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STUDIES ON SN DOPED IN2S3 THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION

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ABSTRACT: In modern times, chemical techniques are frequently employed to create metal chalcogenide thin films due to their affordability, ease of usage, and suitability for large-scale depositions. In the present study, Sn-doped In2S3 (In2S3: Sn) layers are preparedusing the chemical bath deposition (CBD) method. In2S3: Sn is one of the cutting-edgematerials utilized to create hetero junction solar cells. In the current work, Sn-doped In2S3 thin films at different dopant concentrations (0 – 5.5at. %.) Were deposited onto corning glass substrate at a bath temperature of 70^{o}C. Using the suitable methodologies, the chemical composition, microstructure, optical properties, and electrical properties were investigated. All the layers exhibited cubic-In2S3 structure with (311) as a highest peak.There has been no obvious shift in the preferred orientation with Sn- dopant composition. In the visible spectrum, the films' average optical transmittance was found to be80%.Ata dopant concentration of 4.5 at.%, a reduced resistivity of 3.58x10^{2} cm was obtained. We have reported and discussed the change of grain size, electrical resistivity and optical band gap with doping concentration.

Keywords: Sn doping, In_2S_3 thin films, chemical bath deposition, optical and structural properties.

1. INTRODUCTION

One of the most promising polycrystalline devices for producing electricity among thin film solar cell technologies is the Cu(In, Ga)Se2 based solar cell. Over thedecades the mostly used buffer layer in CIGS solar cell structure is CdS with the reported conversion of 22.6%. However, the sage of CdS limit the photovoltaic device performance due to the toxicity connected with Cd element that harmful to the environment and has the potential cause to manufactures in large scale production.

As a result, significant efforts are being made to resolve this environmental concern with a substitute. In this direction, it is desirable to substitute CdS with other semiconductor material that has a wider band gap. Indium sulphide is one of themost promising alternative buffer layers to CdS. In 2S3, a compound semiconductor that belongs to III-VI group, has optical and electrical characteristics that are comparable to those of CdS. It crystallizes in three polymorphic forms such as α, β and γ dependingupon their preparation conditions. Among these three forms, □-In2S3 is the most stable structure at room temperature. In2S3finds many applications in the preparation of greenand red phosphors and in the manufacture of picture tubes for color television and drycells. In addition to its stability, In2S3 has an attractive fundamental property suitablefor device applications, particularly for photovoltaic cells as a buffer layer as well as window layer. In our earlier investigations, we have studied un doped indium sulfide layers grown by close spaced evaporation that demonstrated very favorable properties for use as a buffer layer in solar cells. These layers showed high resistivity although the composition and thickness are modified. It is highly beneficial to use conductive layers

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of In_2S_3 as a window layers in order to reduce the inter face defects and band bending at the buffer/window interface. Thus, the chemical bath method (CBD) wasused in this work to deposit pure and Sn-doped In_2S_3films on corning glass substrates, and the impact of dopant concentration on the physical properties of In_2S_3layers was investigated. Among the various methods used to deposit In_2S_3 films, the CBD approach is an easy and affordable way to produce large area thin films compared to other vacuum processes. A uniform and pin hole free films are prepared using CBD method. Usually, this technique is used at room temperature and atmospheric pressure. The chemical reaction that took place in aqueous solution acts as a driving force for film growth in this technique, which was widely used for the deposition of metal chalcogenides. The basic reaction species are ions instead of atoms and the processing parameters such as precursor concentration, reaction temperature, time etc. are easily controlled. The technique requires very simple equipment, a hot plate with magnetic stirrer and uses cheap chemicals as precursors. The doping of In_2S_3films toalter their structural and electrical properties has not received much attention in theliterature. Barreau et al. reported the incorporation of Na on In_2S_3 films that resultedin widening the energy band gap with better conductivity. Becker et al. prepared Sn-doped In_2S_3filmsbychemicalvaportransportmethod.Thephysicalandopticalproperties of Sn doped In_2S_3thin films by vacuum thermal evaporation was reported by Alsulamei et al Mathew et al studied Ag-doped In_2S_3 films by spray pyrolysis and they obtained enhanced crystallinity, conductivity and photosensitivity. The present paper reports on the dependence of composition, microstructure, optical and electrical properties of Sn-doped In_2S_3 films grown by CBD method.

