Investigation of structural and optical sensing studies of Mn-doped CuO nanostructures film for optoelectronics applications

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Abstract

In this study, the impact of Mn on structural, morphological and optical of p-type copper oxide nanostructures is investigated. Mn-doped CuO thin film developed via chemical spray Pyrolysis technique. Developed film was characterized using by x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and UV – vis spectroscope. XRD pattern confirms the monoclinic CuO crystal structure without any extra phases. In addition, broadening of diffraction peaks indicated the prepared film has nana sized phase. Average crystallite size of Mn-doped CuO is found to be 4.81 nm. Optical energy band gap of Mn-doped Cuo film was 2.15 eV.

Keywords: Mn-doped CuO; Spray Pyrolysis; FESEM; optical study.

1. Introduction

Current research is very interested in transition metal oxides at the nanoscale zone due to their intriguing characteristics and wide range of applications. One significant p-type transition metal oxide among them is cupric oxide (CuO), which has a narrow band gap (E_g = 1.2–1.9 eV) [1]. CuO's special qualities and broad range of applications in gas sensors [2], biosensors [3], solar cells [4], high Tc superconductors [5], lithium ion batteries [6], catalysts [7], and other fields have drawn a lot of attention recently. To improve its performance, numerous attempts have been undertaken to create nanostructured CuO materials, such as nanoparticles, nanorods, nanowires, nanoplates, and nanotubes [8 -10]. In addition, a variety of substances can be added to materials as doping agents to improve their chemical and physical characteristics. Despite a lot of study on doping nanostructured films, producing high-quality crystalline films with superior physical and chemical characteristics of doped CuO nanostructures is still difficult. Copper oxide has garnered significant interest among transition metal oxides due to its exceptional catalytic activity as well as optical properties. Mn is also renowned for being a superb catalyst and photovoltaic applications.

A few numbers of papers on Mn-doped bulk and/or nanostructure CuO were discovered through the literature review [11]. For example, Y. Gu¨len et. Al. [10] reported that the optical band gap of the films increases with increasing Mn-doping concentrations of CuO. The conventional solid-state reaction method was utilized to create the ceramic targets of $Mn_xCu_{1-x}O$ [12]. CuO films were coated using a variety of deposition methods, including spin-coating [13], thermal evaporation [14], microwave irradiation [15], electro-deposition [16], solution growth [17], etc. To produce large scale production with low cost and easy to operate spray Pyrolysis is used to prepare thin films, these prepared thin films having different morphology and transport properties.

In this work, 5% Mn doped CuO thin film synthesised using by spray pyrolysis method. The study Mn on structural and optical properties of CuO film. These results are suitable for use in low power and portable electronic devices.

2. Experimental details Mn-doped CuO thin film

Thin film of CuO doped with 5 wt. % of Mn were successfully deposited on non conducting glass substrate using a spray Pyrolysis method. Before deposition, the glass substrate were boiled in chromic acid for 30 min and subsequently cleaned with deionised water, in acetone and finally drying the substrate in an oven for about 1 h at 80 ℃. The precursor solution was prepared by mixing 0.1 M copper acetate (II) monohydrate in 20 ml of double distilled water. For Mn-doped CuO thin film, an appropriate amount of manganese acetate tetra hydrate for preparing 5% was added into the precursor solution. The solution was vigorously stirred using a magnetic stirrer for 20 min. Then the prepared solution was loaded into the spray container and sprayed onto the preheated glass substrates. The nozzle size and the distance between the nozzle and the substrates were 0.25 mm and 28 cm, respectively. Compressed air was used as carrier gas and the spray rate was 3ml/min. All samples were deposited at a constant temperature of 350℃ with the same condition. The thickness of all the films was constantly maintained at approximately 320 nm and confirmed through the weight difference method.

The structural analysis of the Mn-doped CuO thin films was investigated using an X-ray diffractometer (RigakuUltima-IV XRD, CuKα radiation k = 1.5406 Å) in the range of 2θ angle 20^{o} to 80^{o}. The surface morphology of the films wasobtained using field emission scanning electron microscopy (FEI Nova SEM-450). Energy dispersive spectroscopy (EDS: JEOL, JSM-IT 200) was used to study the compositional analysis. The optical properties of the films were studied by UV-VIS spectrophotometer (SHIMADZU UV-1900i) in the 300 nm to 800 nm wavelength range.

