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Effect of Complexing Agent on the Structural, Optical and Electrical Properties of Polycrystalline Indium Sulfide Thin Films Deposited by Chemical Bath Deposition

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Indium sulfide (β-In_2S_3) thin films are synthesized by chemical bath deposition method using three different complexing agent volumes, triethanolamine (TEA) (0.30, 0.45, and 0.60 ml). The effect of complexing agent on the structural, morphological, optical and electrical properties of chemically deposited indium sulfide (β-In_2S_3) thin films have been investigated in this work. The characterization of the present films is carried out using X-ray diffraction, scanning electron microscopy, UV-vis spectroscopy and electrical measurements. The structure of the films is polycrystalline with a cubic phase of β-In_2S_3. Firstly, the band gap of the film decreases from 3.74 eV to 3.15 eV by adding 0.30 ml TEA. Then, it increases to 3.79 eV with increasing TEA. Nevertheless, previously, the refractive index of the films increases from 2.13 to 2.67 for the 0.30 mL TEA and then it decreases to the value of 2.11 with increasing TEA. Extinction coefficient, real and dielectric constant of the films are calculated using the absorption and transmittance spectra. Firstly, the electrical resistivity of the films decreases from 3.46×10^8 Ω cm to 1.33×10^7 Ω cm by adding 0.30 ml TEA. Then, it increases to the value of 2.16×10^9 Ω cm with increasing TEA. Eventually, the more conductive film with worm-like morphology detected from the scanning electron microscopy is synthesized using 0.30 ml TEA. These results show that complexing agent has an important effect on the structural, morphological, optical and electrical properties of the deposited films.

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1. Introduction

In recent years, β-In_2S_3 thin films have been extensively studied as a window material in thin film solar cells due to its exceptional optical and electronic properties, non-toxicity, chemical stability, and low cost [1]. Because of having hazard to the environment, cadmium sulfide (CdS) has been replaced by β-In_2S_3 layer in the copper–indium–gallium–diselenide (CIGS) heterojunction in order to improve the solar conversion [2]. β-In_2S_3 is an n-type semiconductor that belongs to the III–VI group of compounds with an optical bandgap in the range of 2.00 eV–3.91 eV [3]. Because of its high photosensitivity and photoconductivity, this material has also attracted intense interest as a potential visible-light photocatalyst [4]. Pomaska et al. [5] fabricated chalcopyrite-based solar cells using In_2S_3 thin layers. The β-In_2S_3 exist in three crystallographic modifications α, β and γ. Cubic structure of β-In_2S_3 is a stable phase at room temperature. Thin films of this material have been prepared by different methods such as spray ions layer gas reaction (ILGAR) [5], radio frequency (RF) magnetron sputtering [6], chemical spray pyrolysis [7], sol-gel [8] and chemical bath deposition (CBD) [9].

Moreover, there are also other techniques for producing nanocrystalline structure of the III–VI and II-VI group of compounds such as dip coating [10], electrodeposition [11], electrospinning process [12], thermal barrier coatings [13], mechanical alloy [14] and two-step chemical etching process [15].

Among them, the CBD technique is a more attractive technology which is well suited for coating large surfaces, low temperature processing, simple and inexpensive. In this technique, the preparation parameters can be controlled easily such as precursor concentrations, bath temperature, pH, substrates and film thickness.

In this work, we report that β-In_2S_3 thin films are synthesized by CBD technique. The effects of complexing agent on the structural, morphological, optical, and electrical properties of the films are investigated. The structure properties of the samples have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Moreover, the optical parameters and electrical properties of deposited films are studied.

2. Experimental details

The β-In_2S_3 thin films are deposited onto microscope glass substrates (7.6 cm $\times$ 2.6 cm $\times$ 0.1 cm) at room temperature (30 °C) using CBD method. In the present work, 10 ml of 0.1 M indium chloride ($InCl_3$, Aldrich, > 99.99% purity), 3.15 M TEA ($(HOCH_2CH_2)_3N$) as a complexing agent, 20 ml of 0.2 M acetic acid (CH_3COOH, Merck, 100% purity) and 20 ml of 0.4 M thioacetamide (TAA, CH_3CSNH_2, Merck, ACS. Reag.) have been used. By adding deionized water, the total volume of the solution

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is completed to 50 ml. The films are obtained from the acidic bath (pH = 3.88). Cleaned substrates are placed vertically to the bottom of the beakers and waited for 69 h. After deposition, the films are rinsed with deionized water to remove loosely adhered particles on the film surfaces and then dried in air. TEA volume has been changed as 0.30, 0.45, and 0.60 ml to see the effect of complexing agent on the physical properties of the deposited films. Preparation conditions for deposited films are listed in Table I.

