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Structural, optical and electrical properties of Zr-doped In_2O_3 thin films

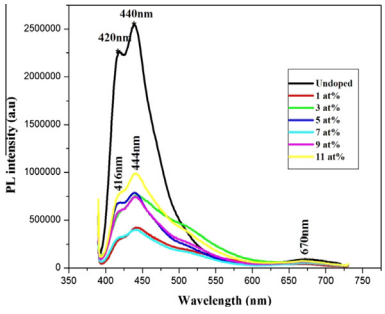
C. Manoharan [a], M. Jothibas [b,*], S. Johnson Jeyakumar [b], S. Dhanapandian [a]

[a] Department of Physics, Annamalai University, Annamalai Nagar 608 002, India
[b] Department of Physics, T.B.M.L. College, Porayar 609 307, India

HIGHLIGHTS

- Spectroscopic properties of Zr doped In_2O_3 thin films were examined.
- The crystallographic parameters; micro strain, dislocation density and lattice constant were estimated.
- The emission spectra show a strong blue emission band around 416–444 nm in all samples.

GRAPHICAL ABSTRACT



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ABSTRACT

Undoped and zirconium doped indium oxide (ZrIO) thin films were deposited on glass substrate at a substrate temperature of 450 °C by spray pyrolysis method. The effect of zirconium (Zr) dopant concentration (0–11 at.%) on the structural, morphological, optical and electrical properties of n-type ZrIO films were studied. X-ray diffraction (XRD) results confirmed the polycrystalline nature of the ZrIO thin film with cubic structure. The grain size was decreased from 25 to 15.75 nm with Zr doping. The scanning electron microscopy (SEM) showed that the surface morphology of the films were changed with Zr doping. The surface roughness of the films was investigated by atomic force microscopy (AFM) and was found to be increased with the increasing of Zr doping percentage. A blue shift of the optical band gap was observed. The optical band was gap decreased from 3.50 to 3.0 eV with increase in Zr concentrations. Room temperature photoluminescence (PL) measurement of the deposited films indicated the incorporation of Zr in In_2O_3 lattice. The film had low resistivity of 6.4×10^{-4} Ω cm and higher carrier concentration of 2.5×10^{20} was obtained at a doping ratio of 7 at.%.

Introduction

Indium oxide (In_2O_3) has several properties that make it a useful material. These properties include high density, hardness, electrical conductivity, wear resistance, low thermal conductivity, relatively high dielectric constant, and extreme chemical inertness [1]. In_2O_3 is an essential material in optics due to its excellent optical properties, such as a high refractive index, large optical band-gap, low optical loss and high transparency in the visible and near-infrared regions. It is being used for high refractive mirrors, broadband interference filters, and active electro-optical devices [2]. Additionally, In_2O_3 is the most frequently used material for anti-reflection (AR) coatings in optical industries.

In_2O_3 thin films are deposited by electron beam evaporation [3], sputtering [4], pulsed laser deposition [5], chemical vapor deposition [6], sol-gel processing [7], and spray pyrolysis deposition [8]. The physical properties of the In_2O_3 thin films strongly depend on the deposition techniques and the ex situ thermal treatment process.

* Corresponding author. Tel.: +91 9994197383.
E-mail address: joejothi_1980@rediffmail.com (M. Jothibas).

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Spray pyrolysis is a versatile deposition method because it allows the use of inexpensive precursor materials, good control of layer stoichiometry and most importantly-large-area coatings can be obtained by using low-cost equipments, in low energy consuming conditions. In spray pyrolysis the deposition rate, thickness and uniformity of the films are the consequence of nucleation and crystal growth processes which are mainly influenced by the deposition temperature and precursor solution concentration. On the other hand, the precursor type and carrier gas pressure influence the solvent evaporation rate within the aerosol droplets, and the droplets speed up through modification of superficial tension. To the author's knowledge this is the first attempt to prepare Zr-doped Indium oxide films using spray pyrolysis methods.

In this paper, highly transparent conductive In_2O_3:Zr thin films are deposited by spray pyrolysis method. The effect of doping concentrations on the structural, morphological, electrical and optical properties of In_2O_3:Zr thin films are investigated in detail.

Experimental details

Both un-doped and doped (In_2O_3:Zr) films were deposited onto microscopic glass substrate using spray pyrolysis technique. The precursor of Indium (III) acetate (0.1 M) was dissolved in deionised water. A few drops of concentrated hydrochloric acid was added for complete dissolution and sprayed onto microscopic glass substrates with dimensions of 75 × 25 mm^2 at optimized substrate temperature (T_s = 450 °C). At this optimum temperature, Zirconium was doped on In_2O_3 thin film using $ZrCl_4$ (0–11 at.%) as the dopant source. The substrates were first cleaned with a water bath, followed by dipping in con. HCl, acetone and ethanol successively. Finally the substrates were rinsed with deionised water and allowed to dry in a hot air oven. In the spray unit, the substrate temperature was maintained with the help of heater, controlled by a feedback circuit. During the spray, the substrate temperature was kept constant with an accuracy of ±5 K. Spray head and substrate heater were kept inside a chamber provided with an exhaust fan, for removing gaseous by-products and vapors from the solvent. The spray head was allowed to move in the *X*–*Y* plane using the microcontroller stepper motor, in order to achieve a uniform coating on the substrate. The spray head could scan an area of 200 × 200 mm with *X*-movement at a speed of 20 mm/s and *Y*-movement insteps of 5 mm/s simultaneously. In the spray unit, there was a provision for controlling the spray rate of the solution as well as the pressure of the carrier gas. The microcontroller device was communicated with PC through the serial port; the data of each spray could be stored in the PC. The deposition parameters like solution flow rate, carrier gas pressure and nozzle to substrate distance were kept as 2 ml/min, 1.0 kg/cm^2 and 20 cm, respectively. This spray system can be used for large area of deposition with better uniformity.