3. Results and discussion

Fig. 1 presents the X-ray diffraction (XRD) pattern of 5% Mn-doped CuO thin film. The XRD pattern shows the presence of diffraction peaks associated with the (110), (002), (111), (-202), (020), (202), (-113), and (220) crystal planes in Mn-doped CuO sample. The diffraction peaks exhibit polycrystalline with the monoclinic crystal structure.

The XRD pattern obtained from the samples good agreement with Joint Committee on Powder Diffraction Standards (JCPDS) card no. 89-5897 [18]. The average crystallite size was determined for Mn-doped CuO sample by using the Scherrer formula [19].

$$D = \frac{0.91\lambda}{\beta cos\theta} \qquad (1)$$

Where λ is the wavelength of CuK_α radiation (λ=1.5406Å), β is the full width at half maximum (FWHM) and θ is the Bragg diffraction angle. The value of average crystallite size for 5% Mn-doped CuO films is found to be 4.81 nm. M. Babu et al. [20] also observed a similar variation in crystallite size with Mn.

The lattice constant ($a \neq b \neq c$, $\alpha = \gamma = 90^0 \neq \beta$) for monoclinic structure, can be derived from XRD using the following formula:

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2 sin^2\beta} + \frac{k^2}{b^2 sin^2\beta} - \frac{2hkcos\beta}{absin^2\beta} + \frac{l^2}{c^2}\right) \qquad (4)$$

Where *a*, *b*,and *c* are the lattice parameters, *d* is interplanar distance, and *h*, *k*,*l* are Miller indices of the crystalline plane. The value of lattice constants a, b, and c are found to 4.1781 Å, 3.4504 Å, and 5.0414 Å respectively.

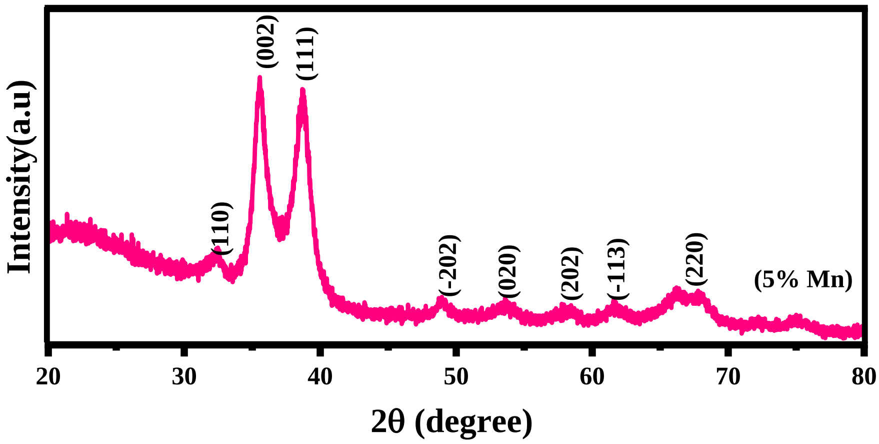

Fig. 1 XRD pattern of Mn-doped CuO sample.

3.2. Surface morphology and compositional analysis

Fig. 2(a) shows Field Emission Scanning Electron Microscopy (FE-SEM) images of 5% Mn-doped. From the FE-SEM images, it is observed crack-free and randomly distributed spherical agglomerated nanoparticles (NPs) particles. The average grain size is calculated by Image J software and found to be 125.77 nm for 5% Mn-CuO thin film. The elemental compositions of synthesized films were determined by EDS and are shown in Fig. 2(b) Mn-doped CuO films existence of Cu, Mn, and O in the sample confirms the incorporation of Mn into CuO lattices. In addition, no extra peaks corresponding to impurity elements were observed, thereby confirming the purity of synthesized Mn-doped CuO film.