TABLE I

Preparation condition and EDS analysis [at%] of β-In_2S_3 thin films synthesized with various TEA volumes [ml]. pH=3.88, $T = 30\,^{\circ}C$, deposition time = 69 h.

TEA	Thickness [nm]	In	S	S/In
0.00	394	61.63	38.37	0.62
0.30	355	55.78	44.22	0.79
0.45	300	70.52	29.48	0.42
0.60	247	56.41	43.59	0.77

The XRD measurements are carried out on a Bruker AXS D8 X-ray diffractometer with Cu K_α (λ = 0.15418 nm). Surface morphology of the films are taken on a EVO40-LEO SEM system and the composition ratio of In and S were obtained by energy dispersive X-ray spectroscopy (EDS). The room temperature optical absorption spectra in the wavelength range of 300–1100 nm is recorded by using a Perkin Elmer Lambda 4S UV-vis spectrophotometer. Keithley 2400 current–voltage (I–V) source measuring system using computer-controlled 2-point probe technique is performed to get electrical resistivity values of the synthesized films. The thicknesses of the films (t) are determined by gravimetric method using $t = m/\rho A$ with a precision microbalance, where m is the mass of the film, A is the surface area of the deposited film and ρ is the bulk density of cubic β-In_2S_3 (4.6 g cm^{-3}) [16].

3. Results and discussion

Figure 1 shows the SEM images of the films prepared with different TEA volumes. In Fig. 1a, we observe that the particles can be clearly distinguished with some clusters and the average grain size of the particles is measured as 24 nm. Figure 1b shows worm-shaped structure with cracks which has different morphological features from the others. In Fig. 1c and d, as TEA volume increases from 0.45 ml to 0.60 ml, these "worms" become shorter, being converted into grains whose diameter is about 66 nm and 22 nm, respectively. As can be seen from these morphologies, the smooth and well defined grains are obtained for the film synthesized at 0.60 ml TEA.

The compositional analysis of the films is obtained by EDS attached to the SEM and listed in Table I. The average ratio for atomic percentage of S/In is 1.5. This ratio changes in the synthesized films in the range 0.42–0.79. This means that our films show a large amount of sulfur deficiency.

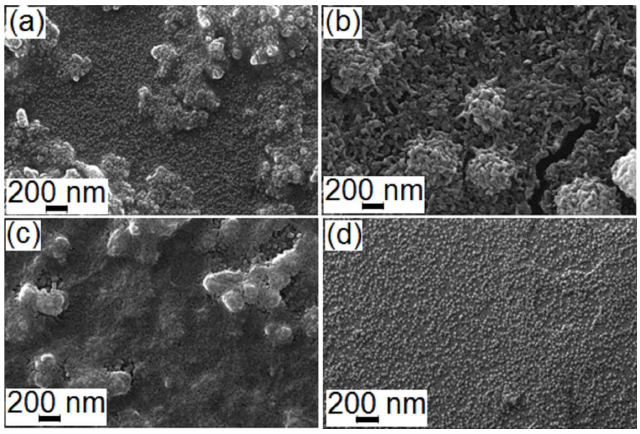

Fig. 1. SEM micrographs of β-In_2S_3 thin films obtained at 100k× magnifications synthesized with different TEA volumes: (a) 0.00 ml, (b) 0.30 ml, (c) 0.45 ml, and (d) 0.60 ml.

The structural analysis of the films is performed by means of XRD patterns. Figure 2 shows the XRD patterns of β-In_2S_3 thin films with different TEA volumes. As can be seen from these figures, the broad hump between 15° and 40° is due to amorphous nature of β-In_2S_3 thin films. When compared with the observed and standard 2θ values, it is concluded that the formed compound is β-In_2S_3 with cubic structure (PDF no. 32-0456). XRD results are consistent with previous data by Zhao Yang Zhong et al. [3], in which In_2S_3 thin films were synthesized by thermal evaporation process.

