Influence of Film Thickness on the Optical Properties of Antimony Sulphide Thin Films Grown by the Solution Growth Technique

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ABSTRACT

In this study, the effect of film thickness on the optical properties of antimony sulphide (Sb_2S_3) thin films grown on soda-lime glass substrate using the solution growth technique is reported. The film thickness was varied by altering the deposition time. The deposition time was between 1h to 5h and the other deposition variables were kept constant. The results show that the film thickness increased with an increase in the deposition time, and attained a maximum thickness at the deposition time of 4h and decreased thereafter. The film thickness was obtained in the range of 35 nm to 98 nm. The optical properties of the films were investigated using a UV-spectrophotometer to determine the transmittance and absorbance versus wavelength in the range of 400 nm to 1250 nm. Analysis from the optical characterisation reveals that the optical constant; energy bandgap, extinction coefficient, and the optical density varied with the film thickness. The optical energy bandgap was direct and in the range of 2.05 eV to 2.10 eV. The extinction coefficient was in the range $0.01 \leq 0.27$ while the optical density was between $0.01 \leq 0.34$.

Keywords: Film thickness, deposition time, optical properties, solar cell devices
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INTRODUCTION

In recent years, nanotechnology has dominated almost every field of the electronic, optoelectronic, medical and manufacturing industries. In the photonic industry, nanotechnology has been widely utilized in quantum dots solar cells. A proper understanding of the optoelectronic properties of semiconductor materials for photonic device applications is a fundamental step to effective utilisation of such materials for increased efficiency. This is simply because of the fact that the operation of these devices are generally governed by the interaction of light (photons) with certain properties or excitations of the materials that make up those devices in question. In recent years, considerable attention has been drawn to the investigations of antimony sulphide for applications in the electronics, optoelectronic, photonic and in other device applications. Antimony sulphide is a member of the chalcogenides group and is widely known to exhibit the orthorhombic crystal structure [1], and a n-type electrical conductivity [2-3]. Sb_2S_3 is earth-abundant because the constituent materials (Sb and S) are abundant in nature. Sb and S are more environmentally acceptable compared to the Cadmuim-related materials used in the fabrication of some advanced thin film solar cells such as cadmium telluride based devices. One peculiar advantage of antimony sulphide thin films include the possibility of using low-cost and effective deposition technique to grow the films. In the literature, several research groups have grown thin films of Sb_2S_3 for various applications using different methods which includes; spray pyrolysis [4-5], thermal evaporation [6-7], Radio-frequency sputtering [8] successive ionic layer adsorption and reaction-SILAR [9-10], electrodeposition [11], dip method [12], and by solvothermal routes [13].

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Different research groups have used antimony sulphide in several device applications. These includes target material for TV cameras [14-16], microwave devices [17], switching devices [18], decorative coatings [19], and in various optoelectronic applications [20-21]. In the present investigation, we report on the influence of film thickness on the optical properties of antimony sulphide thin films with a view to establish the optimised conditions necessary to obtain Sb_2S_3 layers suitable for use in photonic devices.

MATERIALS AND METHODS

Substrate cleaning is a critical and fundamental step in thin film deposition. The soda-lime glasses used as substrates were thoroughly cleaned with detergent and then degreased with acetone. Further, the sodalime glasses were then subjected to an ultrasonic cleaning to make the substrates completely dirt-free. Details of the substrate and source preparation, and the deposition method have been reported previously [22].

The method utilised by Ubale et al [23] and by other research groups [1] was employed to calculate the film thickness using the gravimetric method or double weight method. A Unico –UV-2102PC spectrophotometer operated at normal incident of light in the wavelength range of 400 nm to 1250 nm was used for the optical spectroscopy (absorbance and transmittance vs wavelength measurements).

