MoO_3- In_2O_3 BINARY OXIDE THIN FILM DEPOSITION FOR TCO APPLICATION IN SOLAR CELL

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ABSTRACT

Transparent conducting binary MoO_3-In_2O_3 as-deposited and annealed thin films, well suited for window layers were fabricated by employing a simple and inexpensive spray pyrolysis technique using perfume atomizer. The effect of Mo concentration (0.2-3 at. %) on the structural, morphological, optical and photoluminescence properties of the binary oxide thin films have been investigated. XRD reveals that the films are polycrystalline with cubic bixbyite structure. An average visible optical transmission of 97% obtained and is well extended in NIR region. A wide optical band gap (for as-deposited-2.84 eV, annealed-3.61 eV) makes the film suitable for solar cell applications. The scanning electron microscope (SEM) measurements show that the surface morphology of the film changes with Mo concentration and AFM ascertains the surface roughness.

Keywords: MoO_3-In_2O_3 binary films, Optical properties, Perfume atomizer, Solar cell, TCO.

I. INTRODUCTION

In recent years, the research on the development of novel transparent conducting oxides (TCO) has been intensified due to their potential applicability in areas like flat panel displays, smart windows, organic LEDs and Solar photovoltaics [1]. Therefore, research in this direction is strongly accelerated by the rapidly rising demand for enlargement in display size and extension of transmission from the visible to NIR region. For instance, the 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 [2]. This urged the photovoltaic research for developing visible to NIR transparent TCOs for its usage in optoelectronics devices such as multifunction Si or $CuIn_{1-x}$ $GaSe_2$, while organic and die sensitized solar cells involve the usage of visible to NIR solar energy [3-5]. Hence, motivated by recent demands, the preparation of the simplified spray deposited MoO_3-In_2O_3 films with low optical absorption and longer wavelength transparency as a function of Mo doping concentration has been considered and their related results are presented. A simple and elegant technique employing a perfume atomizer has been chosen to deposit MoO_3- In_2O_3 films and to the best of our knowledge, the study of MoO_3- In_2O_3 thin films using a cost-effective simplified spray pyrolysis [6] has not yet reported.

II. EXPERIMENTAL DETAIL

The Indium III chloride ($InCl_3$) was used as the source for indium, whereas the molybdenum concentration was achieved using Molybdenum Penta chloride ($MoCl_5$). Microscopic glass plates ($25\times25\times1.2mm^3$) cleaned with acetone were used as substrate. The substrate temperature was fixed at 400° C and $InCl_3$ [0.1 at. %] was dissolved in 2ml of concentrated HCl acid by heating at 90° C for 10 min. The resultant transparent solution diluted with methanol formed the starting solution. For molybdenum oxide, the required amount of $MoCl_5$ was dissolved in double distilled water, which was then added to the starting solution to make up the final spray solution. The as deposited Molybdenum and indium oxide samples were then annealed at 600° C for 30 min in vacuum chamber to investigate the annealing effect.

The X-ray diffraction (XRD) patterns were obtained using the computer controlled Phillips x'pert PRO XRD system (Cukα radiation; λ=1.5405 Å) in Bragg-Brentano geometry ($\theta/2\theta$ coupled). The Joint Committee on Powder Diffraction Standards (JCPDS) database from the International Centre for Diffraction Data (ICDD) was utilized for the identification of crystalline phases. The transmission data were observed in the range of 300-1100 nm using ultraviolet visible near infrared double beam spectrophotometer (Perkin Elmer). The surface morphology was recorded by employing scanning electron microscope (HITACHI S-3000H). Atomic force microscopic images were obtained using AFM Explorer (ThermoMicroscopes, Sunnyvale, CA, USA) and these were then analyzed to estimate the relative surface roughness.

