

Influence of Preparation Conditions on the Dispersion Parameters of Sprayed In_2S_3 films

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Abstract In_2S_3 films were prepared by spray pyrolysis technique at various substrate temperatures (T_{sub}) and the spray solutions were mixtures of indium chloride (InCl_3) and thiourea ($\text{SC}(\text{NH}_2)_2$). The films are preferentially oriented along the (220) plane and are of polycrystalline In_2S_3 with a cubic crystal structure. The refractive index dispersion curves of the films obey the single oscillator model and oscillator parameters changed with substrate temperature. The most significant result of the present study is to indicate that substrate temperature of the film can be used to modify the optical band gaps and optical constants of In_2S_3 films. The effect of T_{sub} on the optical dispersion of these films has been investigated.

Keywords Spray pyrolysis · In_2S_3 · Structural properties · Optical properties

الخلاصة

تم تحضير غشاءات كبريتات الإنديوم In_2S_3 عن طريق تقنية رذاذ الحرق بغياب الأكسجين (SPT) عند درجات حرارة ملقم متنوعة ومحاليل رذاذ عبارة عن مخاليط من كلوريد الإنديوم (InCl_3) والثيوريوريا ($\text{SC}(\text{NH}_2)_2$). إن الغشاءات كانت متجهة بامتياز على جانب مستوى (220)، وهي كبريتات الإنديوم متعددة التبلور مع بنية بلورة مكعبة. وتتبع منحنيات انحلال معامل الانكسار للغشاءات أنموذج المتأرجح المنفرد، وتتغير معاملات المتأرجح مع درجة حرارة الملغم. والنتيجة الأكثر أهمية للدراسة الحالية هي الإشارة إلى أن درجة حرارة الملغم يمكن أن تستخدم من أجل تعديل فجوات الحزم الضوئية والثوابت الضوئية لغشاءات كبريتات الإنديوم. وتم التحقيق في تأثير درجة حرارة الملغم في الانحلال الضوئي لهذه الغشاءات.

1 Introduction

In recent years, there has been a significant increase in the research works on III–VI materials due to their potential applications in optoelectronics and/or photovoltaic device fabrication [1]. Indium sulfide (In_2S_3) is a III–VI compound, originating from II–VI semiconductor [2]. There are a number of techniques that can be used to prepare thin film materials [3,4]. Among them, spray pyrolysis (SP) is a technique that meets the requirements for technologies involved in the manufacturing process for solar cells devices. Many materials have been deposited by this technique, including insulators and semiconductors [5]. Some of the metal chalcogenide materials have optoelectronic properties that suggest its use in photovoltaic structures [6]. A great number of research works have been done on these kinds of materials, especially those that can be prepared by “soft” techniques like SP [4] and chemical bath deposition [7]. Among them, the compounds based on the binary system In–S can be cited. They have received a lot of attention for their potential in optoelectronic device applications, especially in solar cells, which is the case of In_2S_3 . With optimal physical properties,

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the semiconductor material In_2S_3 can meet the requirements to be used as a window material or buffer layer for photovoltaic structures [8]. Indium sulfide (In_2S_3) is a crystalline compound that exists in four allotropic forms, depending on temperature and pressure [9]. Different methods are also used in film preparation, like dry methods: spray pyrolysis [10], metal-organic chemical vapor deposition (MOCVD) [11] and wet methods as chemical bath deposition (CBD) [12]. The In_2S_3 buffer properties are strongly determined by the preparation procedure. There are several studies, where In_2S_3 thin films have been investigated by chemical spray pyrolysis and it may be found that different technological parameters, such as type of precursors, molar ratio of the precursors in the spray solution, growth and annealing temperatures had important effects on the film properties [13–17]. The effect of various substrates on growth and structure of $\beta\text{-In}_2\text{S}_3$ and $\beta\text{-In}_{2-x}\text{Al}_x\text{S}_3$ thin films, prepared using spray pyrolysis technique (SPT), have been studied [18]. It has been found that In_2S_3 thin films prepared by the SPT show optoelectronic properties whose values depend on the deposition parameters. By controlling the deposition parameters, In_2S_3 thin films could be produced with optimized optoelectronic properties. Kamoun et al. [19] have studied the electron diffraction, transmittance and reflectance measurements of these films deposited using the airless spray technique. In this article, we produced the In_2S_3 films on glass substrates by SPT using indium chloride and thiourea as precursors. The present study deals with an experimental investigation of the influences of substrate temperature on the dispersion parameters of In_2S_3 films grown by the spray pyrolysis.