RESULTS AND DISCUSSION

Fig. 1 gives the variation of the film thickness with deposition time. Film thickness is one of the fundamental parameters that govern the behavior of some thin film devices. In solar cell devices, the film thickness of the absorber layer is amongst the principal parameters that determine the solar conversion efficiency in that the film thickness must be of certain magnitude in order to support the contact voltage. As indicated in Fig. 1, the film thickness increased up to the deposition time of 4 h and changed otherwise. Increase in film thickness due to increasing deposition time could be attributed to an increase in the mobility of ad-atoms due to the longer deposition time. This could consequently increase the crystallite/grain size or other related effects, leading to an increased film thickness. In the literature, different authors have reported on variation of film thickness with different/similar deposition parameters for antimony sulphide or other related chalcogenides [24-29]. It could be possible that the decrease in the film thickness at the longer deposition time was caused by a fragmentation of crystallites or to other related phenomena.
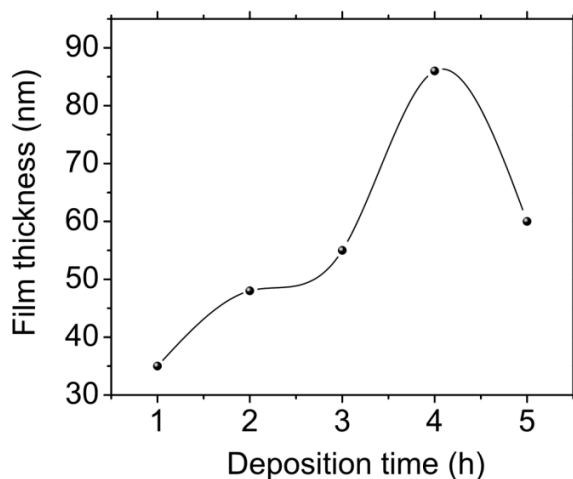

Fig. 1: Variation of film thickness with deposition time.

Fig. 2 gives the variation of the absorbance of the films with wavelength at the different film thickness. The analysis indicate that the absorbance decreased sharply with wavelength up to a critical wavelength (around 498 nm to 505 nm), and then become relatively constant (wavelength regions > energy bandgap) as indicated in Fig. 2. The absorbance spectra for film thicknesses between 35 nm to 55 nm is relatively similar, exhibiting a different behaviour at the highest film thickness (86 nm).
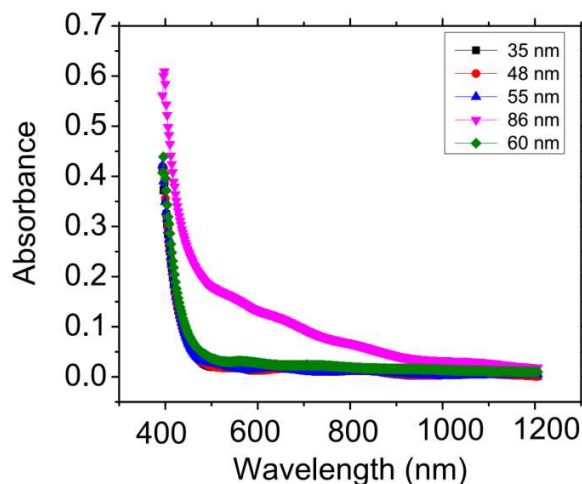
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Fig. 2: Plot of absorbance vs wavelength at different film thickness.

The variation of the absorbance of the Sb_2S_3 thin films with wavelength at different deposition variables has been reported by other authors [30]. Fig. 3 gives the variation of the transmittance with wavelength. As shown on Fig. 3, the films were more uniform for thicknesses ≤ 55 nm because of the clear interference patterns exhibited by the plots at those thicknesses. However, at the highest thickness (86 nm) the interference pattern was relatively less vivid. Existence of interference pattern in the transmittances of Sb_2S_3 thin films has been reported by other authors [31-32] independent of the deposition techniques.
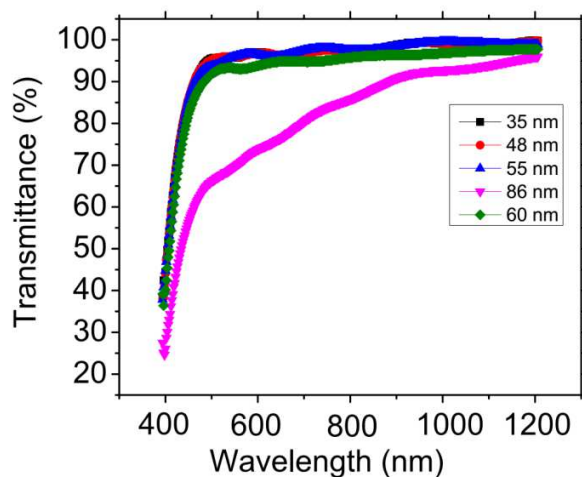

Fig. 3: Plot of transmittance vs wavelength at different film thickness.