III. RESULT AND DISCUSSION

3.1 XRD Analysis

MoO_3-In_2O_3 binary thin films prepared for different cationic ratios were characterized using XRD in order to get the information about the crystallographic evolution of spinel structure and orientation of crystallites. The XRD patterns of as-deposited and annealed MoO_3-In_2O_3 binary films are shown in Fig. 1(a) and (b). The samples of as-deposited MoO_3-In_2O_3 binary films at different concentration with constant temperature 400° C are labeled as MI1, MI2, and MI3. The films prepared for the cationic ratio-0.2 at. % contains both In_2O_3 and MoO_3 phases and exhibited peaks at 2θ=12.76˚, 23.39˚, 25.67˚, 27.34˚ and 38.9˚ respectively for (0 1 1), (2 2 0), (6 0 2), (6 1 2) and (0 4 1) planes that correspond to molybdenum oxide phases(Fig. 1(a)). Although (0 2 0), (1 2 1) and (1 2 9) planes are similar to indium oxide phase, no change was observed in In_2O_3 and MoO_3 phases and also in diffraction planes even when the cationic ratios were increased to 0.25 and 0.3 at. %. The peak position of In, MoO_3 phases were compared with the standard card [97-064-4063]. The planes of MoO_3-In_2O_3 films coincide well with the JCPDS data [04-010-8422]. The intensity of diffraction peak has increased as the concentration level increased from 0.25 to 0.3 at. %. XRD patterns of as-deposited (Fig. 1(a)) MoO_3-In_2O_3 shows the presence of diffraction planes, which are not reported in earlier work [7-11].

The samples of as-deposited MoO_3-In_2O_3 binary films annealed at 600° C for 30 min are labeled as MIa1, MIa2 and MIa3 respectively to investigate the annealing effect. The annealed film prepared with 0.3 at. % contains both In_2O_3 and MoO_3 phases(Fig. 1(b)). In (0 1 1), (2 2 0), (6 0 2), (6 1 2) and (0 4 1), all these planes are coherent to molybdenum oxide phases. The planes (0 2 0), (1 2 9) and (6 4 0) are in indium oxide phase, and the same diffraction patterns and phases appeared even in 0.2 and 0.25 at. %. In 0.25 at. % one more plane (0 4 4) is found to be in indium oxide phases. At 0.2 at. % there are four more peaks, with (2 1 1) and (8 0 4) in indium oxide phase, remaining two planes (1 1 7), (2 2 3) in molybdenum oxide phase as shown in Fig. 1(b). The annealed binary films were oriented along (0 1 1), (6 1 2) and (6 0 2) planes in which (0 1 1) orientation is found to be more predominant. According to the literature, as the dopant occupies interstitial sites of the respective ion, there is a change in the intensity of preferred orientation. However, the dopant occupies additional interstitial sites which are unoccupied and more intense preferred growth takes place as reported by Agashe et al. [12].

In the present study, it seems that Mo replaces indium at its regular lattice sites upto 0.3 at. % of the Mo doping level. At higher Mo doping level, perhaps the Mo incorporated on additional interstitial sites results (0 1 1) plane which is more prominent in the films. The foregoing discussions lead to the comparison of as-deposited and annealed films. The diffraction peaks of annealed films are sharp and it shows better crystalline behavior than as-deposited films which is shown in Fig. 1(b). The particle size was evaluated using the full width half maximum (FWHM) data according to the Scherrer formulae [13].