After the deposition, the films were allowed to cool slowly to room temperature and washed with deionised water and then dried. The structural characterizations of the films were carried out by X-ray diffraction technique on SHIMADZU-6000 (monochromatic Cu kα radiation, λ = 1.5406 Å). The XRD patterns were recorded in 2θ interval from 10° to 80° with the steps of 0.05° at room temperature. Fourier transform infra red (FT-IR) spectra were recorded in the 4000–400 cm^{-1} range with a SHIMADZU. FT Raman spectra were recorded on a BRUKER: RFS 27 instrument using a 100 nm excitation laser. Wave numbers in the 100–3700 cm^{-1} range were obtained at room temperature. The surface topological studies were carried out using Atomic force Microscope (Nano surf Easy scan2). Optical absorption spectrum was recorded in the range 300–1200 nm using JASCO V-670 spectrophotometer. The photoluminescence spectrum (PL) was studied at room temperature using plorolog 3-HORIBAJOBINYVON with an excitation wavelength of 375 nm. The Electrical resistivity, mobility and carrier concentration were measured at room temperature using standard Hall Effect system equipment (ECOPIA HMS–3000) in Van-der Pauw configuration.

Results and discussion

Structural analysis

The X-ray diffraction patterns of un-doped and Zr doped In_2O_3 films with different concentrations (1, 3, 5, 7, 9 and 11 at.%) are shown in Fig. 1. All the films exhibit polycrystalline nature with cubic structure. The peak positions are in good agreement with In_2O_3 (JCPDS card No: 06–0416). No extra peaks are observed due to the addition of zirconium in indium oxide films which indicates the absence of an impurity phase in the films. There are three prominent peaks of (222), (440) and (400) planes in XRD pattern reveal the cubic structure. From the figure, it was clear that the intensity of peaks is increased sharply with increasing Zr doping concentration up to 7 at.%. The increase in intensity of the peaks is due to the improvement of crystallinity. However, the intensity of the peak is decreased sharply and slightly shifted to higher diffraction angle with increase of doping content above 7 at.%. The decrease in intensity at higher doping level is due to structural deformation in the crystal structure [9]. The 'shift' of strong (222) peak position to higher angle region is due to the residual stress developed in the films because of difference in the ionic radius between In^{3+} (0.088 nm) and Zr^{4+} (0.074 nm) [10]. The calculated lattice constant values are less than the standard value which is the strong indication of stress in the films observed and the shift of (222) diffraction peak position with increase in doping content of zirconium (see in Table 1).

The lattice parameters ($a = b = c$) are determined by the equation [11]:

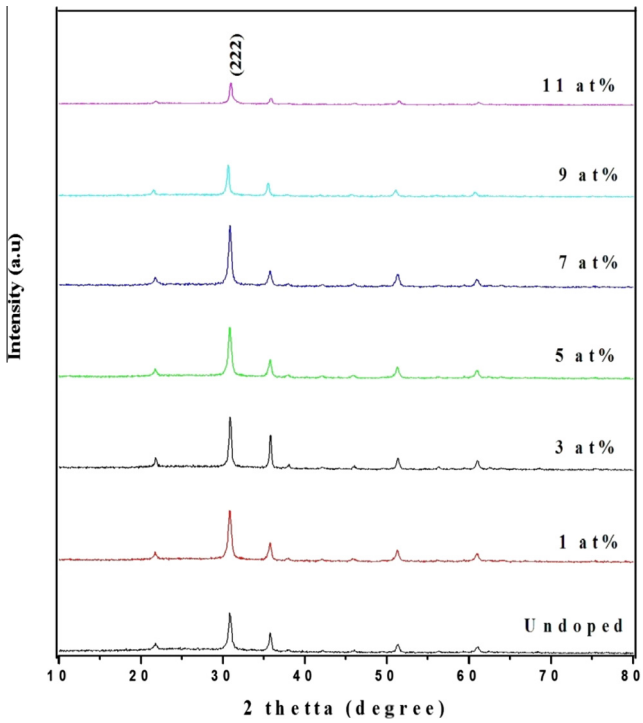

Fig. 1. XRD spectrum of Zr doped In_2O_3 thin films at different doping concentrations.