Information extracted from the transmittance vs wavelength plots was used to generate the plots of $(\alpha h\nu)^2 \ versus \ h\nu$ as shown on Fig. 4. From the plots (Fig. 4), there is no kinks/shoulders for regions of energy $< E_g$ or for regions $> E_g$, which points to the fact that a direct energy band gap is expected and also that other phases of antimony sulphide is not present. It is on this premise that the energy bandgap was calculated using the relation [33-35] given in equation (2) as;

$$\alpha = B(h\nu - E_g)^n \qquad \qquad (2)$$

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In equation 2, B is an energy independent constant, E_g is the energy bandgap and the index   n = 0.5 for direct allowed transition and 1.5 for indirect allowed transition [34].

It is generally understood that the energy band gap can be obtained from the graph of $(\alpha h\nu)^2$ *versus* $h\nu$ by the linear extrapolation of the intercepts on the $h\nu$ -axis. This gives the energy bandgap in the range 2.05 eV to 2.10 eV. The close values was due to the proximity of the film thicknesses. The values of the energy bandgap obtained in this study is within the range reported by other authors [1, 23, 30] in the literature.
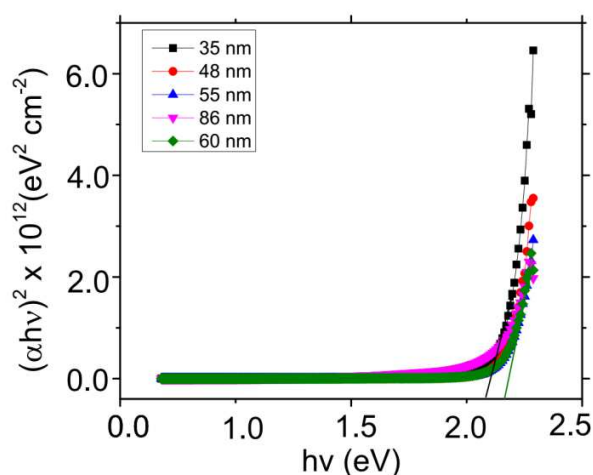

Fig. 4: Plots of $(\alpha h\nu)^2$ *versus* $h\nu$ **at different film thickness.**

Fig. 5 gives the plots of the extinction coefficient with the wavelength. The extinction coefficient is directly related to optical absorption coefficient and the wavelengths of the region under study for that particular material. Generally when light is incident on a thin film material, there is an interplay of reflection, transmission and absorption. According to the literature [34], the absorption coefficient α, gives information on the extinction coefficient k, and is related as;

$$k = \frac{\alpha\lambda}{4\pi}$$
(3)

where α is the optical absorption coefficient, λ is the wavelength, and π is a constant.

The results show that the extinction coefficient, k was in the range 0.01 to 0.27, exhibiting a less steep curve for the films with the highest thickness (86 nm). However the plots all show a similar trend of a decrease with lower photon energies (higher wavelengths). Similar behaviour has been reported by other authors in the literature [36-37], independent of the deposition techniques.

It has been established that the optical density is related to the film thickness and the optical absorption coefficient [38]. Fig. 6 gives the variation of the optical density ρ_{opt} , with the wavelength under investigation. The optical density was calculated using the formula [38], given as;

$$\rho_{opt} = \alpha t$$
(4)

