

Investigations on high visible to near infrared transparent and high mobility Mo doped In_2O_3 thin films prepared by spray pyrolysis technique

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ABSTRACT

High visible to near infrared (NIR) transparent Mo (0–1 at%) doped In_2O_3 (IMO) thin films with high carrier mobility were deposited on Corning-1737 glass substrates at 400 °C by spray pyrolysis experimental technique. The films were annealed in vacuum ($\sim 1 \times 10^{-4}$ mbar) at 550 °C for 45 min. XRD analysis confirmed that indium oxide belongs to cubic bixbyite structure. The preferred growth orientation along (2 2 2) plane for low Mo doping level shifts to (4 0 0) for higher Mo doping levels. Crystallite sizes extracted from the XRD data corroborate the changes in full-width at half-maximum due to the variation in Mo doping. Scanning electron microscopy study illustrates the evolution in surface microstructures as a function of Mo doping. The negative sign of Hall coefficient confirmed n-type conductivity. Films with high mobility of $\sim 149 \text{ cm}^2/(\text{V s})$, carrier concentration of $\sim 1.0 \times 10^{20} \text{ cm}^{-3}$, resistivity of $\sim 4.0 \times 10^{-4} \Omega \text{ cm}$ and high figure of merit of $\sim 1.02 \times 10^{-2} \Omega^{-1}$ were observed for post-annealed films (0.5 at% Mo). The obtained high average transparency of $\sim 83\%$ in the wavelength range 400–2500 nm confirms that transmittance is well extended into the NIR region.

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1. Introduction

Transparent conducting oxide (TCO) thin films are key materials in various optoelectronic devices such as thin film solar cells, light-emitting diodes, flat-panel displays and transparent thin film field effect transistors (TTFTs) [1,2]. Such devices require TCOs with high carrier mobility (μ) and high transmittance (T) in the entire visible–near-infrared (NIR) region without sacrificing electrical conductivity (σ) [3–5]. Therefore, research in this direction is strongly accelerated by rapidly rising demands for enlargement of display size and to extend the T from the visible to NIR region. For example, solar cells having wide-range spectral sensitivity suffer from optical loss in the NIR region due to free carrier absorption (α) in the conventional TCO electrodes such as Sn-doped In_2O_3 (ITO), F-doped SnO_2 and Al- or Ga-doped ZnO films [6]. This has forced the photovoltaic research on developing visible to NIR transparent TCOs for use in optoelectronics devices such as multifunction Si or $\text{CuIn}_{1-x}\text{GaSe}_2$, while organic and die sensitized solar cells involve the usage of visible to NIR solar energy [7–9]. Further, high μ TCOs are required to derive high current and fast device operating speeds for TTFT display applications [2]. Since μ is a measure of the efficiency of electron movement (in solids) under the application of an electric field,

high μ results in enhancing the device speed and thereby making the films to sustain high currents. In devices, high current effects quick charge or discharge of capacitive loads to yield high operating speeds. Basically, high μ translates into a wide range of application possibilities [10].

In recent years, the research community makes ample efforts to develop new TCOs with superior electrical and optical properties in comparison with conventional ones. Attempts have been made to prepare TCOs with high μ to increase σ without sacrificing T . Increasing σ by increasing carrier density (n) in TCO results in deteriorating T . As confirmed in Drude model computer simulations [3], increasing σ without compromising T is possible only by increasing μ rather than n [3]. Alternatively, an increase in T can be achieved without deteriorating σ but by decreasing n as follows:

$$\sigma = ne\mu = \frac{ne^2\tau}{m_c^*} \quad (1)$$

where μ is a function of electron relaxation time (τ) and carrier effective mass (m_c^*). The degree of scattering increases with increasing n but with decreasing τ . A longer τ and/or smaller m_c^* can yield higher μ . Increasing τ involves attacking extrinsic issues, whereas decreasing m_c^* requires finding new semiconductors with lower m_c^* that cannot be externally modified. A decrease in m_c^* will shift free-carrier absorption band towards the visible spectrum [5]. Hence, the widespread consensus on the best approach for enhancing the quality of TCOs is to improve μ . Increase in τ

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reduces scattering effect of the doping element, whereas the dopant must provide a large electronic valence difference between the dopant and substituted ions. This would allow enough n to achieve high μ and low α with low impurity atom concentration in the solid matrix. Increasing μ not only improves the electrical properties but also improves T until the NIR region due to lesser n . Indium molybdenum oxide (IMO) thin films have the unique combination of low resistivity (ρ), high μ and high visible to NIR transmittance. However, available reports on these films have not been studied in detail on these aspects [11–13]. The authors have highlighted this point in their recent short communication [14]. Further, the available reports confirm inadequate work on these films in employing the conventional and economic spray pyrolysis technique [15,16]. An attempt is made in the present study to obtain the aforementioned unique combination of properties in IMO films deposited by spray pyrolysis experimental technique.

