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Investigation of optical properties of Sb_2S_3 thin films grown based temperature

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Abstract – In this study, Sb_2S_3 thin films grown at 275 °C, 300 °C and 325 °C temperature using the ultrasonic Spray Pyrolysis method were examined related to optical properties. The energy band gaps of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films were obtained as 2.36 eV, 2.47 eV and 1.84 eV, respectively, using UV-Vis spectrophotometer measurement system between 300-1100 nm. Amount of photon value of the fabricated Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films calculated using absorbance values. , the extinction coefficient, skin depth, optical conductivity spectra were obtained depending on the wavelength (λ) over a wavelength range of 300-1100 nm in the spectrum and photon energy in this work. The refraction indices and dielectric constants of the samples were calculated by Herve and Vandamme, Moss and Ravindra relations. E_g values for Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films have been determined and reported in this work to be 1.59 eV, 2.75 eV and 0.43 eV, respectively.

Keywords – Sb2S3 Thin Film, Temperature, Optical, Refraction Indice

1. Introduction

Antimony sulphide (Sb_2S_3) samples have acquired significant consideration during the past two decades owing to their unique behaviour including their high refractive index [1], quantum size effects [2], photosensitivity and thermoelectricity behaviour [3,4]. A study of the optical behaviors of Sb_2S_3 thin films on $LiNbO_3$ substrates has recently been published for use in applications such as resonant laser cavities [1]. As a result, it was determined that Sb_2S_3 films with different transmittances after heat treatment could be used for laser cavities to design reflective coatings. As the vacuum evaporated Sb_2S_3 thin films on the used substrate were annealed in atmosphere of sulfur, they became polycrystalline structure. The electrical and optical behaviors of evaporated Sb_2S_3 samples were studied associated with the influence of substrate temperature [5]. It has neen noticed and reported thatsamples have been structred in nearly amorphous nature depending on the applied substrate temperature near to 200 °C even it is some what higher than 200 °C (≈200 °C) while those fabricated at around 225 °C have polycrystalline nature. The effect of a thermal treatment change on the crystalline and optoelectronic behaviors of vacuum evaporated antimony sulphide samples was detailed investigated [6]. After being irradiated with electron beams at accelerating voltages of 15 to 30 kV, evaporated amorphous Sb_2S_3 thin films exhibited a surface modification [7]. Various techniques are used to obtain Sb_2S_3 thin films including SILAR method [8], chemical fabrication method [9], spray pyrolysis (SP) [10], pulse electrodeposition [11], and chemical bath deposition technique [12]. Previous studies indicates that Sb_2S_3thin film fabrication techniques and conditions changed the optical, structural and electrical properties of obtained films. For example, Salem *et al*. [2] have shown that obtained Sb_2S_3 thin film using chemical deposition technique has both direct and indirect band gap. They have also indicated optical absorption energy uniformly upsurged from 2.2 eV to 3.8 eV depending on the decrease in particle size of film. Garcia *et al*. [13] obtained Sb_2S_3 thin films annealed at 300 °C using Pulse electrochemical storage technique. They have also indicated that the obtained thin film has a high absorption coefficient and optical band gap decreased from 2.03 eV to 1.65eV. The optical properties of Sb_2S_3 thin films are widely discussed in literature using different deposition techniques. In this study, optical properties of temperature dependence of Sb_2S_3 thin films (275 °C, 300 °C and 325 °C) are limited using the ultrasonic spray pyrolysis (USP) technique. Ultrasonic spray pyrolysis (USP) technique is an important because of simple to use and inexpensive and it provides the opportunity to make controlled films. For this reason, optical properties of temperature dependence of Sb_2S_3 thin films detailed investigated related to absorption, energy band, Urbach energy, the refraction indices and dielectric constants.