2. EXPERIMENTAL DETAILS

Using the CBD approach, thin films of In_2S_3 were formed onto glass substrates atvarying concentrations of Sn doping, ranging from 0 at. %. to 5.5 at. %. Acetic acid (AcOH) was utilized as a complexing agent of the metallic In^{3+} ion. The samples weregenerated by CBD from aqueous solutions of 0.025 M indium chloride ($InCl_3$) and 0.5 Mthioacetamide (TA) (CH_3CSNH_2) as sources for In^{3+} and S^{2-}, respectively. Tin chloride ($SnCl_2$: $2H_2O$) was used as the dopant source, and the amount of Sn-chloride needed foreach doping concentration was adjusted accordingly. A few drops of HCl were added to the solution to bring its pH down to 2.5. The low pH is necessary to avoid the hydroxides in the precipitate. The solutions were stirred thoroughly using a glass rod at each stage to ensure a homogenous mixture of the solution. The bath composed of different reaction mixtures for In, Sn and S with appropriate volumes. The ultrasonically cleaned substrates were vertically positioned within the beaker holding the solution. For a reaction time of40 min, the deposition was done a ta bath temperature of 70^0C. The growth of In $2S_3$ films occur either by condensation of In and S ions on the substrate surface or by the adsorption of colloidal particles. Once the samples were deposited, they were removed, cleaned with de-ionized water to get rid of the powder precipitates that had adhered loosely to the solution, and then dried. The films were annealed at 250 ^{o}C for 1 hour in a tubular furnace under argon flow. In order to explore the composition, microstructural, optical, and electrical properties, the deposited films were analyzed.

The deposited films were characterized in order to look into their optical, electrical, microstructural, and compositional characteristics. The energy dispersive X-rayanalyzer (EDAX) from Oxford Instruments was used to determine what was contained in each layer. The crystallinity of In_2S_3 thin films was evaluated with an X-ray diffractometer equipped with a Cu-Kf_0 radiation source (λ=1.54 Å). The morphological characteristics of the films were assessed with a Ze is sEVO50 scanning electron microscope (SEM). To measure optical transmittance, a Hitachi UV-Vis-NIR spectrophotometer was used. Silver flakes were used as the electrodes in a four-probe method for the electrical characterization.

3. RESULTS AND DISCUSSION

The grown films appear in pale yellow color and were strongly adherent to the substrate. Because the films were made without the use of a vacuum, the surface contamination caused by CBD and/or the incomplete reaction of the bath mixes might be the reason for the presence of oxygen in the layers.

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The chemical composition of Sn-doped In_2S_3films grown at different dopant concentration was determined using EDAX analysis. Fig.1 shows the EDAX spectra of Sn-doped In $_2S_3$films at a dopant concentration of 4.5 at.%. The EDAX analysis primarily identified In, S, and Sn elements, respectively. The chemical composition of the as-deposited film was found to be S =53.76 *at*. %and In = 46.24*at*. % where as for doped layers the atomic percentage of the elements were S = 53.73 *at*. % and In = 41.89*at*. % and Sn = 4.38 *at. %*. Because the films were made without the use of a vacuum, the surface contamination caused by CBD and/or the incomplete reaction of the bath mixes might be the reason for the presence of oxygen in the layers. The presence of Sn peaks in the EDAX indicates the incorporation of Snin to the hostlattice sites.

The low crystallinity of the layers caused due to some amorphous broadening in the as-grown films and no well-resolved peaks were seen, which inhibited determinationof the structure of the In $_2S_3$ films formed from the bath. In this view, the films wereannealed in furnace at a temperature of 250 ^oC for 1hour and the corresponding X-ray diffraction patterns of Sn-doped In_2S_3 films prepared for various dopant concentrations is shown Fig. 2. It clearly shows that the dopant concentration influences the formed layers' crystalline nature. All the films prepared by CBD method exhibited thepolycrystalline cubic phase of □-In $_2S_3$ structure (JCPDS#32-O46). A comparable result of cubic β-In_2S_3 structure was observed by Yahmadiet. al for the films grown by CBD method. It is observed from Fig.2 that all the films exhibited the (311) peak as thepredominant at □27.65□ of cubic In_2S_3. Alsulamei et al. observed similar behavior related to preferred orientation for Sn doped In_2S_3 films deposited using vacuum thermalevaporation. In relation to the concentration of dopants, the layers did not exhibit any appreciable change in growth direction. There was an increase in the (311) plane's intensity when the Sn-dopant percentage increased to 4.5 at. %; this could be because the films' crystalline equality improved. Analogously, MKranietal reported thecrystallinity of Sn-doped In_2S_3 films made by chemical spray pyrolysis increasing withdopant concentration. The crystallinity of the films appeared to decrease at higher dopant concentration, > 4.5 at. %, which might be due to the formation of powdery colloids. However, there was no change in the position of the preferred (311) peak as the levels ofSn-doping in the layers rise. This is probably due to the similarity in the ionic radii of In^{3+}(0.71 Å) and Sn^{4+} (0.81 Å). The average crystallite size (D) of the films was calculatedusingDebye–Scherrer formula[11] using the full width at half maximum of the (311)

