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Effect of co-doping concentration on structural, morphological, optical and electrical properties of aluminium and indium co-doped ZnO thin films deposited by ultrasonic spray pyrolysis

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ABSTRACT

In this work, we reported a chemical approach to prepare aluminium and indium co-doped ZnO thin films (AIZO) by ultrasonic spray pyrolysis. Film depositions were carried out on soda lime glass substrates at 425 °C by using a spray solution containing zinc acetate as zinc precursor, aluminium acetylacetonate as Al dopant source and indium (III) acetate as In dopant source. Physical properties such as structural, morphological, optical and electrical properties were studied with respect to the equal variations in co-dopants concentration (0.5–3 at%). X-ray diffraction patterns proved that films are poly crystalline with (002) preferential orientation. Scanning electron microscopy analysis showed that AIZO films grown like hexagonal nanopyramids, elongated grains and irregular trigonals. Optical transmittance ~85% and a minimum resistivity of 1.3×10^{-3} Ω cm, are achieved for films when co-doped with 1.5 at% of Al and 1.5 at% of In, confirm that AIZO films are suitable for transparent conductive oxide (TCO) applications.

1. Introduction

Transparent conductive oxides (TCO) films are optically transparent and electrically conductive. TCOs are widely investigated for various applications, such as solar cells, liquid crystal displays, light emitting diodes and window thermal coatings [1–5]. Zinc oxide (ZnO), a wide bandgap semiconductor, is preferred for its low-cost, non-toxicity and rich availability over other TCO materials, such as SnO_2, In_2O_3, CdO, PdO, NiO and CuO [6]. However, intrinsic ZnO is highly resistive. In order to enhance the electrical properties of ZnO thin films, aluminium (Al), indium (In), or gallium (Ga) are the dopants preferred since their ionic radius is near to that of zinc (Zn) [7–9]. The ionic radius of Al^{3+}, In^{3+}, Ga^{3+} and Zn^{2+} ions are 0.054, 0.080, 0.062 and 0.074 nm respectively [10,11].

There are various deposition techniques followed to prepare ZnO thin films such as thermal evaporation [12], sputtering [13], chemical vapor deposition [14], sol–gel [15] and ultrasonic spray pyrolysis (USP) [16]. Among these, ultrasonic spray pyrolysis has numerous advantages such as cost effectiveness, simple experimental setup and large area depositions [17–19]. From the literature, we noticed that several authors reported ZnO doped with single element (Al/In/Ga) deposited by spray pyrolysis [20–27]. They obtained minimum resistivities for Al-doped ZnO, In-doped ZnO and Ga-doped ZnO were 5×10^{-3}, 3.4×10^{-3} and 9.3×10^{-3} Ω cm respectively. In recent times, to enhance the properties co-doping is preferred by investigators [28]. However, no research has been carried out to prepare co-doped films by USP. Aiming at, low resistivity and high transmittance, we have deposited Al and In co-doped ZnO thin films (AIZO) by USP. In this work, we have investigated the structural, morphological, optical and electrical properties of the films with respect to equal variations in co-dopants concentration.

2. Experimental

AIZO thin films were deposited on soda lime glass substrates by ultrasonic spray pyrolysis. The precursor solution (0.2 m) was prepared by dissolving zinc acetate dihydrate ($Zn(OOCCH_3)_2 \cdot 2H_2O$, Alfa Aesar, 98–101%) in a mixture of acetic acid (50 ml), deionized water (50 ml), and methanol (900 ml). Al

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dopant solution (0.1 m) was prepared by dissolving aluminium acetylacetonate ($C_{15}H_{21}AlO_6$, Alfa Aesar, 99%) in 100 ml of methanol. In dopant solution (0.2 m) was prepared by dissolving indium (III) acetate ($In(OOCCH_3)_3$, Alfa Aesar, 99.99%) in a mixture of deionized water (50 ml) and acetic acid (50 ml). The spraying solution was prepared by adding equal at% (0.5%, 1%, 1.5%, 2% and 3%) of the dopant solutions (Al and In) in the precursor solution and ultrasonically sprayed on glass substrates for 10 min at 425 °C. The samples were identified based on the co-dopants at% as S0.5, S1, S1.5, S2 and S3 (For e.g, S0.5 sample has 0.5 at% of Al and 0.5 at% of In).

PANalytical diffractometer with CuKα radiation was used for structural analysis. The morphological characteristics were examined by using Zeiss (Auriga-39–16) scanning electron microscope. The thickness measurements were carried out with the help of KLA Tencor P-15 Profilometer. The optical transmittance of the samples was measured in Shimadzu 2401 PC spectrophotometer. Sheet resistance was measured in a Veeco four point probe instrument. Presence of dopants was confirmed by depth analysis through IMS-6F CAMECA Secondary Ion Mass Spectroscopy (SIMS).

3. Results and discussion

3.1. Structural properties

The XRD spectra of AIZO thin films deposited at 425 °C is shown in Fig. 1. All the films are polycrystalline and confirmed the formation of hexagonal wurtzite structure, irrespective of dopants proportions. The preferential orientation is (002), confirms that the growth of the films is along c-direction [29,30]. No other peaks belong to either aluminium or indium phases are observed in the spectra, in turn indicate that both Al and In are incorporated well into the ZnO lattice [31].

