GROWTH AND CHARACTERIZATION OF OPTICAL AND SOLID STATE PROPERTIES OF ANNEALED ANTIMONY SULPHIDE (Sb_2S_3) THIN FILMS.

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Antimony sulphide (Sb_2S_3) thin films were grown on glass substrates from baths containing antimony trichloride ($SbCl_3$) and sodium thisulphate ($Na_2S_2O_3$) dissolved in acetone (CH_3CO). Some of the film samples deposited at both room temperature and 55 ^oC in an oven were annealed at different temperatures of 100, 200 and 400 ^oC. Measurements of spectral absorbance and transmittance for annealed and un-annealed samples were performed in the NIR-VIS-UV regions of the electromagnetic spectrum using a spectrophotmeter (D model Avantes Spec 2048 version 7.0). Other properties were evaluated using mathematical relations. For room temperature deposition, the un-annealed sample has optical conductivity of 2.5 x 10^7 s^{-1} while samples annealed at 100 ^oC and 200 ^oC have optical conductivities of 7.6 x 10^7 s^{-1} and 9.8 x 10^7 s^{-1} respectively. For deposition at 55 ^oC, the optical conductivity increased to 1.0 x 10^9 s^{-1} for200 ^oC annealing temperature. Energy band gaps obtained for un-annealed and annealed samples at room temperature deposition ranged from E_g^d of 1.8 -2.6 eV and E_g^i of 0.7 – 2.5 eV and for deposition at 55 ^oC the values were E_g^d of 2.0-2.1 eV and E_g^i of 2.4-2.5 eV. These results and more are reported in this paper.

(Received November 28, 2011; accepted December 7, 2011)

Keywords: Antimony sulphide, Annealing , absorption coefficient, Sodium thiosuphate, Energy band gap.

1. Introduction

Thin films of chalcogenide glass of Sb_2S_3 are very promising materials whose attractive physical properties can be changed in controlled manner by annealing at varying temperatures or doping with different impurity elements [1,2]. This makes them useful semiconductor materials for applications in electronic devices especially for the videocon type of television camera tubes, switching, microwave and optoelectronic devices [3,14]. The effects of annealing temperatures on optical and solid state properties of chalcogenide glasses have been reported by many researchers [4-7]. Such effects are strongly dependent on the composition of the glass [8-11]. In this paper, the growth and characterization of Sb_2S_3 thin films deposited at both room temperature and oven temperature of 55 ^oC and annealed at various temperatures are discussed.

2. Experimental details

2.1 Film Deposition

Stoichiometric measurements of antimony tri-chloride ($SbCl_3$), sodium thiosulphate ($Na_2S_2O_3$) and a comlpexing agent, acetone (CH_3CO) were prepared in aqueous solution using

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CBD technique as follows: 1.3g of $SbCl_3$ was dissolved in 5 ml of acetone in a 50 ml beaker and then 25 ml of 1 M sodium thiosulphate was added and stirred before 20 ml of distilled water was added to the bath. Degreased glass slides were inserted vertically into the bath with a synthetic foam which partly covers the top of the bath. Deposition in different baths were formed and left for different hours undisturbed to check the effect of deposition time.

2.2 Characterization of the deposited Sb_2S_3 thin films

Characterization of the Sb_2S_3 thin films following their successful deposition was carried out at Sheda Science and Technology Complex (SHESTCO), Gwagwalada, Abuja with the assistance of technologists. Measurements of the spectral absorbance and transmittance were performed in the NIR-VIS-UV region of the electromagnetic spectrum using a spectrophotometer (D model Avantes Spec 2048 version 7.0).

3. Results and discussion

3.1 Sb_2S_3 thin films deposited at room temperature

Fig. 1 shows the spectral absorbance of the Sb_2S_3 thin film samples deposited at room temperature. The un-annealed sample AB_1 has peak value of 1.5 in the ultraviolet region of 300 nm wavelength. Samples AB_2 and AB_3 annealed at 100 ^oC and 200 ^oC have respective peak values of 2.3 at 350 nm wavelength and 1.7 at 300 nm wavelength. Fig. 2 shows the transmittance of the Sb_2S_3 thin film samples. Sample AB_3 has the most pronounced transmittance of 80 % at a wavelength of 700 nm which drops to zero between 300-400 nm wavelength and rises to 25 % at 250 nm wavelength. Un-annealed sample AB_1 has consistent higher transmittance (40-46 %) as compared to AB_2 annealed at 100 ^OC with transmittance of 15-22 %. Thus, annealing temperatures produce distinctive effects on the absorbance and transmittance of Sb_2S_3 thin films.