2 Experimental

In_2S_3 films were prepared by spraying an aqueous solution of InCl_3 and $(\text{SC}(\text{NH}_2)_2)$ on the highly cleaned glass substrate whose temperature was varied in the range of 200–350 °C. These samples are grown by a fine spray of the source solution using compressed air as a carrier gas. The atomization of the chemical solution into a spray of fine droplets is effected by the spray nozzle. Totally, 100 cm³ of solution was used and sprayed at different deposition time between 45 min and 4 h. Details of the sample preparation are given elsewhere [20]. During the spraying process the substrates were heated by an electrical heater. The distance between the nozzle and the substrate was maintained at 35 cm and the substrate temperature was controlled within ± 5 °C using an iron–constantan thermocouple. The crystallinity of the films was characterized by X-ray diffraction (XRD) using a Philips X-ray powder diffractometer equipped with $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.5418$ Å). Optical transmission and reflection spectra of the investigated samples were measured using Shimadzu UV 3101 PC; UV–VIS–NIR double-beam

spectrophotometer with reflection attachment of V–Ntype (incident angle 5°). The optical measurements were carried out in the wavelength range from 400 to 1,000 nm. In addition, optical dispersion characteristics of In_2S_3 films were evaluated.

3 Results and Discussion

3.1 Structural Characterization

The XRD patterns of sprayed In_2S_3 films prepared at different substrate temperatures are shown in Fig. 1. The diffractograms indicate the presence of all prominent peaks (109), (220) and (309) reflections belonging to $\beta\text{-In}_2\text{S}_3$ phase with tetragonal structure. From Fig. 1, it is observed that the featureless spectra of the films deposited at substrate temperatures 200 °C possess an amorphous structure whereas the presence of peak in the (220) direction of the film deposited at higher substrate temperature 350 °C reveals that the film is crystalline in nature. Also, it is observed that the XRD patterns of all In_2S_3 films show mostly a preferred orientation along (220) plane. As the substrate temperature is increased, the peaks intensity is increased, indicating the formation of more crystallites with well-defined orientation along (220). The intensity of the (220) peak and its narrowing with increasing in the substrate temperature up to 350 °C indicated an improvement in the degree of crystallinity of the films. At 250 °C, In_2S_3 (220) peak is observed and it increases

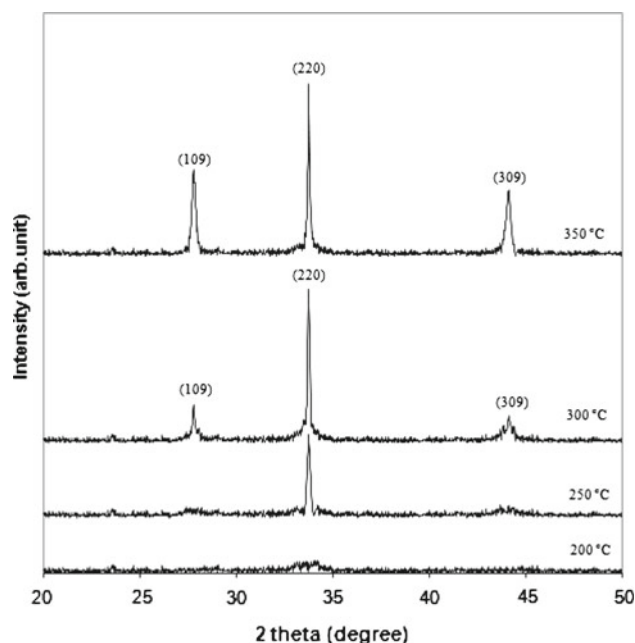


Fig. 1 XRD patterns of In_2S_3 films at various substrate temperatures, a 200 °C, b 250 °C, c 300 °C, d 350 °C