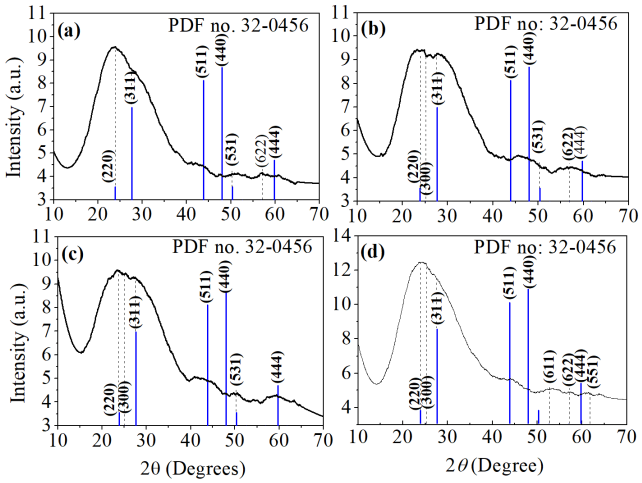

Fig. 2. XRD patterns of β-In_2S_3 thin films synthesized with various TEA volumes: (a) 0.00 ml, (b) 0.30 ml, (c) 0.45 ml, and (d) 0.60 ml.

The film thicknesses of chemically deposited β-In_2S_3 thin films are calculated by gravimetric method listed in

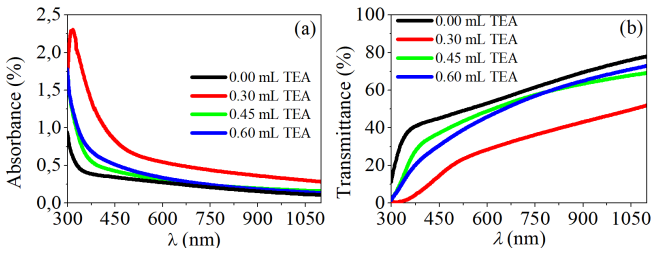

Fig. 3. (a) Absorbance and (b) transmittance spectra of β-In_2S_3 thin films synthesized at different TEA volumes.

Table I. The absorbance and transmittance spectra of the films with different TEA volumes are shown in Fig. 3a and b, respectively.

The absorption coefficient α is determined from the transmittance T spectra using the relation $I = I_0 \exp(-\alpha t)$ where t is the thickness of the film, I and I_0 are the intensities of the transmitted and incident light, respectively. The optical band gap of the β-In_2S_3 films is calculated using the relation given by $\alpha h\nu = B\left(h\nu - E_g\right)^n$ [17], where B is a constant and $n = 1/2$ for allowed direct transition. A plot of $(\alpha h\nu)^2$ against photon energy $h\nu$ shows a straight line portion, and the interception point of this linear portion on the energy axis at which $(\alpha h\nu)^2$ is equal to zero gives the direct band gap of the material. The $(\alpha h\nu)^2$ plots of the films deposited at different TEA volumes are shown in Fig. 4. Firstly, the band gap of the film decreases from 3.74 eV to 3.15 eV with adding 0.30 ml TEA. Then, it increases to 3.79 eV with increasing TEA volume. The estimated band gap values are listed in Table II. These results are in good agreement with previous works related to In_2S_3 thin films [3, 6, 7].

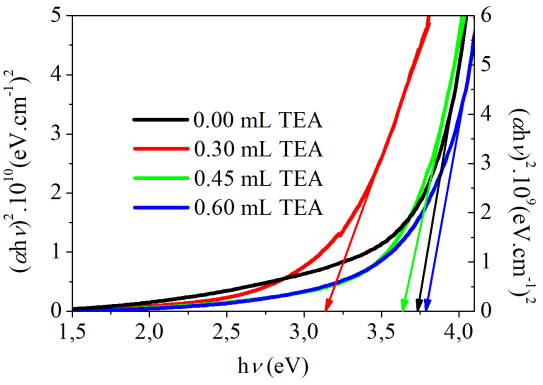

Fig. 4. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for β-In_2S_3 thin films synthesized at different TEA volumes.