2. Experimental

To deposit Sb_2S_3 thin film on soda lime glass substrate (SLG) using USP technique, first 0.05 M antimony (III) chlorate and equimolar sulfur was solved in deionize water. To obtain a homogeneous solution, these solutions were vibrated at room temperature on magnetic stirrer. These homogenous solutions were added at a ratio of 1:1 and stirrer again for 1 hour under the same conditions. Obtaining a high quality clean and homogeneous Sb_2S_3 thin film, glass materials we use for storage first, 5:1:1 H_2O, NH_3 and 5:1:1 H_2O, NH_3 and in H_2O_2 and then boiled. 5:1:1 H_2O in H_2O_2 and HCl under the same conditions. Then the materials were mixed in acetone and ethanol respectively for 3 minutes and washed with pure water from the cleaning process. Then it was dried with N_2 gas. Ultrasonic spray system USP to obtain film (SonoTek Exacta–Coat) was used Sb_2S_3 thin at three different temperatures (275 °C, 300°C and 325 °C) and the systematic of this process given in Figure 1. The device distance between spray tip and substrate 10 cm is set to obtain thin film. Ultrasonic system spraying It was operated at 125 kHz and flow rate of solution set at 1 mL per minute. After the thin films are completed, it was annealed in H_2S:Ar (1:10) environment at 500 °C. Using UV-3600 spectrophotometer, absorbance, energy band gap, Urbach energy values of the thin films were calculated in the range of 300-1100 nm wavelength. Amount of photon value of the obtained thin films calculated using absorbance value. Depending on the wavelength and photon energy, the extinction coefficient, skin depth, optical conductivity spectra were obtained in this work.

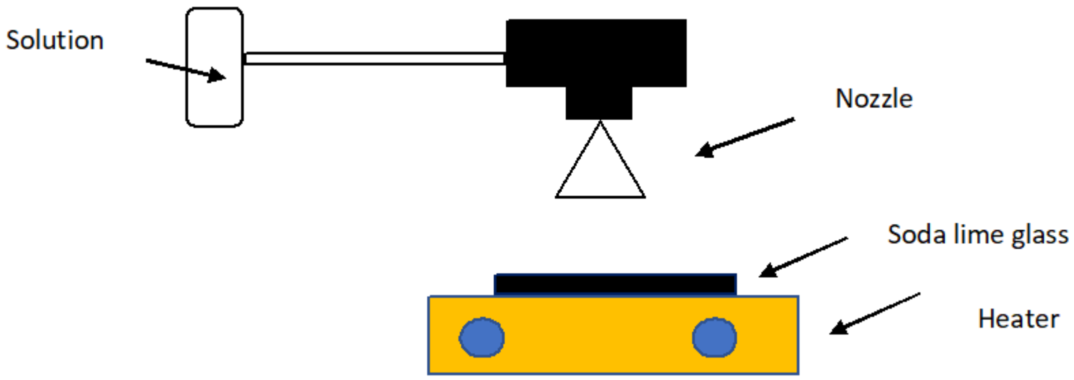

Figure 1. Systematic of the ultrasonic spray pyrolysis technique for thin films

3. Result and Discussion

3.1.The Optical Properties of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C films