peak for all the samples. The evaluated average crystallite size was varied from 18.3 nmto 54.8 nm with increase of Sn dopant concentration from 0 at.% to 4.5 at.%. These films showed maximum crystallite size of 54.8 nm ata dopant concentration of 4.5 at.%, beyond which the crystallite size decreased. This implies that the level of Sn-doping in In $_2S_3$films highly influences the growth kinetics of these films. The change incrystallite size with concentration of Sn dopants is similar to that of the literate data. The grains were crystallized in cubic□-In_2S_3structure and the evaluated lattice parameters were a = b = c =10.723Å. The XRD spectra showed that the dopant species were uniformly distributed throughout the host lattice matrix because there was no other peak in addition to In_2S_3. Fig.3 shows the SEM images of the films synthesized at different Sn-doping densities. There were no voids or faults on the film surface, and the grains in each layer were continuous and homogeneous. The surface morphology of the samples is found to be changed with dopant concentration. The rise of 'Sn' doping concentration in the films, the surface of the layers was found to be smooth and the grains became irregular in shape. The addition of dopant changed the grain morphology from spherical shape to whiskers shape with the appearance of rod/stick like structures unevenly distributed over the film surface. The presence of different grain shapes in the layers could be because of various physical and chemical states of the reactants arriving at the substrate surface during the course of chemical reaction, which led to different growth mechanisms and morphologies. The grain size was found to be maximum at a Sn-doping concentration of 4.5 *at.*% and further at higher dopant level the grain size started to decrease. Grain size and shape variations with doping concentration suggest that the addition of "Sn" to the solution may have some impact on the chemical reaction, nucleus formation, and coalescence phases of the film growth. For In-doped CdS films, a similar result of grain development with a change in dopant concentration was reported.

The optical transmittance spectra of undoped and various Sn-doped In $_2S_3$ filmsthat were annealed for one hour

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at 250°C are displayed in Figure 4. In the visible range, pure In_2S_3 films have an average transmittance of roughly 68%, while 4.5 at.%Sn-doped films had an 80% transmittance that dropped to73% as the doping level was increased to 5.5 at.%. Better crystallinity, structural homogeneity, and reduced scattering effects maybe the causes of the greater transmittance shown in the layers. The greater defect density that caused the layers' poor crystallinity may be the cause of the transmittance decrease at higher doping concentrations. The optical energy band gap, *Eg* of the films was determined using the relation

$$\alpha h\upsilon = A\left(h\upsilon - E\right)^{1/2}, \qquad (1)$$

Where *A* is constant depending on the transition probability. The value of Eg was determined by extrapolating the linear portion of the $(\alpha h\upsilon)^2 Vs h\upsilon$ plot onto the energy axis. The in set of Fig.4shows the $(\alpha h\upsilon)^2 h\upsilon$ plot for In_2S_3 layer that had a Sn concentration of 4.5%. The evaluated band gap decreased with the increase of Sn concentration. The variation of band gap is found to be nominal within therange,2.68–
2.61 eV for Sn-dopant concentration upto 4.5 at.%, while a considerable decrease of band gap to 2.23 eV was observed for doping concentration, > 4.5 at.%. The reduction in band gap at > 4.5 at.%. dopant concentration might be explained due to the formation of additional phases in the bath that results in the generation of structural defects such as voids and dangling bonds, leading to the formation of undesirable localized states in the band gap. However, the X-ray diffraction spectra didn't show any additional phases due to their limited presence below the detection limit in the instrument.