The complex refractive indexes of the β-In_2S_3 thin films are described as follows:

$$\hat{n} = n(\lambda) + \mathrm{i}k(\lambda), \tag{1}$$

where n is the real part and k is the imaginary part of complex refractive index and given by $k = \alpha\lambda/4\pi$. The reflectance R is described by the Fresnel formulae [18]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \tag{2}$$

If one solves Eq. (2) via elementary algebraic manipulation, the refractive index is obtained as below

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2}. \tag{3}$$

The dependence of n on wavelength for the β-In_2S_3 thin films is shown in Fig. 5a. In the visible range of wavelength ($\lambda = 600$ nm), the refractive index varies between 2.11 and 2.67 in Table II. These values are in good agreement with the previous report (2.5) [19] and higher than in Ref. [20] (1.6–1.84). The variation of extinction coefficient with wavelength of the present films is also seen in Fig. 5b. At wavelength of 600 nm, it changes between 0.33 and 0.72 and these values are higher than the reported value (0.01) [20].

The real (ε_1) and imaginary (ε_2) dielectric constants are given by $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$, respectively. Figure 5c and d shows the plots of ε_1 and ε_2, respectively. At $\lambda = 600$ nm, it can be seen that ε_1 and ε_2 change between 4.03–6.62 and 1.40–3.87, respectively.

TABLE II

Film thickness and optical parameters ($\lambda = 600$ nm) of β-In_2S_3 thin films with various TEA values.

TEA [ml]	E_g [eV]	n	k	ε_1	ε_2	ρ [$M\Omega$cm]
0.00	3.74	2.13	0.33	4.44	1.40	346
0.30	3.15	2.67	0.72	6.62	3.87	13.3
0.45	3.64	2.15	0.49	4.38	2.10	557
0.60	3.79	2.11	0.64	4.03	2.72	2160

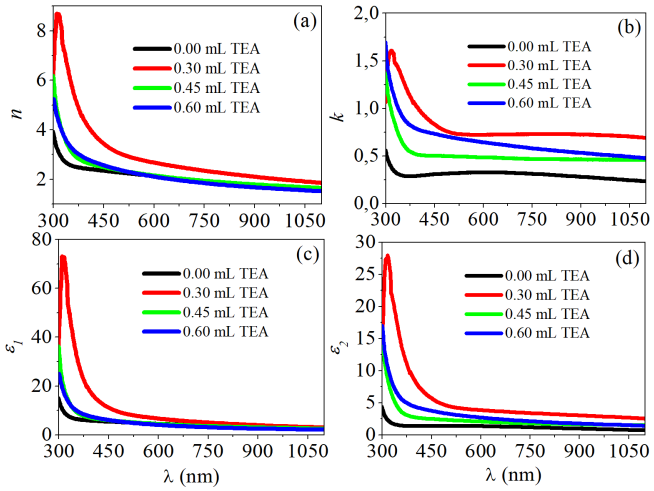

Fig. 5. The variation of (a) refractive index, (b) extinction coefficient, (c) real and (d) imaginary dielectric constant for the β-In_2S_3 thin films synthesized at different TEA volumes.

The resistivities ρ of the films as a function of different TEA volumes are listed in Table II. A definite effect of the TEA on the electrical transport of the β-In_2S_3 thin films is observed. Initially, using 0.30 ml TEA causes a decrease from 3.46×10^8 Ω cm to 1.33×10^7 Ω cm in the resistivity of the films, but then a further increase in the pH leads to less conductive films with higher resistivities increasing from 1.33×10^7 Ω cm to 2.16×10^9 Ω cm. Eventually, the film deposited at 0.30 ml TEA becomes two orders of magnitude more conductive than the others. Resistivity values are consistent with reported data [17, 21, 22]. One possibility that might affect the resistivity is the morphology change in the films. As shown in the SEM images, the film with worm-shaped structure is synthesized using 0.30 ml TEA and it has different morphology than the others.