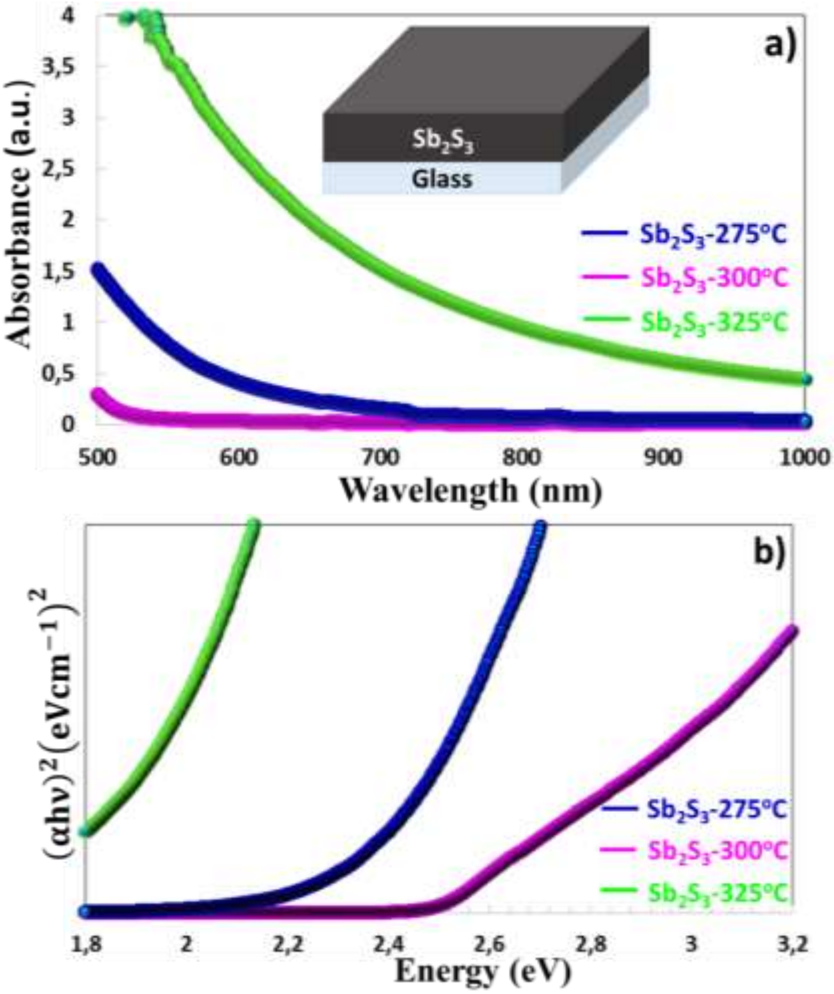

Figure 2. a) The absorption spectrum and b) Tauc Plot of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films

The absorption spectra of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films are presented in Figure 2a. Sb_2S_3 thin film grown at 325 °C temperatures absorb more photons than other thin films. Because kinetics of particles increases at high temperatures, they can combine with each other to form large particles. Thus, Sb_2S_3-325 °C thin film can have absorbed more photons. However, Sb_2S_3-300 °C thin film absorbs the least number of photons. At 300 °C, particles may have moved to different regions and moved away from each other, instead of combining with each other, making the sample more transparent. The band gap of thin films can be calculated with $\alpha h\nu = A(h\nu - E_g)^{1/2}$ Tauc equation. According to plot drawn using Tauc equation in Figure 2b, band gaps of Sb_2S_3-275 °C, Sb_2S_3 -300 °C and Sb_2S_3-325 °C samples have been obtained to be 2.36 eV, 2.47 eV and 1.84eV, respectively, [14]. While the band gap of Sb_2S_3-325 °C sample is smaller because it absorbs more photons, the band gap of Sb_2S_3-275 °C thin film is larger because it absorbs lower number of photons.