2. Experimental details

The authors have earlier reported IMO films [17] deposited by spray pyrolysis technique [18], where InCl_3 was dissolved using methanol as solvent. Joseph Prince et al. [19] have demonstrated that indium oxide (IO) films with good properties can be grown at relatively low temperature (380 °C) using ethanol–water mixture as a solvent. Consequently, the films reported in the present study were deposited on Corning-1737 substrates using ethanol: double distilled water (1:3 ratios) as the solvent. The films deposited with substrate temperature (T_s) ranging 450–500 °C were opaque with milky white in color [19], and have significantly deteriorated T . A probable reason is that pyrolytic decomposition is taking place in the hot air layer above the substrate [20] in this T_s range, which is probably substantiated by the transparent films when the T_s is reduced to 400 °C. Hence, the films reported in this study were all deposited at 400 °C. Further, molybdenum (Mo) doping range in the solution was narrowed between 0 and 1 at% (in comparison with our previous work [17]) in order to study the effect of doping in detail. The value of Mo doping referred throughout this work is the ratio of Mo to In in the spray solution. InCl_3 and MoCl_5 were used as precursors for the source of In and Mo, respectively. The estimated quantity of these precursors was dissolved in ethanol (99.9%) and doubly distilled water. Optimized spray parameters such as spray nozzle–substrate distance (30 cm), spray angle (about 45°), spray time (1 s), spray interval (20 s) and carrier gas pressure (compressed air, 40 kg/cm²) were kept constant. Further, the deposited films were post-annealed in vacuum ($\sim 1 \times 10^{-4}$ mbar) at 550 °C for 45 min following the experience obtained from the literature survey [21]. These annealed IMO films were characterized for their structural, electrical and optical properties and the results are discussed in this work.

X-ray diffraction (XRD) patterns were obtained using the computer controlled PAN Analytic X pert PRO X-ray diffraction system (Cu K α with a wavelength of 1.5406 Å) in Bragg–Brentano geometry ($\theta/2\theta$ coupled). The electrical parameters were measured using Hall measurement setup (ECOPIA-HMS 3000 Hall system—room temperature) with a permanent magnet of 0.57 T. Hall voltage of 1 mA and delay time of 0.5 s were fixed constant. The T was measured using a double beam spectrophotometer (Shimadzu UV-3100) with a bare substrate in the path of the reference beam. Hence, all the transmittance spectra reported in this study refer only to film transmittance. Thickness of the films was measured by the reflection method using filmetrics F20, which is in agreement with values obtained by the weight-gain method. Surface microstructure was examined by scanning electron microscopy (SEM, FSI Serion). Composition of different

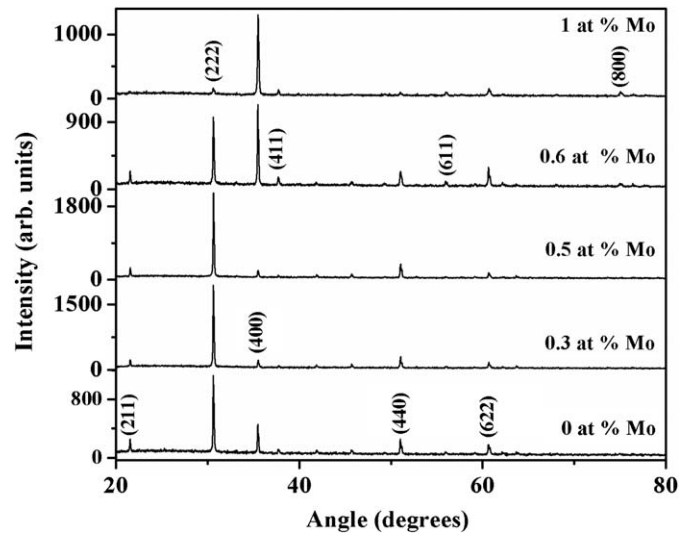


Fig. 1. XRD patterns of post-annealed IMO thin films with different Mo concentrations.

constituents in the deposited films was estimated using energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

Thickness of all the films was found to be ~ 300 nm. XRD studies confirmed the cubic bixbyite structure of polycrystalline IO [22] and the obtained patterns are shown in Fig. 1 as a function of Mo doping. The obtained diffraction peaks were identified as marked on the corresponding XRD patterns (Fig. 1) by matching with the standard data [22]. The obtained diffraction peaks substantiate the polycrystalline nature of the IMO films, while their intensities suggest a more uniformly distributed orientation of crystallites. It is perceptible that the (2 2 2) peak emerges as the strongest orientation for IO films, which is retained until 0.5 at% of Mo doping. Increased intensity of (2 2 2) diffraction peak (I_{222}) probably suggests an improvement in crystallinity. When the Mo doping is increased to 0.6 at%, the intensity of (4 0 0) diffraction peak is significantly increased and it tends to emerge as the strongest orientation when the Mo doping is increased to 1 at%. This change in the strongest orientation due to the variation in Mo doping is discussed in our earlier work [17]. In the present work, the change in strongest orientation of XRD peak is correlated with the change in grain shapes as observed by SEM analysis (explained later). Elangovan et al. [23,24] have made similar correlations for fluorine and antimony doped tin oxide ($\text{SnO}_2:\text{F}$ and $\text{SnO}_2:\text{Sb}$) thin films prepared by spray pyrolysis technique. Irregular shaped grains are strongly oriented along the (2 2 2) diffraction peak, and regular octahedron shaped grains are oriented along the (4 0 0) peak. This probably indicates that the amount of Mo doping influences the evolution of microstructures and thereby reflects on the strongest orientation observed by XRD studies. The foregoing discussion leads to the conclusion that the intensity of diffraction peaks can be varied and the strongest orientation can be shifted between the planes by varying the Mo doping level.

The data extracted from the XRD analysis are summarized in Table 1. The full-width at half-maximum (FWHM) value obtained from (2 2 2) and (4 0 0) diffraction peaks of IMO thin films ranges between $\sim 0.0669^\circ$ and 0.2676° for the various Mo dopings. The crystalline size (L) was calculated using Scherrer's formula [25] and the obtained values change as a function of Mo doping. The

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