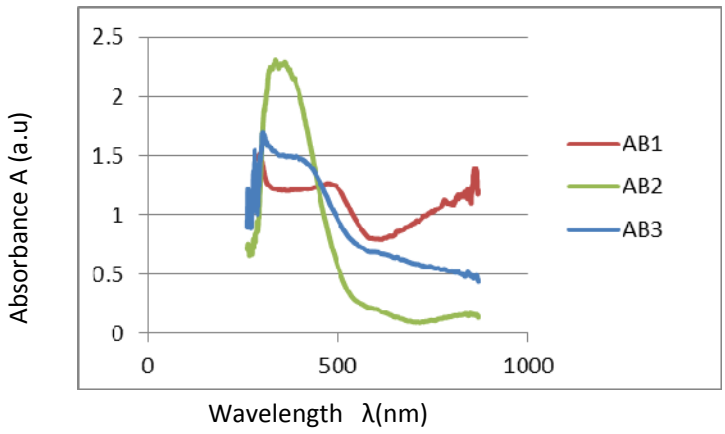


Fig. 1 Absorbance as a function of wavelength for annealed Sb_2S_3 thin films deposited at room temperature with AB_1(As Grown), AB_2(100 ^OC) and AB_3(200 ^oC).

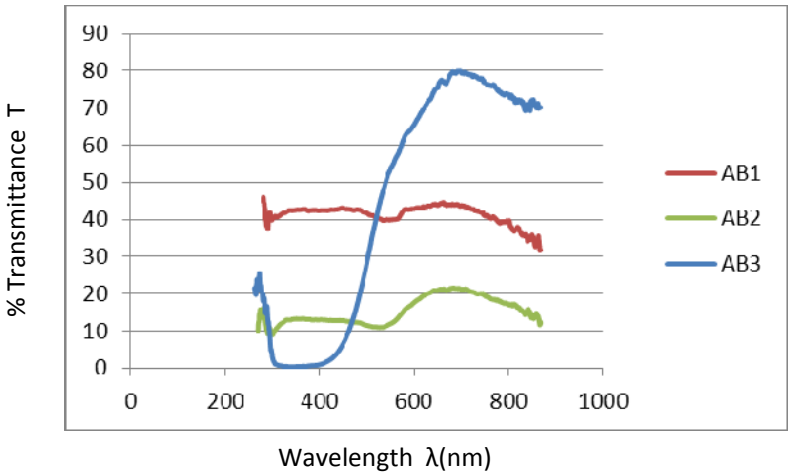


Fig. 2: Transmittance as a function of wavelength for annealed Sb_2S_3 thin film samples deposited at room temperature with AB_1(As Grown), AB_2(100 °C) and AB_3(200 °C)

The absorption coefficient α representing the fractional decrease in intensity of the radiation per unit increase in distance traversed in the film material is obtained using the relation [14].

$$\alpha = 4\pi k/\lambda \quad (1)$$

where λ is the corresponding wavelength and k is the extinction coefficient.
The index of refraction n is obtained from

$$n = \sigma\lambda/2k \quad (2)$$

and the optical conductivity σ is given by

$$\sigma = 2nk/\lambda \quad (3)$$

The graphs of these parameters whose peak values are contained in table1 are shown in Fig.3 (a, b, c, d).

Table. 1: Peak values of optical and solid state properties of annealed Sb_2S_3 thin film samples.