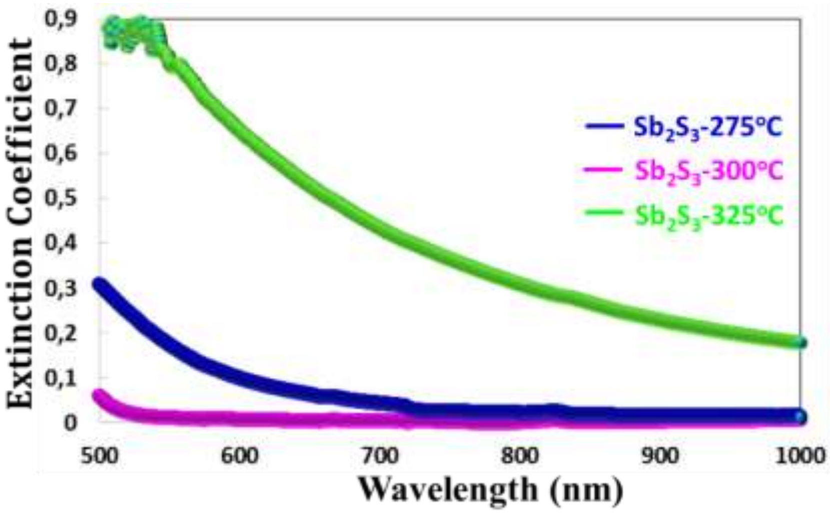

Figure 3. Extinction Coefficient spectra of Sb_2S_3-275 ºC, Sb_2S_3-300 ºC and Sb_2S_3-325 ºC thin films

$$k = \frac{\alpha\lambda}{4\pi} \quad (1)$$

The photon that diffuses through thin film can be lost by absorption or scattering. This light loss is defined by Extinction Coefficient (k) [15]. k value of samples is calculated by equation (1). α and λ given in the equation define the absorption coefficient and wavelength, respectively. Since Sb_2S_3-325 ºC samples absorbs more photons, it presents higher extinction coefficient in Figure 3. In contrast, k value of Sb_2S_3-300 ºC thin film absorbing lower number of photons is reduced. At a wavelength of 500 nm, k values of Sb_2S_3-275 ºC, Sb_2S_3-300 ºC and Sb_2S_3-325 ºC thin films are 0.30, 0.06 and 1.125, respectively.

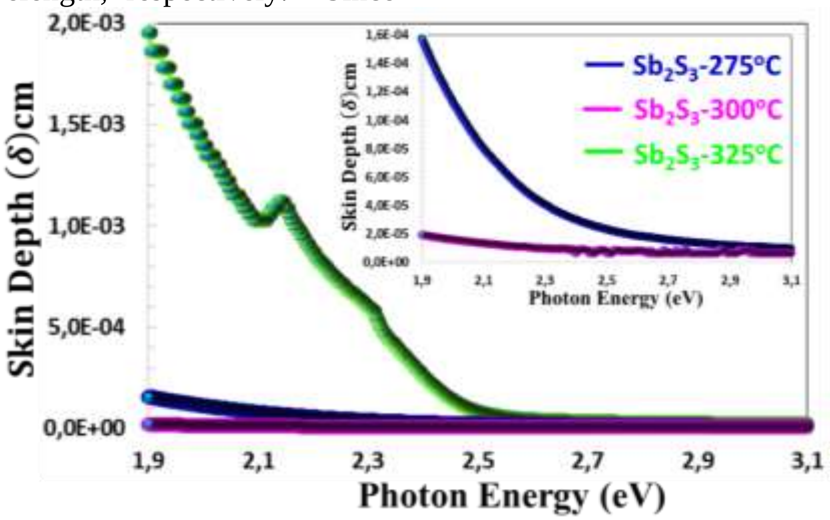

Figure 4. Skin Depth spectra of Sb_2S_3-275 ºC, Sb_2S_3-300 ºC and Sb_2S_3-325 ºC thin films

Light incident on the sample travels a certain distance through the thickness of the film, depending on k and λ. This distance is called Skin Depth. Skin Depth (χ) is determined by the equation (2):

$$\chi = \frac{\lambda}{2\pi k} \quad (2)$$

Depending on some factors such as particle size, density and shape in thin film, the distance the light travels through thin film may vary. According to absorption spectra as shown in Figure 4, χ value increased from wide band gap (bg) to narrow bg. In particular, the larger χ of Sb_2S_3-325 ºC thin film indicates that it is more suitable for use in solar cells absorber layer. The possibility of formation of photo-excited charge-carriers in deeper region may increase the charge density of carrier.