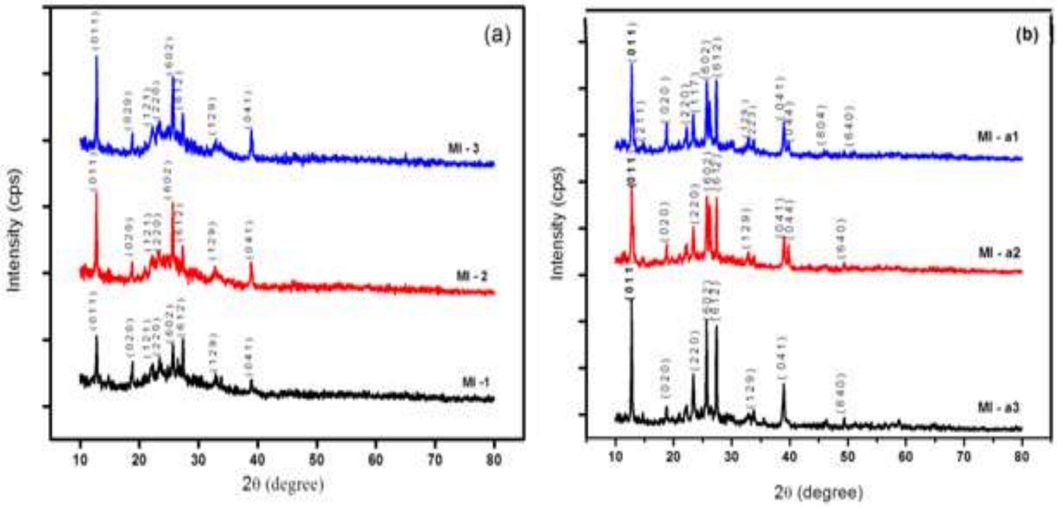

Fig. 1. XRD patterns of (a) as-deposited and (b) annealed MoO_3-In_2O_3 binary thin films.

The FWHM (in radians) is inversely proportional to the particle size and is related to the degree of crystalline in polycrystalline thin films [13]. The FWHM values decrease initially upto 350 nm thickness as shown in Fig 2.(a). The increase in grain size can be attributed to the improved crystallinity. As the degree of crystallinity of annealed films are better than as-deposited films, FWHM reaches film thickness of 812 nm [14] and is shown in Fig. 2(b). According to Liu et al.[15], the reason for the improvement in crystallinity is due to the increased ability of the atoms to move towards stable sites in the lattice. The lack of any peak shifting also supports this since incorporation of atoms into interstitial sites should result in some change in the overall lattice parameters of the polycrystalline structure.

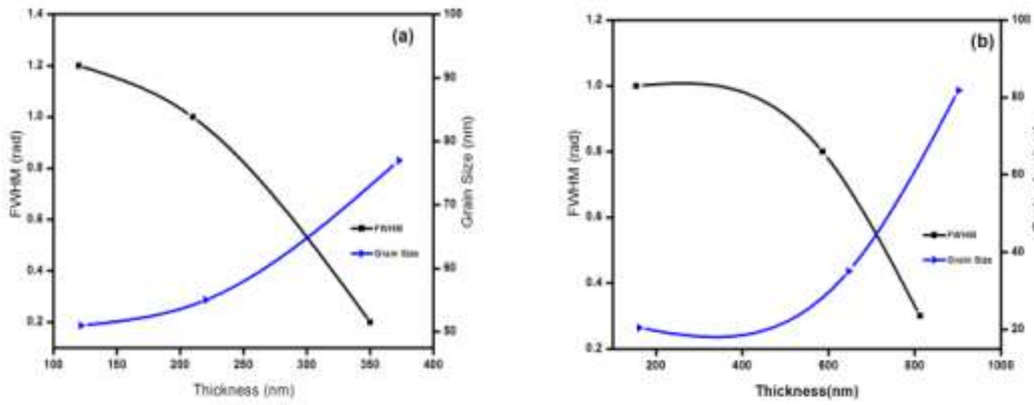

Fig. 2. Variation of FWHM and grain size as a function of thickness shown for (a) as-deposited and (b) annealed MoO_3-In_2O_3 binary films.

