–650 K. The samples were analyzed by the following characterization studies. The samples were analyzed by the following characterization studies done using x-Ray powder diffraction (XRD) (XPERT-PRO (Model: PW-3710) operated at 45 kV and 40 mA with a Cu-K_α radiation source of wavelength 1.5406 Å), scanning electron microscope (SEM) (Model: JSM6100), transmission electron microscope (TEM: Hitachi-Model: H-7500) and DC electrical conductivity measurements using KEITHLEY source meter (model 2400).

2.3. Different relations used for measurement of properties

Q3 The lattice constants of pure and Co doped ZnO nanocrystals were determined using following formula

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left[\frac{4}{3}(h^2+hk+k^2)+\frac{a^2l^2}{c^2}\right] \tag{1}$$

where ‘θ’ is the angle of diffraction, ‘λ’ is wavelength, ‘a’ & ‘c’ are lattice constants and h, k and l are miller indices. Considering the first order approximation (n = 1) for the (100) plane, the lattice constant ‘a’ is obtained through the relation

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \tag{2}$$

Lattice constant ‘c’ is derived for the plane (002) by the relation

$$c = \frac{\lambda}{\sin\ \theta} \tag{3}$$

The volume of unit cell can be calculated using equation,

$$V = 0.866 \times a^2 \times c \tag{4}$$

The parameter ‘u’ can be calculated by the formula doping-induced effect of bond length ZnO is analyzed.

$$u = \frac{a^2}{3c^2} + 0.25 \tag{5}$$

Average crystallite sizes were estimated using Debye–Scherrer’s equation

$$D = \frac{K\lambda}{\beta\cos\ \theta} \tag{6}$$

Strain induced broadening ($\beta\varepsilon$) is given by the Wilson formula:

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \tag{7}$$

where ‘ε’ is the root mean square value of the micro strain. The readings were recorded during slow cooling after heating cycle and the electrical conductivity (σ) was calculated by the formula:

$$\sigma = \left(\frac{\mathrm{I}\times\mathrm{t}}{\mathrm{V}\times\mathrm{A}}\right) \tag{8}$$

where ‘V’ is the applied voltage, ‘I’ is the measured current; ‘A’ is the area of the pellet and ‘t’ the thickness of the pellet.

3. Results and discussions

3.1. X-ray diffraction study

Fig. 1 shows x-ray diffraction patterns (XRD) of pure and Co doped ZnO nanoparticles. The XRD peaks are located at angle (2θ) corresponds to (100), (002), (101), (102), (110), (103), (112), (201) and (004) planes attributed to ZnO. The XRD peaks show the hexagonal (wurtzite) crystal structure of all prepared samples. In reported literatures the spinel Co_3O_4 peaks are observed as a secondary phase even for the lowest dopant concentration x = 0.1 at sufficiently high calcination temperature of 600 °C [23,24]. Fig. 1 confirms no extra or any impurity phases evident in Co doped ZnO

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