Using the four probe method, the films' electrical resistivity was examined. The resistivity of the un doped films was $2.65x10^4\Omega$cm, which decreased to $3.58x10^2\Omega$cmwith the increase of dopant concentration up to 4.5 at. % and it improved thereafter with the rise of doping. The change in resistivity with dopant concentration can be explained in terms of solubility limit of the precursor solutions. For dopant concentrations lowerthan 4.5 at.%, Sn substitutes In atom in In_2S_3 lattice contributing an extra electron to theconductionbandasthevalencedifferencebetweenSn^{4+}andIn^{3+}is1.However,duetothe limited solubility of Sn, the dopant atoms are unable to occupy the indium sites in theIn_2S_3 lattice after a certain level of doping. Alternatively, intermediate precipitates can beformed in the solution and hence the surface of the film is found to be non-uniform and showed the presence of island like structures at higher dopant concentrations > 4.5 at.%. Therefore, the reason for the rise in resistivity at higher doping levels could be attributed to the formation of additional secondary phases that might result in impurity / grain boundary scattering. A detailed analysis of the electrical properties is necessary to find out the scattering mechanisms that are under progress.

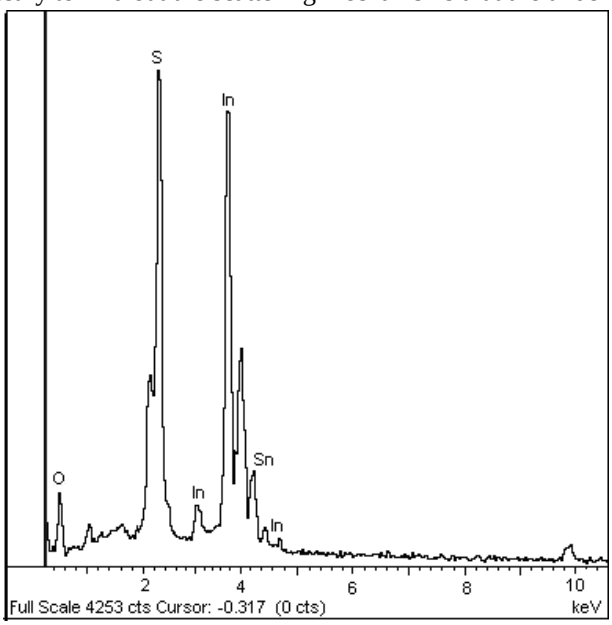

Fig.1.EDAX spectra of Sn-doped at 4.5at.% In $_2S_3$ film annealed at 250°C

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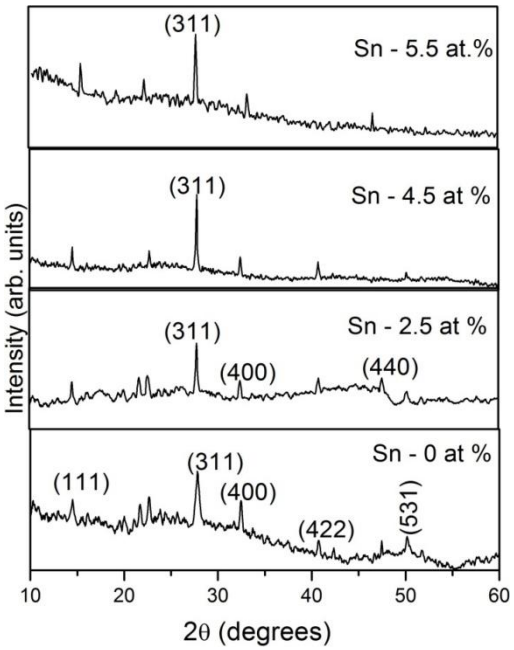
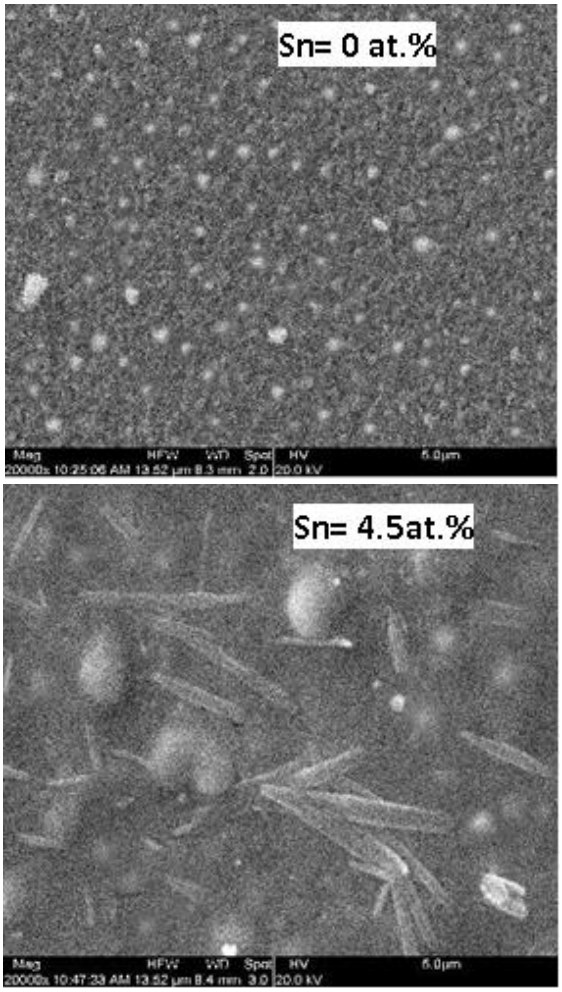