3.2 UV-Visible Spectra

The transmission spectra of as-deposited and annealed MoO_3-In_2O_3 binary thin films recorded in the wavelength range of 300-1100 nm is shown in Fig 3. (a) and (b). It is observed that as-deposited MoO_3-In_2O_3 films acquired transmittance ~51-79% in the visible region. A maximum average visible transmittance (AVT) of ~86% is observed at 800 nm for the films doped with 0.3 at. % and moderately higher transmittance 69-90% in the visible-infrared region and is depicted in Fig. 3(a). The transmittance is significantly increased upon annealing the MoO_3-In_2O_3 films at 600° C for 30 min. It is observed that the annealed MIO films have obtained transmittance 65-84% in the UV-Visible region and the maximum average visible transmittance (AVT) of 86% is observed at 675 nm and moderately higher transmittance 75-97% is obtained in the visible infrared region as shown in Fig. 3(b). The transparency of both as-deposited and annealed MoO_3-In_2O_3 binary thin films extends well into near-IR range. So, it is clear that all the samples have very high transmittance in the wavelength region ≥ 1000 nm. From the results of optical analysis, it is shown that the transmission rate is higher in the NIR region (97%), which is a better result obtained from our investigation as it has not yet been reported in earlier works [6- 10]. The optical band gap (E_g) is estimated from the plot of $(\alpha h\upsilon)^2$ *Vs* ($h\upsilon$). A value of 2.84 eV is obtained for as-deposited films while the band gap value got increased to 3.61 eV for annealed films. Hence, the wide band gap and highest transmittance of MoO_3-In_2O_3 binary films fabricated by simplified spray technique, make these films possible candidate for window layer of solar cells and also in optoelectronic and solar cell applications.

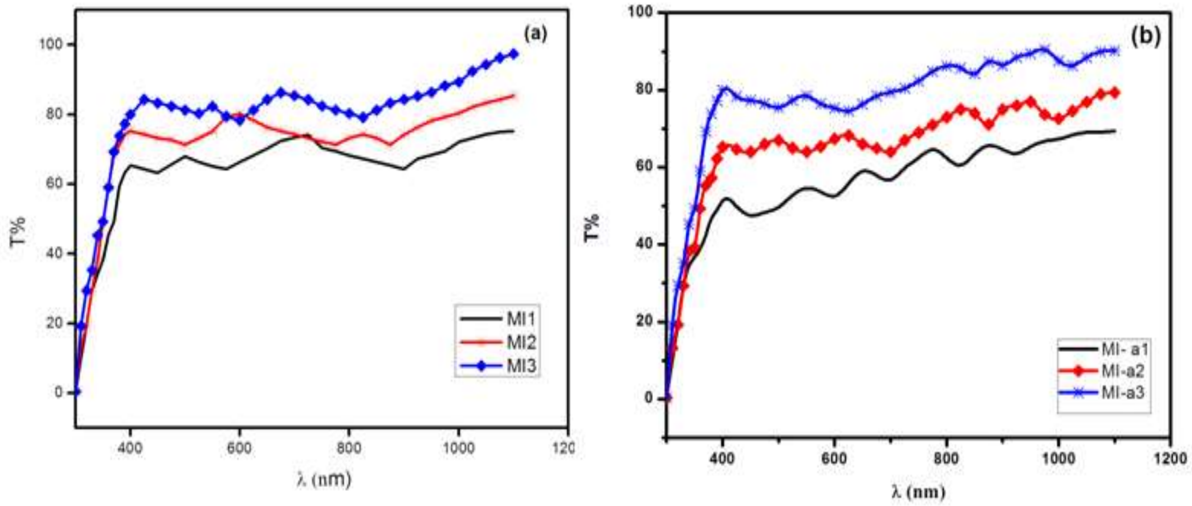

Fig. 3. Variation of transmittance (T %) with wavelength λ (nm) of MoO_3-In_2O_3 binary thin films for: (a) as- deposited and (b) annealed at 600° C for 30 min.