Sample/Annealing Temperature	n	α(m^{-1})	K	σ(10^7 s^{-1})	E_g^d (eV)	E_g^i (eV)
AB_1(As Grown)	1.10	1.0	800	2.5	1.8	0.7
AB_2(100 °C)	1.50	3.0	1480	7.6	1.8	1.0
AB_3(200 °C)	1.25	5.5	1530	9.8	2.6	2.5

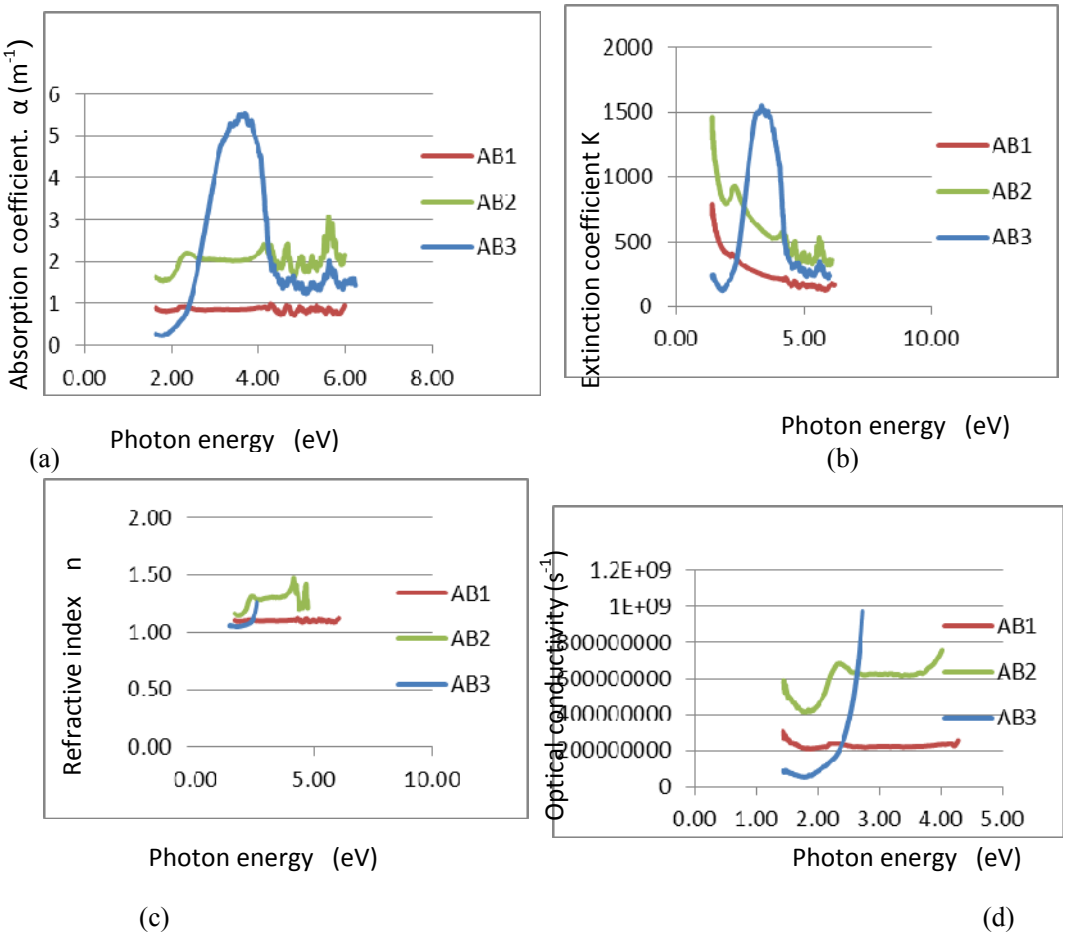
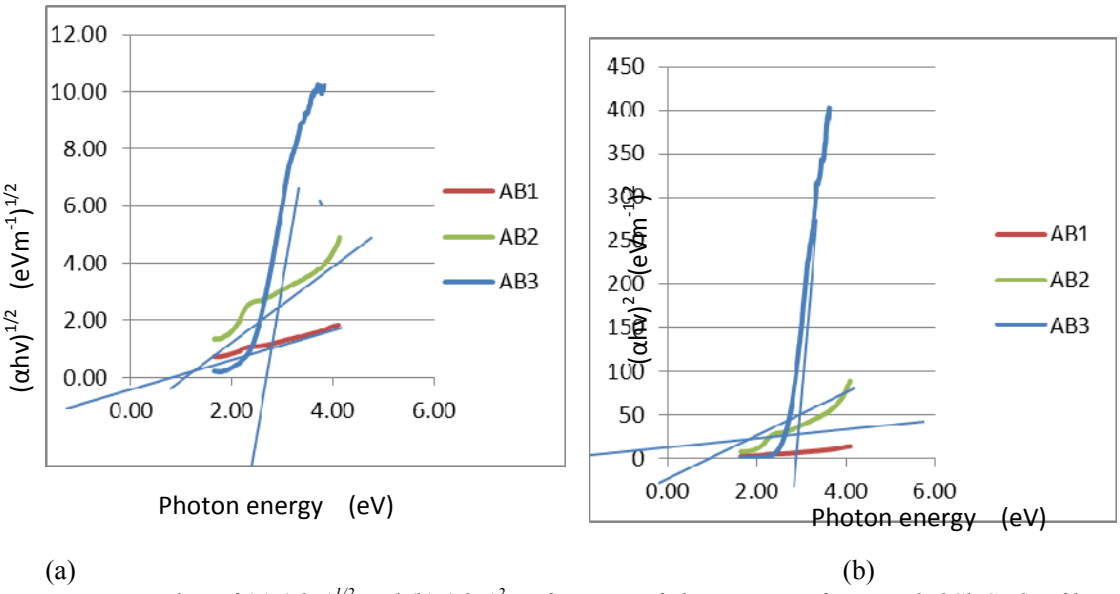


