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Optical properties of sprayed Bi_2S_3 nanocrystalline thin film

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Bismuth Sulfide (Bi_2S_3) thin film was prepared by spray pyrolysis on glass substrate at 270 °C, by using bismuth chloride ($BiCl_3$) and Thiourea (CS $(NH_2)_2$). The optical constants and thickness were extracted using the pattern search optimization technique. The optical constants confirm that the Bi_2S_3 film has a direct gap of 1.56 eV. The dispersion of refractive index in Bi_2S_3 was analyzed using the concept of the single oscillator model. The dielectric constants represented by the lattice dielectric, the dispersion parameters E_0 and E_d, and the rth moments, M_{-1} and M_{-3} were determined. It is interesting to note that Bi_2S_3 appears to fall into the covalent class. The values ratio of the carrier concentration to effective masse and plasma frequency were also evaluated.

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Keywords: Thin film, Optical Constants, Single oscillator model, Bi_2S_3

1. Introduction

Semiconducting chalcogenide thin films have attracted extensive interest in recent years due their outstanding optical and electrical properties, which are useful in various optoelectronic devices. Bismuth sulfide is one of thin chalgogenide films in group V-IV. The optical band gap of Bi_2S_3 single crystal is found to be 1.1-1.3 eV and varies from 1.3 -1.7 eV in its polycrystalline structure [1,2]. Bi_2S_3 exhibit orthorhombic structure with lattice parameters, a= 11.19 Å, b=11.303 Å and c= 3.975 Å [3].

The Bi_2S_3 films were prepared with different techniques. Among these techniques, one may note the gas-solution interface [4], electrodeposition [5] and spray pyrolysis [6] techniques. The latter technique is simple, economical, and allows the preparation of large surface thin films. According to our Knowledge, the opto-electronic parameters of Bi2S3 thin films have not been reported. In this work, we have evaluated the various opto-electronic parameters such as refractive index, extinction coefficient, dielectric constants, the ratio of the carrier concentration to effective mass and plasma frequency.

2. Experimental

Bi_2S_3 thin films were obtained by sprtay pyrolysis in air atmosphere on the glass substrate at 270 ° C. The starting chemical solution was prepared using 0.1 N pure bismuth chloride ($BiCl_3$) and Thiourea (CS $(NH_2)_2$). The prepared solutions of tin chloride and thiourea were appropriately mixed to obtain Bi:S proportion of 2:3. The obtained solution was pulverised on glass substrates with compressed air (2 bars) and at flow rate of 8ml/min. The distance from the spray nozzle to the heater is kept approximately at 29 cm. Under these deposition conditions, good films were obtained. They were uniform and very adherent to the substrates. Structural characterization has been carried out at room temperature using a Philips 1830 X-ray diffractometer with a C_uK_α peak λ=1.546Å. The optical transmittance and reflectance were recorded from 200 to 2500 nm wavelength using an UV (Ultra-Violet) Visible JASCO type V-570 double beam spectrophotometer. Morphology was carried out by a Joel JSM 5800 scanning electron microscope.

3. Results and discussion

Fig. 1 demonstrates the X-ray diffraction pattern of nanocystalline Bi_2S_3 thin film deposited on glass substrate. All the diffraction peaks can be indexed to orthorhombic crystalline phase of Bi_2S_3 with lattice parameters a= 11.143 Å, b= 11.196 Å and c= 3.974 Å, which is in good agreement with the experimental ASTM X-ray powder data files (Card No. 17- 0320). The grain size (G) of nano-crystallite has been estimated from Scherrer formula [7], using the full- width at half –maximum of the more intense diffraction peak. The determined value of the grain size from the peak (310) is about 19 nm.

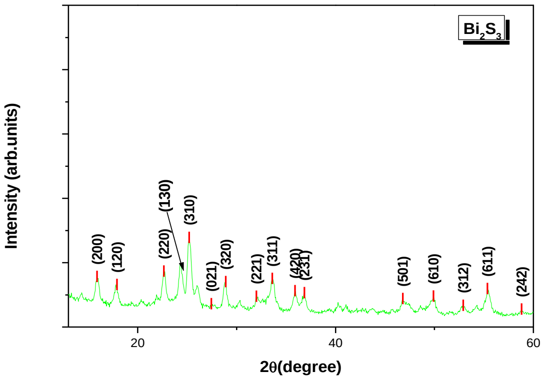

Fig. 1. X-ray diffraction patterns of Bi_2S_3 prepared by spray pyrolysis method

Fig. 2 shows the scanning electron micrograph of Bi_2S_3 thin film. It was observed that film was homogenous and was composed of platelets which are grown perpendicularly to the glass substrate.