Semiconductor'refractive index (n) is a significant optical limit which effects the performance of optoelectronic device. A band gap (bg) is used to calculate n value of an object, and the Moss relation is used to calculate it.

$$E_g n^4 = k \quad (3)$$

The constant k, is equal to 108 eV. Addition, Herve and Vandamme use Eq. (4) to express the relationship between n and E_g;

$$n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2} \quad (4)$$

where A (13.6 eV) and B (3.4 eV) constants. Besides Moss, Herve, and Vandamme relations, Ravindra stated an remarkable equation between and the value of refractive index using as Eq. (5) [16].

$$n = 4.16 - 0.85E_g \quad (5)$$

The value of refractive index (n) of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films obtained using Eqs. (3), (4) and (5) are demonstrated in Table 1. When the bg value of the obtained samples decrease, their refractive index increases, according to Herve and Vandamme's (H-M_s), Moss and Ravindra's (M-R_s) relationship. Aside from that, the value of refractive index (n) and dielectric coefficient (ε_o) theoretically evaluated by Herve and Vandamme (H-M) are more similar to each other and the values theoretically calculated by Ravindra are a little lower.

A key parameter defining the charge accumulation in application of solar cells is the value of ε_o, which is determined by the electric field (E_f)between charges in thin films. In this work, values of both high frequency (ε_∞) and value of the static dielectric constant (ε_o) were theoretically investigated by using Eq. (6) and Eq. (7), respectively [2]:

$$\varepsilon_\infty = n^2 \quad (6)$$

$$\varepsilon_o = 18.52 - 3.08E_g \quad (7)$$

Among all Sb_2S_3 thin films, Sb_2S_3-325 °C has a high dielectric value leading to enable charge shifts, change the charges' lifetime and stabilizes mobility of the charge in the samples because of the possibility of formation of large particles and the possibility of decreasing the number of grain boundaries [17].

Table 1. the value of the optical parameters of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C

Samples	E_g	Moss relation		Herve&Vandemme		Ravindra		
	(eV)	n	ε_∞	n	ε_∞	n	ε_∞	ε_o
Sb_2S_3-275 °C	2.36	2.60	6.76	2.56	6.57	2.15	4.63	11.25
Sb_2S_3-300 °C	2.47	2.57	6.61	2.52	6.36	2.06	4.24	10.91
Sb_2S_3-325 °C	1.84	2.76	7,66	2.78	7.73	2.59	6.73	12.85

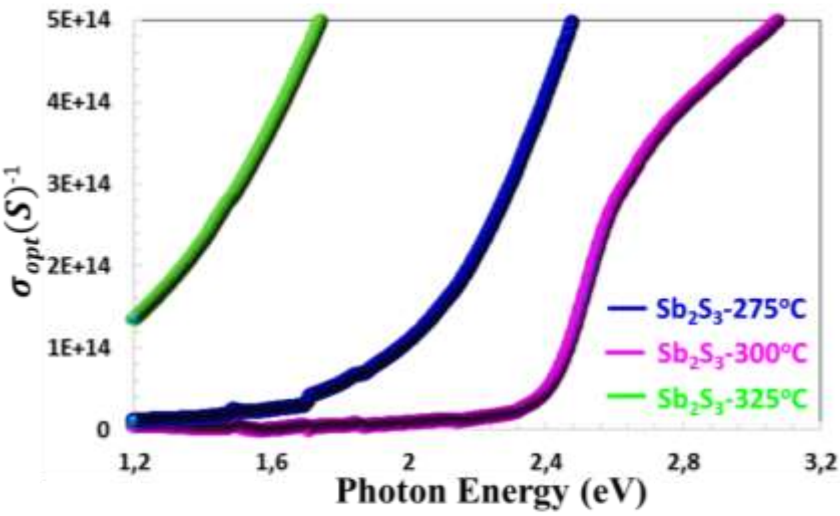

Figure 5. The optical conductivity ($\sigma_{opt}(S)^{-1}$) spectra of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films

The optical conductivity (σ_{opt}) of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C samples is regulated related to Eq. (8);

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \quad (8)$$

where c is the light speed. σ_{opt} value defines the change in photo excited electrons' density [18]. The value of σ_{opt} of Sb_2S_3-325 °C thin films is higher in the lower energy regions, while that of Sb_2S_3-300 °C thin film is higher in larger energy region as seen in Figure 5. The optical conductivity of Sb_2S_3-325 °C is higher than that of Sb_2S_3-275 °C and Sb_2S_3-300 °C samples. Sb_2S_3-325 °C has higher optical conductivity because of the fact that more photo-excited electrons were shaped round the lower energy band gap. Since Sb_2S_3-300 °C thin film absorbs fewer photon, its σ_{opt} value is lower.