Fig. 3: Plots of (a) Absorption coefficient, α (b) Extinction coefficient, k (c) Refractive index, n and (d) optical conductivity, σ as functions of photon energy for annealed Sb_2S_3 thin film samples deposited at room temperature with AB_1(As Grown), AB_2(100 °C) and AB_3(200 °C).

Fig. 4 (a,b) show graphs of $(\alpha h\upsilon)^n$ as functions of photon energy for n = ½ (indirect transition) and n = 2 (direct transition) using the following relation [12,13]:

$$(\alpha h\upsilon)^n = A(h\upsilon - E_g) \quad (4)$$

where A is a constant. The corresponding indirect and direct band gap energies are obtained by extrapolating the straight portions of the graphs to the hυ axis.

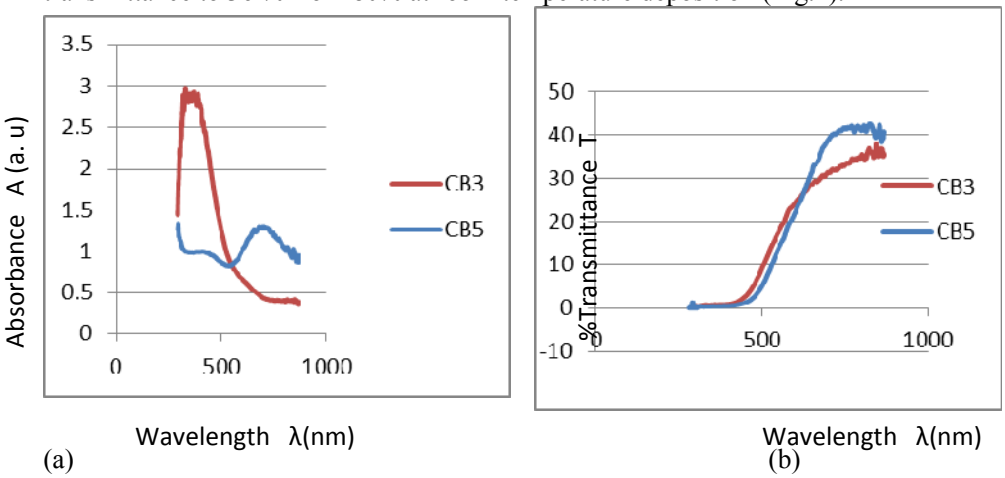


(a) (b)

Fig. 4: Plots of (a) $(\alpha h\upsilon)^{1/2}$ and (b) $(\alpha h\upsilon)^2$ as functions of photon energy for annealed Sb_2S_3 thin films deposited at room temperature with AB_1(As Grown), (AB_2 100 °C) and (AB_3 200 °C).

3.2: Sb_2S_3 thin films deposited at 55 °C

Fig. 5 (a,b) show the results for the absorbance and transmittance of Sb_2S_3 thin film samples CB_3 and CB_5 deposited at 55 °C and annealed at 200 °C and 400 °C respectively. Clearly, higher deposition temperature of 55 °C with annealing temperature of 200 °C increased the peak absorbance to 3.0 from 1.7 at room temperature deposition (Fig.1) and decreased the peak transmittance to 36 % from 80% at room temperature deposition (Fig.2).