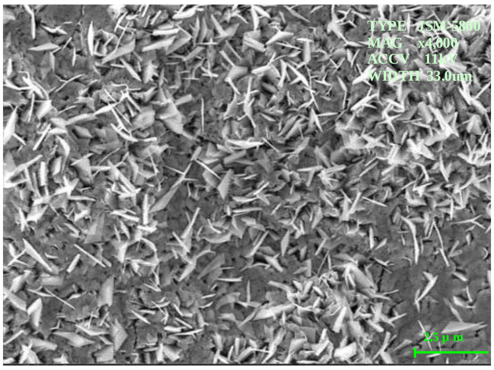

Fig. 2. SEM image of Bi_2S_3 nanocrystalline thin film deposited at 270 ° C

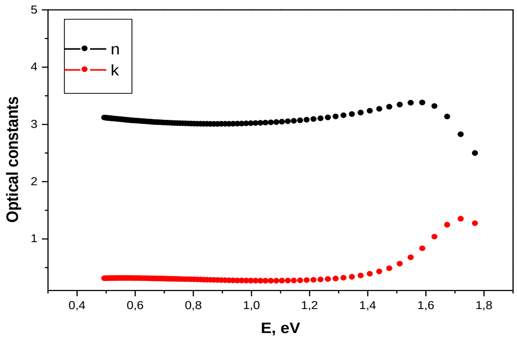

Fig. 3. Refractive index and extinction coefficient from fitting of a two-term Lorentz dispersion equation

The optical constants (n, k) and the thickness (d) were obtained with the spPS (seed preprocessing Pattern search) technique [8] combined with Lorentz oscillator model. The accuracy of calculations of optical constants has been obtained for $\varepsilon=10^{-6}$.

The layer thickness and surface roughness are found to be 80 nm and 15 nm, respectively. The extracted refractive index n and extinctive coefficient k are shown in Fig. 3. The refractive index has a value of 3.39 at high energies and a value around 2.99 at low energies. The peak found at 1.56 eV in refractive index curve represents the direct transitions energy gap.

The fig. 4 demonstrates the relationship of $(\alpha h\upsilon)^2$ versus the photon energy for Bi2S3 thin film. The linear section shown in the curve indicates the allowed direct inter-band transition at 1.56 eV, the value was in good agreement with that mentioned above.

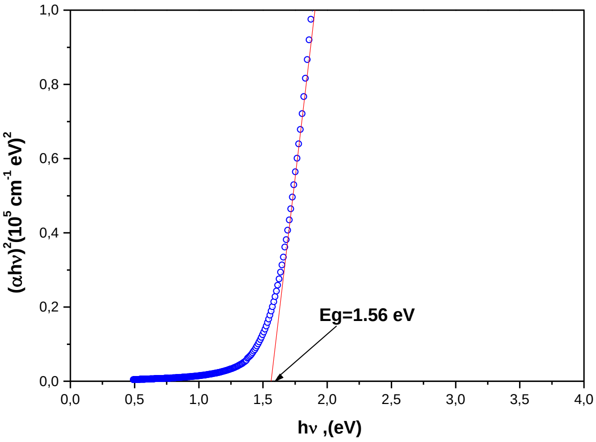

Fig. 4. The plot $(\alpha h\upsilon)^2$ vs.$(h\upsilon)$ for the Bi_2S_3 thin film

The dispersion of refractive index in Bi_2S_3 was analysed using the concept of the single-oscillator model and can be expressed by the relation [9]:

$$n^2 - 1 = \frac{E_0\, E_d}{E_0^2 - E^2} \qquad (1)$$

where n is refractive index, E_0 is the energy of effective dispersion oscillator, E is the photon energy, and E_d is the dispersion energy. This model describes the dielectric response of the inter band optical transitions. E_0 and E_d have a significant association with the crystalline structure and ionicity of ionic or covalent materials. The values of E_d and E_0 are obtained from the intercept and slope resulting from the extrapolation of the curve of Fig. 5 as 25.43 and 3.16 eV, respectively. The value of the refractive index at the IR wavelength was $n_\infty = 3$. This value was significantly lower than that of bulk Bi_2S_3 materials ($n_\infty = 3.6$) . The difference between the two indices is generally interpreted as a consequence of the presence of void inclusions in the layer. From these we estimated the porosity p= 14 %, by using the Bruggeman effective medium approximation (EMA) model [10].

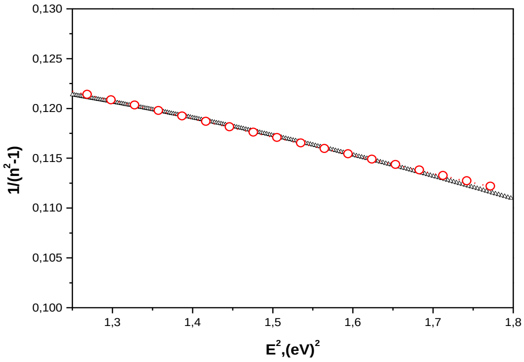

Fig. 5. Plot of $(n^2-1)^{-1}$ *versus* E^2 *of* Bi_2S_3 *thin film*

The rth moment, Mr,of the optical spectrum is defined by relation [11] :

$$M_r = \frac{2}{\pi}\int_{E_t}^{\infty} E^r \varepsilon_2 (E) dE \qquad (2)$$

where Et is the absorption threshold energy. The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the following relations:

$$M_{-1} = \frac{E_d}{E_0} \qquad (3)$$

and

$$M_{-3} = \frac{E_d}{E_0^3} \qquad (4)$$

The calculated values of M_{-1} and M_{-3} were 8.04 and 0.80 eV^{-2}, respectively, for Bi_2S_3 film.