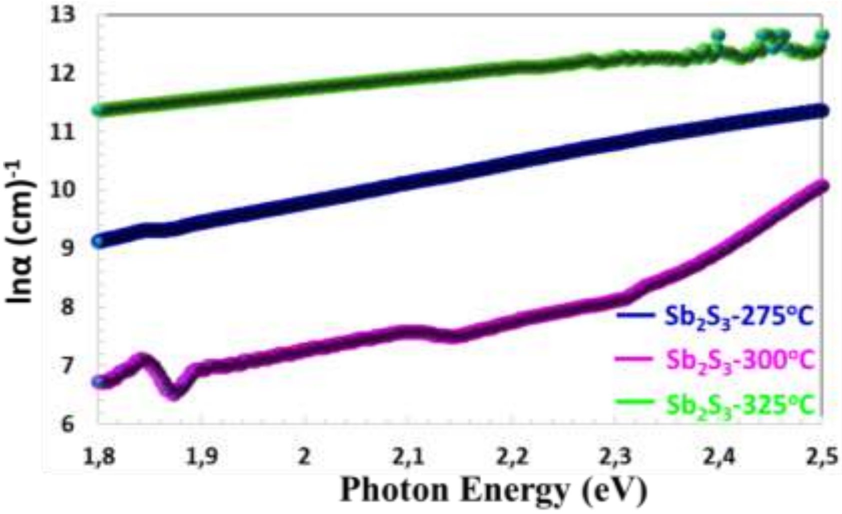

Figure 6. The Urbach energy of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C films

Urbach energy (E_U) states material disorder' change related to conversions between in the conduction band' localized states and of valance band' extended states and E_U is also used to investigate the change in disorder of both low crystalline and amorphous materials. Eq. (9) can be utilized to estimate the disorder in the compound based on the variation in the absorption coefficient (α), as explained below:

$$\alpha = \alpha_o exp(h\nu/E_U) \quad (9)$$

where α_o is a constant. E_U values of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films are 1.59 eV, 2.75 eV and 0.43 eV, respectively. The high E_U value of Sb_2S_3-300 °C shows more phonon disorder compared to Sb_2S_3-275 °C and Sb_2S_3-325. Furthermore, the density of localized states in thin films [19], stoichiometric deviation, and distortion in thin film that expands the band tail [20] and films can all be linked to E_U values.

Conclusions

In this study, the optical changes of Sb_2S_3 samples grown at 275 °C, 300 °C and 325 °C using the Spray Pyrolysis method were examined. The band gaps of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C thin films were obtained as 2.36 eV, 2.47 eV and 1.84 eV, respectively. While Sb_2S_3-325 °C thin film absorbs a high amount of photons, Sb_2S_3-275 °C thin film absorbed a lower amount of photons. Depending on the wavelength and photon energy, the extinction coefficient, skin depth, optical conductivity spectra were obtained. Using Herve and Vandamme, Moss and Ravindra relations, the refraction indices and dielectric constants were calculated. It can be seen that the data obtained with Herve and Vandamme, Moss relations are closer to each other. Sb_2S_3 thin films with high photon absorption have higher refractive index and dielectric constants. E_U values of Sb_2S_3-275 °C, Sb_2S_3-300 °C and Sb_2S_3-325 °C samples were calculated to be 1.59 eV, 2.75 eV and 0.43 eV, respectively.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

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