(a) (b)

Fig. 5: (a) Absorbance (b) Transmittance as functions of wavelength for annealed Sb_2S_3 thin films deposited at 55 °C with CB_3(200 °C) and CB_5(400 °C)

On the other hand, for the same deposition temperature of 55 °C, higher annealing temperature of 400 °C decreased the peak absorbance to 1.3 and increased the peak transmittance to 42 % as compared to 3.0 and 36% respectively for annealing temperature of 200 °C as evident in Fig. 4 (a,b). Also, for annealing temperatures of 200 °C and above, the transmittance is zero in the wavelength range of 300-450 nm.

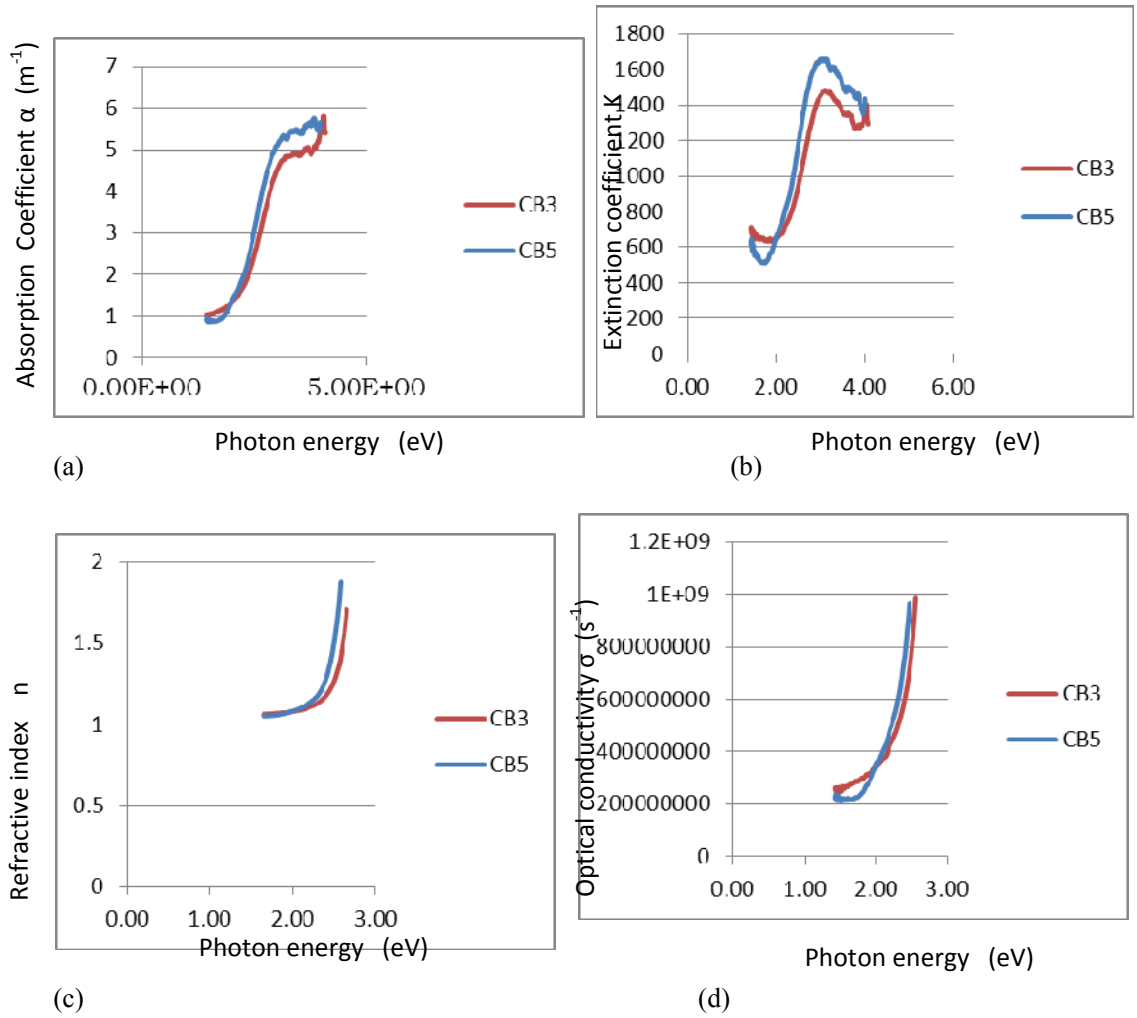


Fig. 6: Graphs of (a) Absorption coefficient (b) Extinction Coefficient (c) Refractive index and (d) Optical conductivity as functions of photon energy for annealed Sb_2S_3 thin films deposited at 55 ^oC with CB_3(200 ^oC) and CB_5(400 ^oC).