as the substrate temperature increases. Other peaks such as (109) and (309) are also observed in the films deposited at higher substrate temperatures and their intensity increases as the substrate temperature increases. These results indicate that the crystallinity is improved in the films deposited at higher substrate temperatures. This is in agreement with the results observed by Masahiro et al. [21]. As the substrate temperature increases, stronger and sharper diffraction peaks were observed. This was thought to occur mostly from the grain growth, resulting in released strains and partly from enhanced homogenization, which increases the amount of stable phases present in the films. Furthermore as the substrate temperature increases, even stronger intensities for some diffraction peaks, namely (220), (309) and (109) can be observed. Hence, it can be assumed that higher substrate temperature enables the atoms to move to the stable sites, which implies that films fabricated at these conditions are rather homogenous, and their crystalline state improves when the substrate temperature increases. It is concluded that the increase in the intensity of XRD peaks by increasing the substrate temperature can be explained by the crystallization of amorphous In_2S_3 , formed beside the crystalline In_2S_3 during deposition as well as an increase in crystallite size as seen from the decrease in the full width at half maximum (FWHM). Therefore, the X-ray diffraction patterns give the most positive evidence for the formation of the desired β -phase of In_2S_3 films. Therefore, the dependence of the In_2S_3 film growth mechanism on substrate temperature can be explained on the basis of the reactions associated with the spray pyrolysis deposition process. Three possible film growth mechanisms, as a function of substrate temperature, explain the growth of In_2S_3 films with different properties in the present work. In the first case, the sprayed droplets impinge on the substrate kept at a low temperature of 250°C , which is not sufficient to initiate reaction in the droplet. Films with foggy nature are formed. In the second stage, 300°C is enough to make precipitates in the droplets and the solvent is evaporated just prior to touching the heated substrate, which initiates the decomposition of the sulphide. At the substrate temperature of 350°C (third stage), a sustained thermal reaction is taking place in which the film formation mechanism is associated with the volatilization of the precipitated indium salt and diffusion of the resulting vapor to the heated substrate, followed by its decomposition to the In_2S_3 film. No residues or powder formation is observed.

The grain size of the In_2S_3 films were estimated using the Scherrer Formula [22],

$$d = \frac{\lambda}{D \cos \theta} \tag{1}$$

where d is the grain size, λ is the X-ray wavelength used, D is the peak full-width at half-maximum (FWHM), and θ is the Bragg's angle. Then the grain size was calculated using the

FWHM of X-ray peak. An increase in grain size from 152 to 226 nm was observed with an increase in substrate temperature from 250 to 350°C . The smaller grain size at low substrate temperature was due to poor crystallinity of the films. As the substrate temperature is increased, the crystallinity of the films is also improved. Therefore, it is observed that the crystallite size of In_2S_3 can be influenced by several factors such as defects, impurities and heating conditions.

3.2 Optical Characterization

Optical parameters of In_2S_3 thin films were calculated from the transmission spectra using Swanepoel's method [23]. Optical absorption studies of In_2S_3 films deposited on glass substrates were carried out in the wavelength range of 400 – $1,000$ nm at room temperature. The optical transmission spectra of the films prepared at different substrate temperatures are shown in Fig. 2.

A weak change in the absorption edge is observed toward higher wavelengths as T_{sub} increases. The film deposited at 200°C substrate temperature exhibits low transmittance. This may be attributed to the fact that the solution droplets form solid phase by evaporation only on reaching the surface of the substrate. It is observed that the transmittance of films is increased as the substrate temperature is increased. This can be attributed to the increase in grain size and roughening. This may be due to the rearrangement of crystallites or grains. It is observed that substrate temperature is the most important factor influencing the film property. The higher transmittance observed in the films was attributed to less scattering effects, structural homogeneity and better crystallinity, whereas the observed low transmittance in the layers might be due to the less crystallinity leading to more light scattering. Interference maxima and minima due to multiple reflections on film surfaces can be observed. The appearance of interference fringes is an indication of the thickness uniformity of the films. The refractive index, n , was found from equation [23]

$$n = \sqrt{N + (N^2 - n_s^2)^{1/2}} \tag{2}$$

where

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \tag{3}$$

where n_s is the refractive index of glass substrate, T_M and T_m are the maximum and minimum values of the transmittance at the same wavelength, respectively.

The refractive index of the glass substrate n_s is determined by

$$n_s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{1/2} \tag{4}$$

where T_s is the substrate optical transmission.