3.3 Surface Morphological Studies

3.3.1 AFM Studies

Surface morphology of the as-deposited and annealed MoO_3-In_2O_3 binary thin films were investigated using AFM technique. The AFM measurements have been performed on all films with scan area of 5µm×5µm. Fig. 4(a) and (b) show the three dimensional surface morphology of as-deposited and post annealed films respectively. The roughness of the film surfaces were calculated for all films and are found to influence by the use of precursor. AFM images of the as-deposited films reveal a discontinuous grain growth (Fig. 4(a)), while in annealed films the surface diffusion was activated and the surface morphology improves with distinct visible grain boundaries (Fig. 4(b)). This observation of enhanced crystalline nature is in good agreement with the XRD measurements(Fig. 1(b)). The as-deposited film exhibits the lowest roughness of about 12.786 nm, while the annealed film has highest roughness of 22.293 nm. Therefore, the annealed film has large size particles with roughness about 33.680 nm. The increase in the roughness of the films might be due to the re-arrangement of polycrystalline structure in grains with larger size [16], which is also indicated in XRD measurements. The calculated particle size from AFM measurements is higher than the values calculated from XRD studies indicating that these particles are probably an aggregation of small crystallites on the surface of the films.

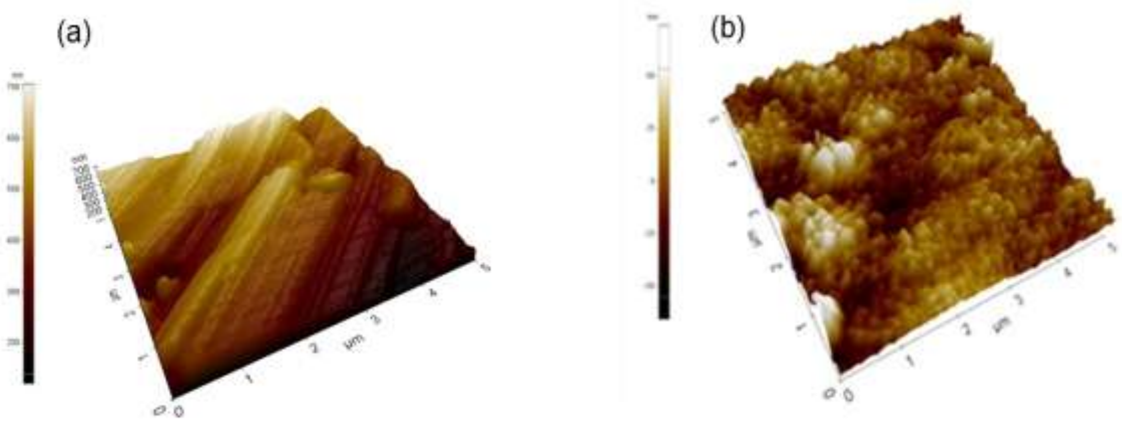

Fig. 4. AFM images of (a) as-deposited and (b) annealed MoO_3-In_2O_3 binary thin films

3.3.2 SEM studies

To probe the effect of the morphological properties of as-deposited and annealed MoO_3-In_2O_3 binary thin films, SEM studies are carried out. From these microscopic images Fig. 5(a) and (b), it is evident that there is small difference found from the films grown on as-deposited and annealed samples. It can be seen that the surface morphology of the films strongly depends on the concentration of the starting materials. The microstructure of the films consisted of many spherical grains distributed throughout the surface. The grain size of films of as-deposited was larger than that of the annealed film. However, the grain size became smaller with increased concentration because the grain growth was suppressed by the compression stresses generated due to the difference in the ionic radii of indium and molybdenum [17].