In addition, the intensity of the peak (002) reduces as the dopants concentration increases, which is a result of reduction in thickness (Table 1). Similar intensity variations with respect to thickness have been previously reported by other authors [32–34]. It is worth to mention that reduction in thickness affects the values of full width at half maximum (FWHM), in turn affects the crystallinity. The crystallite sizes (L) of the samples S0.5, S1, S1.5, S2 and S3 are 49.43, 49.41, 35.3, 29.06, and 24.71 nm, respectively estimated using Scherrer's formula, $L=0.9\ \lambda/\beta\ \cos\theta$ [35], where λ is the wavelength, β is the FWHM in radians and θ is the angle of diffraction. Fig. 2 shows the variations in the FWHM and the estimated crystallite size of AIZO thin films as a function of the doping content in the spraying solution. Sample S0.5 presented the least FWHM, inturn exhibited the largest crystallite size. Identical crystallite size changes with respect to dopant concentration were also observed by S. Pati's group [11].

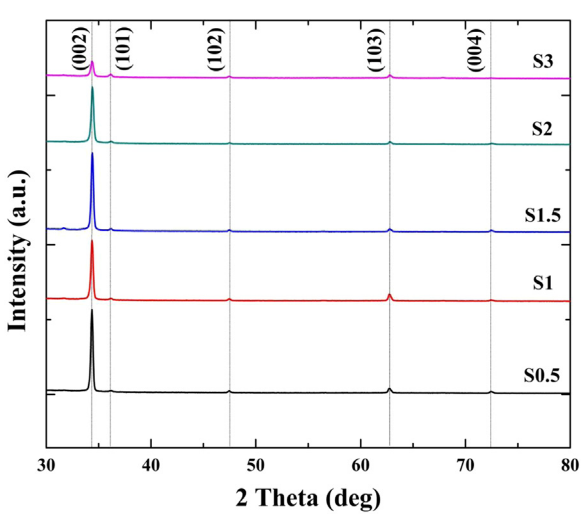

Fig. 1. XRD of AIZO thin films.

Table 1
Optical and electrical characteristics of AIZO films.

Characteristics	Sample ID				
	S0.5	**S1**	**S1.5**	**S2**	**S3**
Thickness (nm)	580	535	509	408	312
Transmittance at 550 nm (%)	74.12	80.18	85.80	90.08	83.78
Band gap (eV)	3.44	3.48	3.49	3.50	3.50
Sheet resistance (Ω/▫)	136.2	45.2	25.5	83.3	67.3
Resistivity (Ω-cm)	7.9×10^{-3}	2.4×10^{-3}	1.3×10^{-3}	3.4×10^{-3}	2.1×10^{-3}
Carrier concentration (cm^{-3})	1.7×10^{20}	3.1×10^{20}	5.9×10^{20}	2.9×10^{20}	3.5×10^{20}
Figure of merit (10^{-3}/Ω)	0.36	2.41	8.47	4.22	2.53

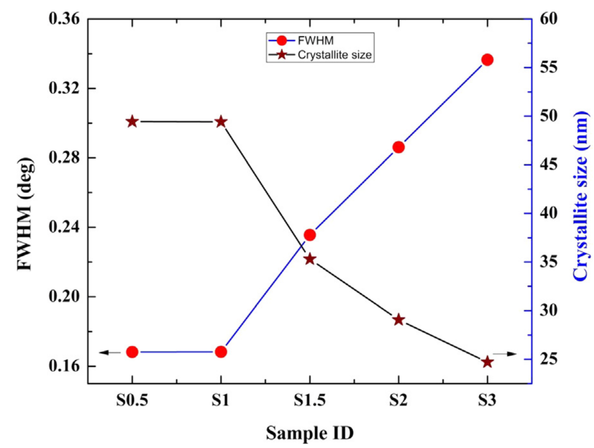

Fig. 2. FWHM and crystallite sizes of AIZO thin films.

3.2. Morphological properties

The morphologies of AIZO samples, S0.5, S1.5 and S3, are shown in the Fig. 3(a–f). Well defined hexagonal nanopyramids, Fig. 3(a–b), are observed for S0.5 sample. These pyramidal structures are found to be uniformly distributed throughout the film. The estimated diameters of the pyramids are in the range of 50 and 250 nm. The diameter of basal hexagon is around 100–120 nm. As the stacks of hexagons grow on the basal hexagon, the diameter of the hexagons is reduced to around 10 nm. From this, we can confirm that, low level doping results in forming hexagonal nanopyramids. Similar nanostructures were observed by Agnes smith for undoped ZnO, sprayed using chlorine free solution [36]. When the concentration level of the dopants is increased (Al: In = 1.5 at%:1.5 at%), surface morphology changes as elongated grains with average dimensions ~200 nm × 100 nm as shown in Fig. 3(c–d). It is worth to note that grains are wider ranging from ~40 to 550 nm. These grains are densely packed structures and have stacks of slices. When doping level is further increased (Al: In = 3 at%:3 at%) the surface of film (S3) is covered with irregular structures of trigonals of different sizes as shown in Fig. 3(e–f). Identical morphology was found for the Al-doped ZnO thin films