The dispersion energy, E_d, describes the dispersion of the electronic dielectric constant and it is related to interband transition strength. Ed is found to obey an empirical relationship [11]

$$E_d = \beta N_c Z_a N_e \qquad (5)$$

where N_c is the coordination number of the cations nearest-neighbor to the anion, Z_a is the formal chemical valency of the anion and Ne is the effective number of the valence electron per anion. $\beta = 0.26 \pm 0.04$ and 0.37 ± 0.05 for ionic and covalent materials, respectively.

For deposited film Bi_2S_3, Nc, Z_a and N_e, respectively, takes the value 3, 2 and 10, substituting theses values in equation (5) we obtained a value for $\beta = 0.42$ indicating an covalent binding in Bi_2S_3.

The relationship between the lattice dielectric constant ε_L , and the squares of refractive index n is given by [12].

$$n^2 = \varepsilon_L - B.\lambda^2 \qquad (6)$$

Where ε_L is the lattice high frequency dielectric constant and $B = \frac{e^2}{\pi c^2}\frac{N}{m_\varepsilon^*}$ was constant. N/m_ε^* is the ratio of the free carrier concentration to the electron effective mass., c is the speed of light, and e is the electron charge. Fig. 6 represents the relation between n^2 and λ^2 for Bi_2S_3 thin film. The values of ε_L and N/m_ε^* were determined from the intercept of the extrapolating straight line with n^2 axis. The obtained values were 9.19 and 9.6 10^{42} K**g**$^{-1}$ m^{-3} for ε_L and N/m_ε^*, respectively.

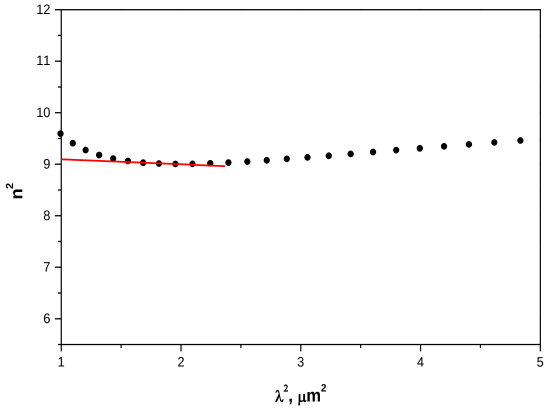

Fig. 6. Plot of n^2 *versus* λ^2 *of* Bi_2S_3 *thin film*

The variation of the real part of the dielectric constant ε_1 with incident photon energy depends on the plasma frequency ω_p. When $n^2 >> k^2$ and $\omega\tau << 1$ the dielectric constant ε_1 can be expressed by the relation :

$$\varepsilon_1 = \varepsilon_\infty - [(\varepsilon_\infty \ \omega_p^2)/\omega^2] \qquad (7)$$

where τ is the relaxation time and ω the angular frequency of the lattice atoms. Fig.7 represents the relation between ε_1 and ω^{-2} for Sn_2S_3 thin films. The values of plasma frequency ω_p and infinite dielectric constant ε_∞ determined from the slop and intercept of the ε_1 versus ω^{-2} plot were $\omega_p = 0.87 \times 10^{14}\ s^{-1}$ and $\varepsilon_\infty = 9 .31$, respectively. According to M.M.El.-Nahass et al. [13] the disagreement between the values of ε_∞ and ε_L may be due to free carrier contribution.

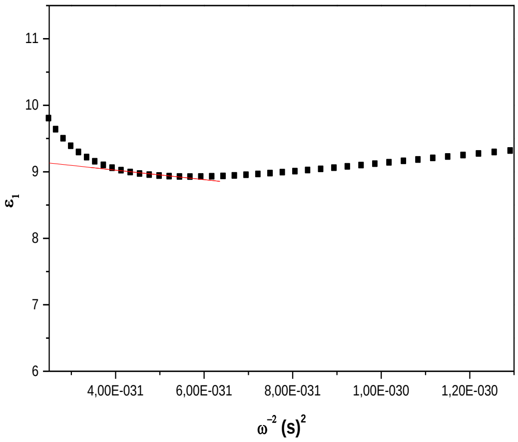

Fig. 7. Plot of ε_1 *versus* ω^{-2} *of* Bi_2S_3 *thin film*

4. Conclusions

Nanocrystalline Bi_2S_3 thin film was prepared on glass substrates by spray pyrolysis technique at the temperature of 270 °C .The pattern search optimization technique was successfully applied to extract the thickness and optical constants. The optical constants confirm that the Bi_2S_3 film has a direct gap of 1.56 eV. The value of dispersion energy E_d determined by single-oscillator model was found to be 25.43 eV. The calculated value of β showed the covalent nature of Bi_2S_3 thin film.. The opto-electronic parameters such as dielectric constants, the ratio of the carrier concentration to effective masse and plasma frequency were also evaluated.

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