Fig. 2 Variation of optical transmittance with substrate temperature, **a** 200 °C, **b** 250 °C, **c** 300 °C, **d** 350 °C

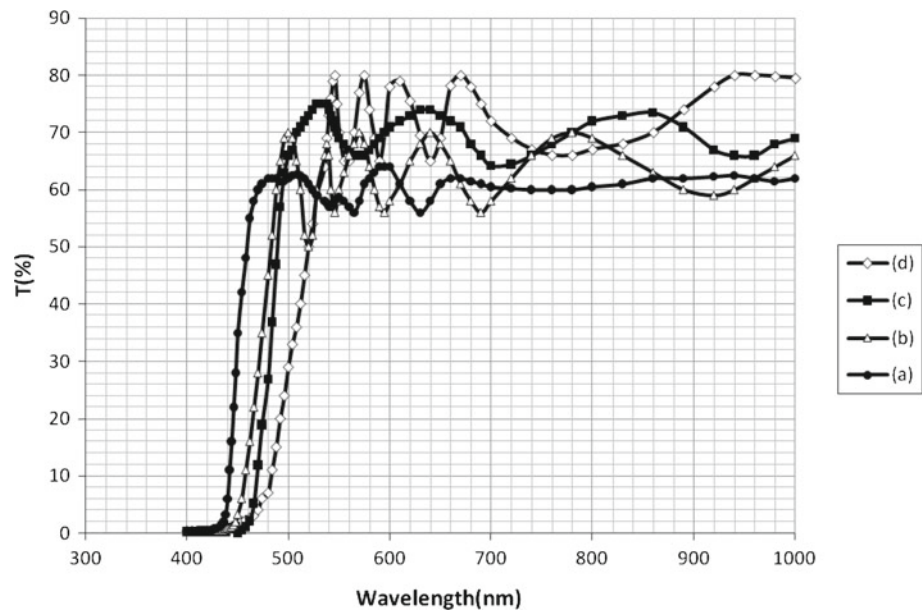


Table 1 The estimated values of the oscillator parameters for In_2S_3 films

Substrate temperature (°C)	Grain size (nm)	Band gap (eV)	Thickness (nm)	E_o (eV)	E_d (eV)
200	–	2.78	510	5.55	23.61
250	152	2.71	535	5.40	24.10
300	180	2.66	555	5.29	24.95
350	226	2.61	580	5.19	25.44

According to Swanepoel's method [23] which is based on creating the envelopes of interference maxima and minima, the value of refractive index in the region of weak and medium absorption ($\alpha \neq 0$) was calculated. The film thickness d is calculated to an accuracy of better than $\pm 3\%$ from interference patterns appearing in the transmission spectrum. If n_1 and n_2 are the refractive indices at two adjacent maxima (or minima) at λ_1 and λ_2 then

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (5)$$

The above equation follows from the basic equation of interference fringes, namely $2nd = m\lambda$. The calculation of refractive index n is described, where n_1 and n_2 are the refractive indices at two adjacent maxima (or minima) at λ_1 and λ_2 . The average value of d , can now be used, along with n_1 , to calculate the order number m for the different extra from the equation

$$2nd = m\lambda \quad (6)$$

The accuracy of d can now be significantly increased by taking the corresponding extra integer of half integer values of m associated with each interference extreme. Furthermore, a simple, complementary graphical method for deriving the value of m and d , based on the basic equation for interference

fringes, was also used [24]. Equation (5) can be rewritten as

$$\frac{L}{2} = 2d \left(\frac{n}{\lambda} \right) - m_1 \quad (7)$$

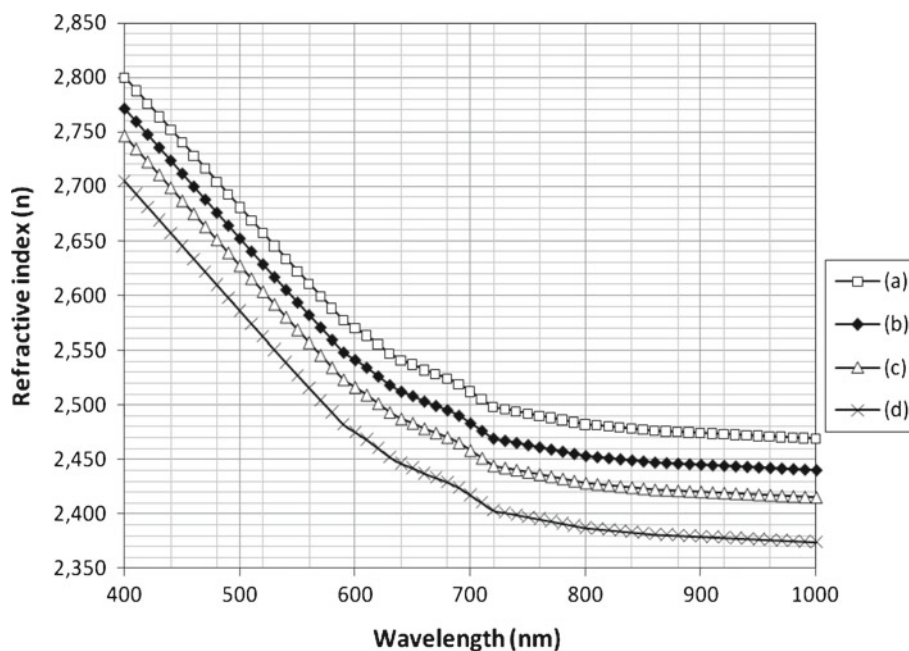
where $L = 0, 1, 2$, and m_1 corresponds to the order number of the first interference extreme of the transmission spectrum. The thickness is determined using transmission interference fringes at wavelength slightly longer than the intrinsic absorption edge, i.e. in a region with relatively high transmission. The all sample thicknesses deposited by different temperatures are presented in Table 1.

