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Study on the physical properties of europium doped indium oxide thin films

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Structural, morphological, optical and electrical properties of europium doped In_2O_3 thin films grown by spray pyrolysis technique are studied in this work. The atomic percentages of europium dopant in In_2O_3-based solution were $y = \left(\frac{[Eu^{3+}]}{[In^{3+}]}\right)_{sol}$ =0; 0.1; 0.3 and 0.5 at%. All films crystallize into the body centered cubic structure. The preferred orientation peak along the (222) plane was changed to (400) after doping. It is further revealed a best crystallinity for y =0.3 at% followed by a noticeable increase of the grain size. Some structural and microstructural parameters are determined using Rietveld refinement of XRD patterns. The optical transmission of doped films was above 68% in the visible range. The optical band gap (E_g) is in the range of [3.43–3.51] eV. Optical constant such as refractive index (n), packing density (p), porosity, oscillator energy (E_0) an$_d$ dispersive energy (E_d) were also studied in this report using envelope method based on transmission-reflection spectra. Electrical properties show a lowest resistivity (ρ) for a doping concentration equals to 0.3 at% reaching 0.031 Ω cm. At this doping ratio, an enhancement of free carrier concentration is also remarked. A heat treatment under nitrogen atmosphere is then applied on optimized In_2O_3:Eu (0.3 at%). A significant decrease of the resistivity is noted at 250 °C during 2 h reaching 0.004 Ω cm. These results lead to conclude that annealed In_2O_3:Eu(0.3 at%) can be a good candidate to be used in many optoelectronic devices and especially as optical window or transparent electrode in solar cells.

1. Introduction

Transparent conductive oxide (TCO) materials exhibit both high optical transparency and low resistivity [1]. Indium oxide has been appeared as an important TCO material used in optoelectronic devices [2,3] and in gas sensor application [4,5]. Intensive studies have been done to improve physical properties of indium oxide thin films especially with doping process. Various atoms have been used as dopant element to be incorporated into In_2O_3 lattice such as molybdenum [6], fluorine [7], iron [8] and zinc [9]. However, few reports have focused on doping In_2O_3 with rare earth atoms. For example, X. Niu et al. [5] have been reported the physical properties of Eu^{3+}, Gd^{3+} (gadolimium) and Ho^{3+} (holmium) doped In_2O_3 powder grown by sol gel method. Further, A. Dakhel et al. [10] have investigated the effect of ytterbium doping on the optical and electrical properties of In_2O_3 thin films grown by evaporation technique. On the other hand, Kim et al. [11] have studied the effect of europium doping on the physical properties of ITO films prepared using sol gel procedure.

Indium oxide thin films can be prepared using several techniques such as: radio frequency sputtering [12], electron beam evaporation [13], sol-gel [14], direct current magnetron sputtering [15] and pulsed laser deposition [16] and the pulverization technique in liquid phase (spray pyrolysis) [17–19]. Among them; spray pyrolysis is a promising method due to its low cost and simplicity. In this work, we have studied the effect of europium doping on the physical properties of indium oxide thin layers grown by spray pyrolysis which is not in our knowledge done before. Furthermore, optimized In_2O_3:Eu thin films were annealed under nitrogen

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atmosphere. The electrical properties of annealed films were also investigated in this study. Europium doped In_2O_3 thin films were characterized using X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), atomic force microscopy (AFM), spectrophotometers, fluorescence spectrometer and Hall Effect measurements. Moreover, XRD patterns were refined using MAUD software [20] based on Rietveld method [20] to determine some structural and microstructural parameters. Among them, we find the micro-strain $<\sigma^2>^{1/2}$, present phases and crystal lattice parameters. Besides, optical constant such as refractive index (n), porosity, packing density (p), oscillator energy (E_0) and dispersive energy (E_d) were studied in this work using envelope method [21].

2. Experimental procedure

Europium doped indium oxide thin films were grown by the pulverization technique in liquid phase (spray). The bi-distilled water was used as a solvent. Indium chloride ($InCl_3$) was used as a source of indium element to grow undoped indium oxide. Eu_2O_3 was added to starting solution as a dopant agent. In fact, Eu_2O_3 was initially dissolved in few drops of HCl according to the following chemical reaction:

$$Eu_2O_3 + 6HCl \rightarrow 2EuCl_3 + 3H_2O \quad (1)$$

$EuCl_3$ was then dissolved in bi-distilled water to obtain Eu^{3+} doping elements and added to the starting solution. In_2O_3:Eu thin films were formed on glass substrates at 500 °C. Compressed air was used as a carrier gas. The solution flow rate is fixed to 2.5 ml min^{-1}. The experimental setup was explained with details in previous work [22]. The atomic concentrations of europium in the sprayed solution were $y = \left(\frac{[Eu^{3+}]}{[In^{3+}]}\right)_{sol} = 0; 0.1; 0.3$ and 0.5 at%. In the following, we have denominated the samples A, B, C and D for respectively doping ratio 0; 0.1; 0.3 and 0.5 at%.