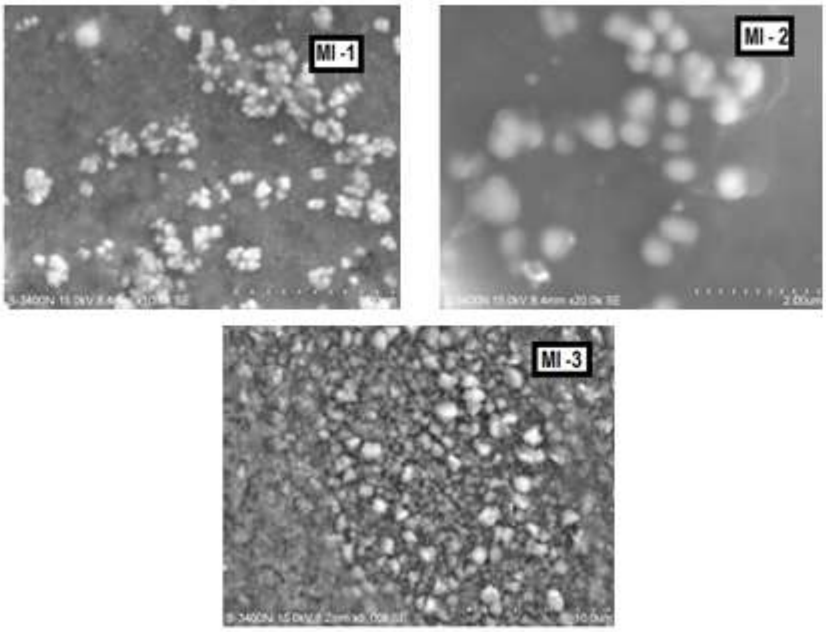

Fig. 5(a). SEM images of as-deposited MoO_3-In_2O_3 binary thin films.

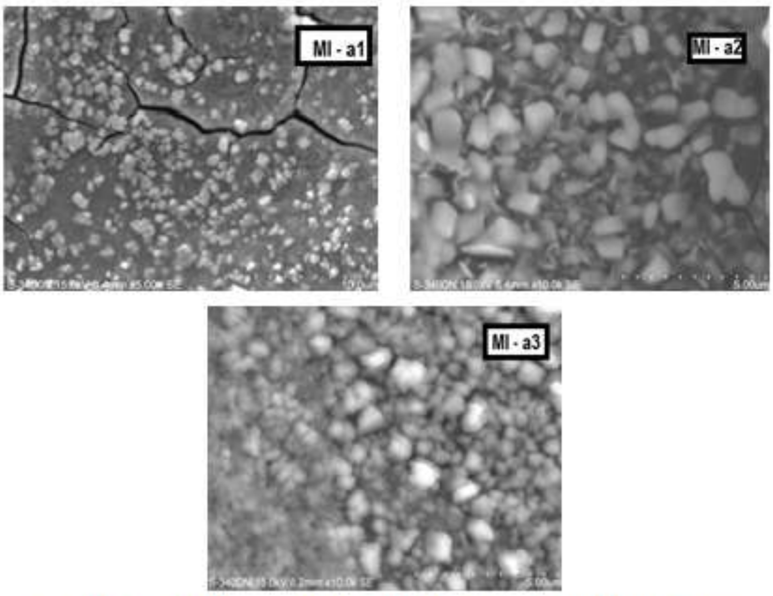

Fig. 5(b). SEM images of annealed MoO_3-In_2O_3 binary thin films.

IV. CONCLUSION

MoO_3-In_2O_3 binary films with good structural, surface morphological and optical properties, suitable for solar cell applications were obtained using an inexpensive, simplified spray pyrolysis technique using perfume atomizer. The XRD studies confirm the polycrystalline nature of In_2O_3 films with cubic bixbyit structure and the presence of Mo or MoO_3. The average NIR transmission is found to be 97% in the wavelength ranging between 1000 and 1100nm and gets increase with increase in concentration. The range of optical transmission and optical band gap (for as-deposited-2.84 eV, annealed-3.61 eV) in these films suggests that the deposited film will be useful in enhancing the performance of optoelectronic device such as TCO application in thin film solar cells. The SEM measurement showed that, upon increasing the concentration, the surface morphology of the films becomes uniform and grains are distributed uniformly throughout the surface. AFM pictures show the porous nature of the films of samples MI3 and MIa3, which make them suitable for gas sensing. The increased thermal energy and larger mobility acquired by the grains during annealing show different surface morphologies. This technique attracts massive production of low-cost, large area MoO_3-In_2O_3 binary thin films for solar cell applications.

V. ACKNOWLEDGEMENT

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