4. Conclusion

In summary, the thin films of β-In_2S_3 are synthesized onto microscope glass substrates with three different TEA volumes using CBD technique. The effect of complexing agent (TEA) on the structural optical and electrical properties of present films is investigated. X-ray diffraction pattern of the deposited films shows the formation of polycrystalline β-In_2S_3 thin films with cubic structure. When adding 0.30 ml TEA, the optical band gap of the films decreases from 3.74 eV to 3.15 eV. Then, with the increase in TEA volumes from 0.30 ml to 0.60 ml, it increases to 3.79 eV. The optical parameters such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant are evaluated and their dependence on TEA is studied. The lowest electrical resistivity value or most conductive film is obtained using 0.30 ml TEA due to the worm-like surface morphology in the film detected from the SEM. It is seen that the use of different TEA volumes can affect the physical and electrical properties of synthesized films.

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References

[1] M.A. Mughal, R. Engelken, R. Sharma, *Sol. Energy* **120**, 131 (2015).

[2] N. Khooshsirat, N.A. Md Yunus, *J. Electron. Mater.* **45**, 5721 (2016).

[3] Zhao Yang Zhong, Eou Sik Cho, Sang Jik Kwon, *Thin Solid Films* **547**, 22 (2013).

[4] X. Zhang, C. Shao, X. Li, N. Lu, K. Wang, F. Miao, Y. Liu, *J. Hazard. Mater.* **283**, 599 (2015).

[5] M. Pomaska, R. Sáez-Araoz, A. Steigert, Y.P. Fu, F. Hergert, I. Lauermann, Th. Dittrich, M.Ch. Lux-Steiner, Ch.-H. Fischer, *Sol. Energy Mater. Sol. Cells* **132**, 303 (2015).

[6] S.S. Wang, F.J. Shiou, C.C. Tsao, S.W. Huang, C.Y. Hsu, *Mater. Sci. Semicond. Proc.* **16**, 1879 (2013).

[7] T. Sall, B.M. Soucase, M. Mollar, B. Hartitti, M. Fahoume, *J. Phys. Chem. Solids* **76**, 100 (2015).

[8] W. Xiang, H. Zhao, J. Zhong, H. Luo, X. Zhao, Z. Chen, X. Liang, X. Yang, *J. Alloys Comp.* **553**, 135 (2013).

[9] X. Meng, Y. Lu, X. Zhang, B. Yang, G. Yi, J. Jia, *Appl. Surf. Sci.* **258**, 649 (2011).

[10] S. Kirtay, *Acta Phys. Pol. A* **128**, B-90 (2015).

[11] İ. Karahan, *Acta Phys. Pol. A* **128**, B-432 (2015).

[12] N. Çiçek Bezir, A. Evcin, R. Kayali, M. Kaşikçi Özen, K. Esen, E.B. Cambaz, *Acta Phys. Pol. A* **130**, 300 (2016)).

[13] I.N. Qureshi, M. Shahid, A.N. Khan, *Acta Phys. Pol. A* **128**, B-314 (2015).

[14] W. Laslounia, M. Azzaz, *Acta Phys. Pol. A* **130**, 112 (2016).

[15] Y. Si Ahmed, T. Hadjersi, R. Chaoui, *Acta Phys. Pol. A* **130**, 385 (2016).

[16] M. Amlouk, M.A. Ben Said, N. Kamoun, S. Belgacem, N. Brunet, D. Barjon, *Jpn. J. Appl. Phys.* **38**, 26 (1999).

[17] N.F. Mott, E.A. Davis, *Electronic Process in Non-Crystalline Materials*, Clarendon, Oxford 1979.

[18] *Optical Properties of Solids*, Ed. F. Abeles, North-Holland, London 1972.

[19] A. Timoumi, H. Bouzouita, *Int. J. Renew. Energy Technol. Res.* **2**, 188 (2013).

[20] T.T. John, C.S. Kartha, K.P. Vijayakumar, T. Abe, Y. Kashiwaba, *Vacuum* **80**, 870 (2006).

[21] P.M.R. Kumar, T.T. John, C.S. Kartha, K.P. Vijayakumar, T. Abe, Y. Kashiwaba, *J. Mater. Sci.* **41**, 5519 (2006).

[22] P. Rao, S. Kumar, *Thin Solid Films* **524**, 93 (2012).