The layers structures were studied using X-ray diffraction (XRD) which are recorded with an automated Bruker D8 advance X-Ray diffractometer with CuK_α radiations for 2θ values over 10–70°. The wavelength, accelerating voltage and current were respectively, 1.5418 Å, 40 kV and 20 mA. The average grain size (d) was calculated using Scherrer formula along the preferred orientation for each doping ratio [23]:

$$\boldsymbol{d} = \frac{0.94\lambda}{\sqrt{\beta - \beta_0} \times \cos\theta} \quad (2)$$

where λ is the X-ray wavelength of Cu Kα radiation ($\lambda = 1.5418$ Å), $\beta_0 = 0.125°$ is the width of the corresponding peak due to the instrumental expansion. β is the experimental full-width at half-maximum (FWHM) preferential diffracted peak measured in radians and θ is the Bragg's angle.

In fact, d is calculated for undoped films (sample A) by using (222) plane however for all doped layers we have used the preferred orientation which is (400) plane. The same method was used in our previous work for Fe-doped In_2O_3 thin films [8].

The dislocation density (δ_{disc}) is determined by using the Williamson and Smallman's formula [24]:

$$\delta_{dis} = \frac{1}{d^2} \quad (3)$$

The number of crystallites per unit surface area (n_c) of elaborated thin films were calculated using the following expressions [25]:

$$\boldsymbol{n_c} = \frac{\boldsymbol{t}}{\boldsymbol{d}^3} \quad (4)$$

where t is the film thickness.

The chemical analysis was carried out using energy-dispersive spectroscopy (EDS) coupled with scanning electron microscope (SEM) Philips SEM XL-30 with secondary electron detector. The film surface morphology was analyzed using Atomic Force Microscopy (AFM, standard Veeco Dimension 3100) used in tapping mode. Optical transmission and reflection measurements were carried out with Perkin-Elmer Lambda 950 spectrophotometer in the wavelength range of 250–2500 nm at room temperature taking air as reference. Photoluminescence (PL) was studied at room temperature with Perkin-Elmer LS 55 Fluorescence spectrometer using 250 and 375 nm as excitation wavelengths. Electrical resistivity, carrier concentration and mobility were determined by Hall Effect in the van der Pauw configuration. The Hall Effect measurements were performed at room temperature using an Accent HL 5500 automated system. Annealing process was carried out using a Jet First Processor™. XRD patterns of europium doped In_2O_3 thin films were also refined by MAUD software [20] which is based on the Rietveld method [20]. In order to reduce the difference between experimental and theoretical diffraction patterns, the fitting procedure is controlled by the Marquardt least square method is used during the fitting procedure to reduce the difference between experimental and theoretical diffraction patterns [20].

3. Results and discussions

3.1. Structural properties

3.1.1. XRD analysis

XRD patterns of europium doped indium oxide thin films for different doping concentration are shown in Fig. 1. Undoped In_2O_3

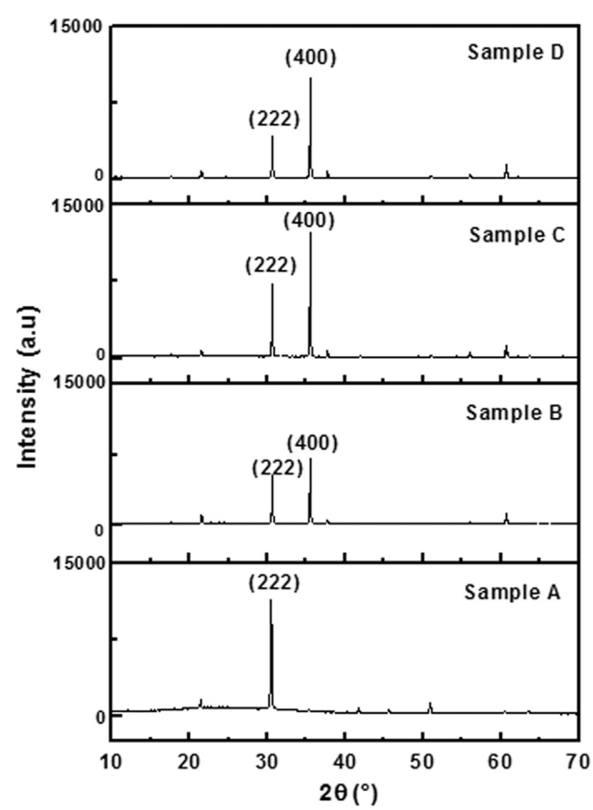

Fig. 1. XRD patterns of undoped and europium doped indium oxide thin films for different doping ratio $y = \left(\frac{[Eu^{3+}]}{[In^{3+}]}\right)_{sol} = 0$ **(A)**; 0.1 **(B)**; 0.3 **(C)** and 0.5 at% **(D)**.