The absorption coefficient (α) as a function of photon energy was calculated and plotted for allowed direct transitions (neglecting exciton effects) using the expression.

$$(\alpha hv)^2 = A(hv - E_g) \quad (8)$$

where hv is the photon energy, E_g denotes the optical energy band gap, and A is the characteristic parameter (independent of photon energy) for respective transitions. The dependences of $(\alpha hv)^2$ as a function of photon energy hv indicate the direct nature of band-to-band transitions for the studied samples. From the best fit of the $(\alpha hv)^2$ versus hv plot and its extrapolation to $(\alpha hv)^2 \rightarrow 0$, the E_g value was calculated for all the samples under analysis. It is observed that

Fig. 3 Spectral dependence of refractive index, n with different substrate temperature, **a** 200 °C, **b** 250 °C, **c** 300 °C and **d** 350 °C



the band gap energy is decreased from 2.78 to 2.61 eV as the deposition temperature was increased from 200 to 350 °C. Similar results were reported by Calixto-Rodriguez et al. [25]. Band gap energy is found to decrease when the crystallite size increases, in a way comparable to that reported for other polycrystalline thin films [26,27]. And the optical band gap of In₂S₃ film is obviously affected by the defects and the crystallinity. In general, there are several factors that influence the band gap of thin films. This includes the band filling effect, quantum size confinement where the band gap increases with the decrease in grain size, charged impurities at the grain boundaries, lattice strain present in the films and the extent of structural disorder. The analysis of the results in the present study suggests that there is a decrease in structural disorder in the films with the increase in substrate temperature from 200 to 350 °C, probably due to a reduction in defects at the grain boundaries of the layers that decreased the band gap. Moreover, the decrease in lattice strain in the films with growth temperature might also have contributed to the decrease in energy band gap in the present study. As the films were deposited at higher temperature, the crystallites began to move and tended to agglomerate easily. As a result, the band gap of crystallites decreases with increasing substrate temperature, which indicates that crystallization would cause the E_g narrowing [28]. It could be explained by crystalline state improvement with increasing the substrate temperature. Also, the shift observed at absorption edge toward lower photon energies for the films deposited on heated substrates could be attributed to the increase in crystallite size and change in the stoichiometry. According to the results, it is apparent that the optical band gap decreases with the decrease in defects and with the increase in grain size. This can be explained by

the fact that free electrons are trapped in the defects and the grain boundaries. The density of defects decreases with the increase in deposition temperature and the density of grain boundaries decreases when the grain size increases at higher deposition temperature. Also the films possess the characteristic features of optical absorption edge of semiconductors. The absorption coefficient is slightly affected by the change of structure at lower energy values, while a sensible change is observed at higher energy values. This behavior is probably due to the crystallization process of films. It is known that intercrystalline boundaries contain structural defects and impurities. These factors have a strong influence on the absorption processes. In the polycrystalline film, the intercrystalline boundaries play an important role in optical absorption.