Table 2: Peak values of optical and solid state properties of annealed Sb_2S_3 thin film samples deposited at 55 ^0C.

Sample/Annealing Temperature	n	α(m^{-1})	K	σ(10^9 s^{-1})	E_g^d (eV)	E_g^i (eV)
CB_3(200 ^{o}C)	1.65	5.8	1500	1.00	2.1	2.5
CB_5(400 ^{o}C)	1.85	5.8	1680	0.98	2.0	2.4

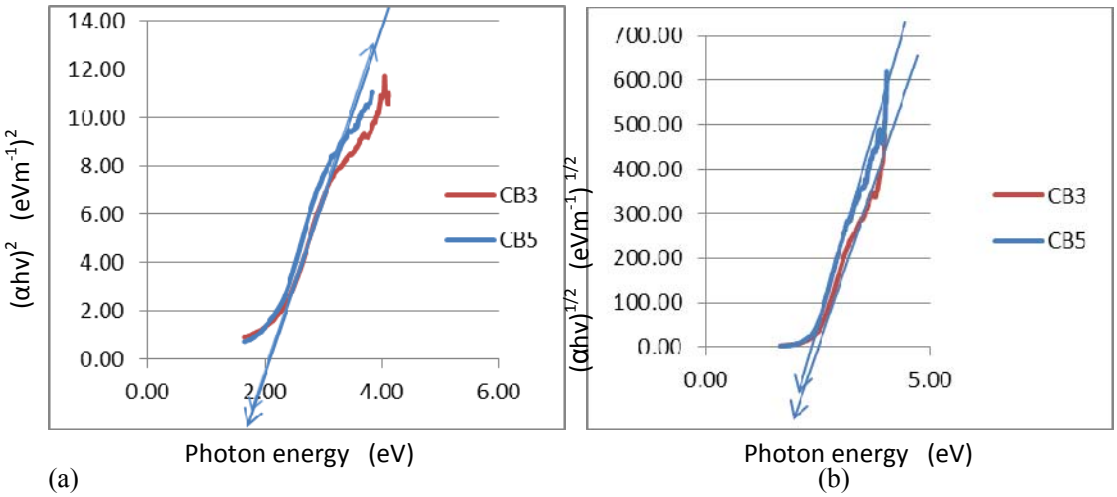


Fig. 7: Plots of (a) $(\alpha h\upsilon)^2$ and (b) $(\alpha h\upsilon)^{1/2}$ as functions of photon energy for annealed Sb_2S_3 thin films deposited at 55 ^{0}C with CB_3(200) and CB_5(400).

Fig. 6 (a,b,c,d) show graphs of absorption coefficient, extinction coefficient, refractive index and optical conductivity as functions of photon energy for the Sb_2S_3 thin film samples deposited at 55 ^{o}C while Fig.7 (a,b) are graphs of $(\alpha h\upsilon)^n$ against photon energy $h\upsilon$ used to obtain the band gap energies E_g^d and E_g^i as in the case of room temperature deposition. The distinct effects of both deposition and annealing temperatures are evident in the peak values of these parameters contained in table 2 when compared to their values in table1.

4. Conclusion

Antimony sulphide, Sb_2S_3 thin film samples have been successfully deposited on glass substrates at both room temperature and 55 ^{o}C, annealed at various temperatures and characterized. At room temperature deposition, energy band gaps after annealing ranged from 1.8-2.6 eV for E_g^d and 0.7-2.5 eV for E_g^i. For deposition at 55 ^{o}C energy band gaps on annealing were 2.0-2.1 eV for E_g^d and 2.4-2.5 eV for E_g^i. Profound effects of both deposition and annealing temperatures on transmittance, absorbance, optical conductivity, refractive index and other properties of the Sb_2S_3 thin films are as reported.

Acknowledgement

The authors are thankful to the Management and Technologists at SHESTCO, Gwagwalada, Abuja, for their assistance and use of their facilities.

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