Fig.2.XRD profiles of Sn doped In 2S3 films



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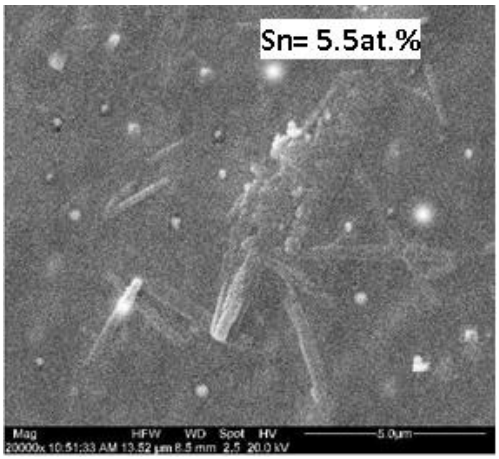

Fig.3.SEMimagesofIn2S3: Sn films

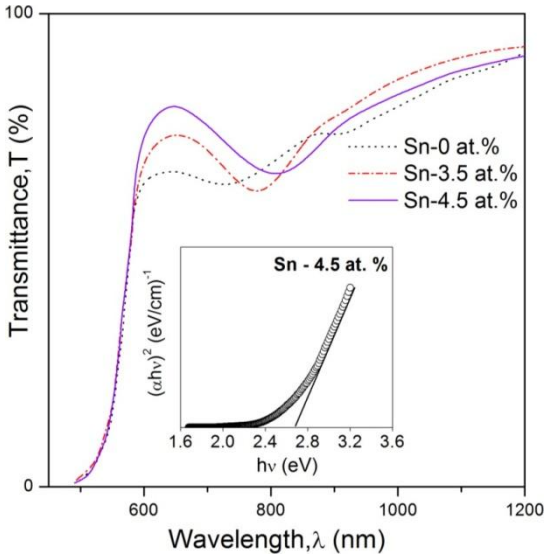

Fig.4.Optical transmittance Vs wavelength spectra of In2S3: Sn films. (Inset shows $(\alpha h\nu)^2$ vs$h\upsilon$ plot for In 2S3:Sn for 4.5at.%).

4. CONCLUSION

Chemical bath deposition has been used to create tin-doped In2S3films with varying Sn-dopant concentrations ranging from 0 to 5.5at.% at a constant bath temperature of 70°C. With the cubic β-In 2S3 structure, all the layers showed a strong (311) plane as the preferred orientation. The crystallinity increases as the "Sn" composition increases, and at a Sn doping of 4.5 at.%, the average crystallite size was found to be 54.8 nm. SEM micrographs revealed that the layers had irregular grains with the presence of stick type structures which were unevenly distributed on the film surface. At a 4.5 at.% Sn-dopant concentration, the films had an average optical transmittance of80%anda2.63eVbandgap.Thesefilmshadaminimum electrical resistivity of3.58x10^2ohm-cm.

CRediT author statement

RN conceptualized, performed the series of experiments, SEM characterization and also writing the original manuscript though vs worked on the various data evaluation andanalyses.TSR participated in the optical data processing and characterization.GPR conceptualized, performed the XRD analysis of the data, including fitting and discussion.KTR conceptualized, reviewed, and edited.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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