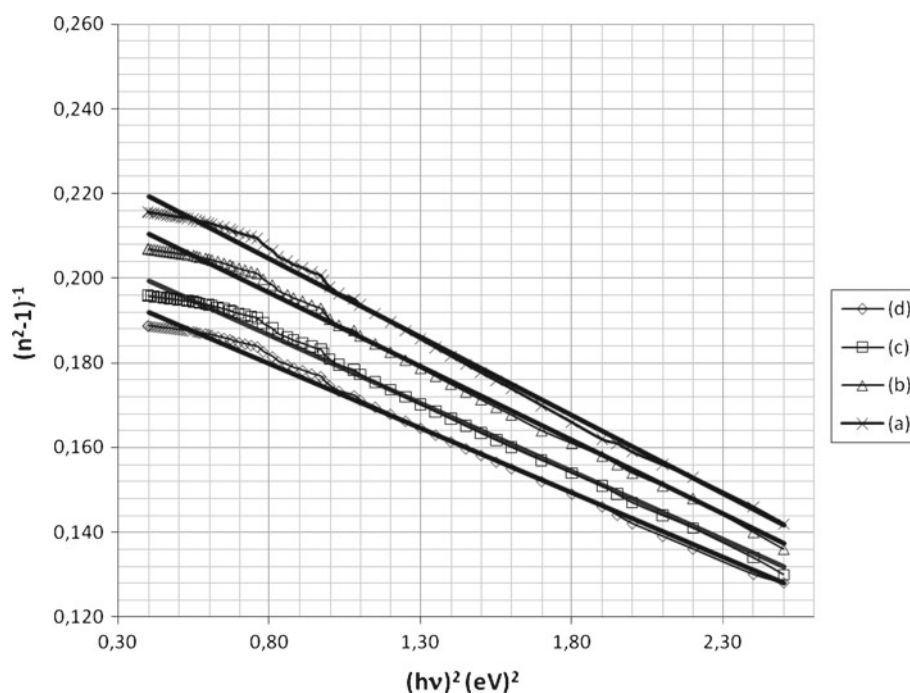
The spectral dependence of refractive index, n , on In₂S₃ films is shown in Fig. 3. The dispersion plays an important role in the research for optical materials because it represents a significant factor in optical communication and in designing devices for spectral dispersion.

The refractive index of polycrystalline films (deposited at 350 °C) is found to be higher than that of the amorphous film (deposited at 200 °C), which may be due to the change in transmittance. The refractive index decreases as the substrate temperature increases, which also results in a better crystallinity and an increases in the crystallite size.

According to a single-oscillator model [29], the relation between the refractive index, n , and photon energy, $h\nu$, can be written as follows

$$n = \left(1 + \frac{E_o E_d}{E_o^2 - (h\nu)^2} \right)^{1/2} \tag{9}$$

Fig. 4 Plot of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ at different substrate temperature, **a** 200 °C, **b** 250 °C, **c** 300 °C and **d** 350 °C



where h is the Planck constant, ν is the frequency, E_o is the oscillator energy and E_d is the dispersion energy or the oscillator strength.

By plotting $(n^2 - 1)^{-1}$ against $(h\nu)^2$ and fitting the data using a straight line for the deviation from linearity at long wavelengths is shown in Fig. 4. E_o and E_d can be determined directly from the slope, $(E_o E_d)^{-1}$, and the intercept E_o/E_d , on the vertical axis. The oscillator energy, E_o , is an “average” energy gap and is related to the optical band gap, E_g , in close approximation by $E_o \approx 2E_g$ [30]. Table 1 summarizes the estimated values of the oscillator parameters, E_o , E_d and E_g .

The higher energy band gap of amorphous In_2S_3 films over those of polycrystalline films is supported by the difference existing in the spectral dependence which suggests that the density of states in the conduction band of the amorphous material is lower, or that the matrix elements for optical transitions are suppressed owing to the lack of long-range order which affect the sensitivity of allowed transitions. The shape and absorption edge depend very much on the conditions maintained during the preparation of In_2S_3 films.

4 Conclusions

In_2S_3 films have been prepared by the spray pyrolysis method on glass substrates at a temperature range of 200–350 °C. The X-ray diffraction measurements of the obtained samples showed that the crystalline state of In_2S_3 is improved with increasing the substrate temperature. However, opti-

cal measurements are featured that the optical band gap is decreased from 2.78 to 2.61 eV when the substrate temperature is increased from 200 to 350 °C, respectively. The decrease in the band gap value with the increase in the substrate temperature is attributed to an increase in grain size. It is observed that to grow films having good structural quality the substrate temperature should be controlled at around 350 °C. It can be concluded that the substrate temperature has a strong influence on the structure and consequently the optical properties of In_2S_3 thin films. The optical constants of In_2S_3 films were determined using the transmission spectra. It is observed that the intercrystalline boundaries play a major role in optical absorption. The single oscillator parameters were calculated and discussed in terms of the Wemple Di-Domenico model. The results have shown that band gap energy, E_g , oscillator energy, E_o , and dispersion energy, E_d , are strongly dependent on the substrate temperature.

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