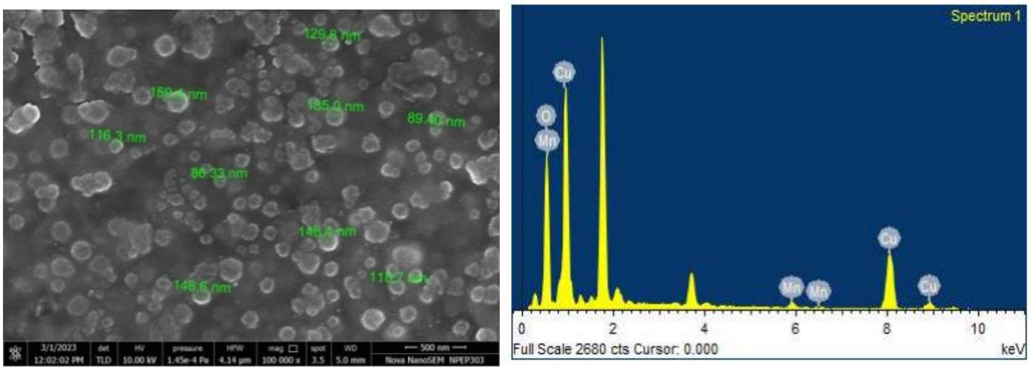

Fig. 2. (a) FESEM image of Mn-doped CuO; (b) EDS spectra of 5% Mn-doped CuO.

3.3 Optical analysis

Fig. 3(a) depicts the transmittance spectra of 5% Mn-doped CuO film in the 300 nm to 1100 nm range. It is observed that optical transmittance 55% due to doping Mn content. The enhancement in optical transmittance after doping may be attributed to the disorder in the doped CuO films [30]. In addition, all spectra illustrate a shift in absorption edge to lower wavelength when Mn content increases. This blue shift indicates the increase of band gap energy which is related to a decrease in crystallite size.

The optical band gap (E_g) for film was calculated using the Tauc equation and by plotting $(\alpha h\nu)^2$ versus (hν) as shown in Fig. 3(b).

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^{1/2} \qquad (5)$$

Where α is the absorption coefficient, A is a constant, and $h\nu$ is the incident photon energy. The extrapolation of the linear part of the curve to the X-axis will give the value of the optical band gap energy of each film. The obtained E_g value is found to be 2.15 ev for 5% Mn-CuO thin film respectively.

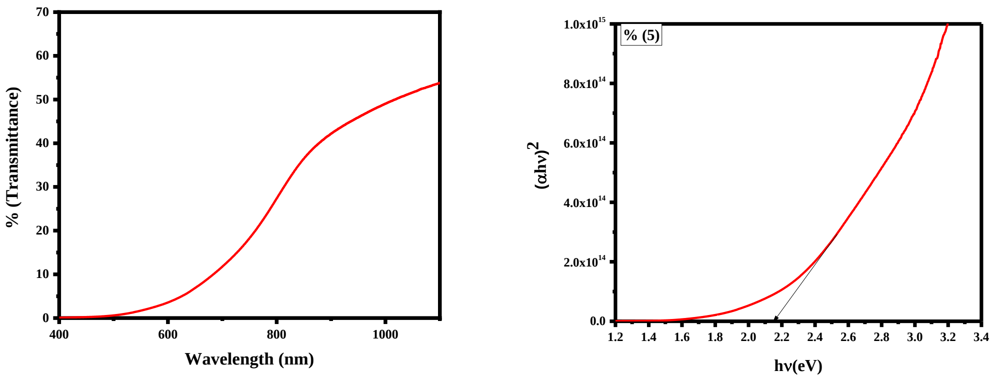

Fig. 3.(a) Transmittance spectra (b) Plot of $(\alpha h\nu)^2$ vs. hν for 5% Mn-CuO thin film.

4. Concussions

Mn-doped CuO thin film was synthesized by the spray pyrolysis method. Film is free of cracks and contains nanoparticles that resemble plates. It was also clear from the FESEM picture that the Mn concentration had an impact on the spherical-like nanostructures'. The Mn-doping percentages of the film exhibited a linear relationship with the Mn ion concentration in the growing solution, according to the EDS analysis. According to the XRD data, film has a monoclinic structure and is polycrystalline. According to the UV-vis examination, the transmission and optical band gap were impacted by the Mn-doping concentration in the film. The optical transmission and optical band gap energy levels rise in tandem with the Mn content. Since Mn and copper oxide are recognized to be ideal opto-electronics applications.

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