where α is the optical absorption coefficient and t is the film thickness. The evaluated optical density was in the range 0.01– 0.34. The optical densities were relatively close to each other for film thicknesses ≤ 60 nm. However, higher values of the optical densities were obtained at lower photon energies (longer wavelengths) for the films with higher thickness (86 nm) at the region of energies < energy bandgap.
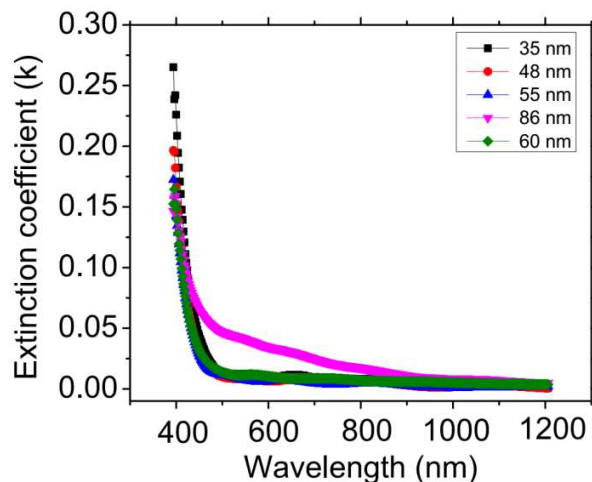
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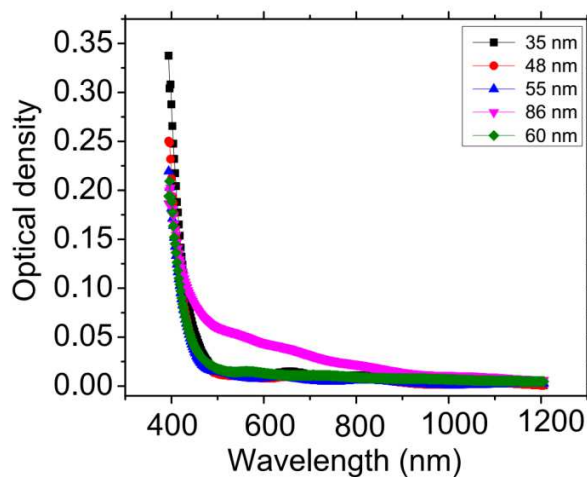**Fig. 5: Plot of extinction coefficient vs wavelength at different film thickness.**

Fig. 6: Plot of optical density vs wavelength at different film thickness.

In the literature, variation of the optical density with similar/different deposition variables has been reported for antimony sulphide thin films grown by same or different deposition methods. Ubale et al [23], observed similar trend of decreasing optical densities with wavelength at different film thickness for Sb_2S_3 thin films grown by the chemical bath deposition technique.

CONCLUSION

Antimony sulphide (Sb_2S_3) thin films were successfully grown using the solution growth technique and optical spectroscopy was used for the characterisation. The results show that the optical constants (energy band gap, extinction coefficient, optical density) is within the range reported by other authors. The evaluated optical constants (extinction coefficient and the optical density) were observed to decrease with increasing wavelength while the trend observed for the variation of the transmittance and absorbance with wavelength is in line with current literature. The values of the energy bandgap of the films were in the range suitable for application as window layers in solar cell devices and in other optoelectronic applications.

REFERENCES

[1] H Megharaoui-Meherzi; T Ben Nasr; N Kamoun; M Dachraoui. *Physica B*, **2010**, 405, 3101.

5

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[2] KF Abd-El-rahman; AAA Darwish. *Curr. Appl Phys*, **2011**, 11, 1265.

[3] JS Curran; R Philippe - Fourth EC Photovoltaic Solar Energy Conference, 1982 – Springer.

[4] KY Rajpure; CH Bhosale; CD Lokhande. *Thin Solid Films*, **1997**, 311,114.

[5] KY Rajpure; CD Lokhande; CH Bhosale. *Mater. Chem. Phys.,* **1997**, 51, 252.

[6] AE El-Shaazy; MAM Seyam; MM El-Samanoudy; AH Ammar; EM Assim. *Appl. Surf. Sci*, **2002**, 189, 129.

[7] IK El Zawawi; A Abdel-Moez; FS Terra; M Mounir. *Thin Solid Films*, **1998**, *324*(1), 300.

[8] MY Versavel; JA Haber. *Thin Solid Films*, **2007**, 515(18), 7171.

[9] BR Sankpal; HM Pathan; CD Lokhande. *J. Mater. Sci. Lett.,* **1999**, 18, 1453.

[10] HM Pathan; CD Lokhande. Bull. Mater. Sci., **1994,** 27(2), 85.

[11] NS Yesugade; CD Lokhande; CH Bhosale. *Thin Solid Films*, **1995**, 263, 145.

[12] BB Nayak; HN Acharya; TK Choudhuri; GB Mitra. *Thin Solid Films*, **1982**, 92, 309.

[13] W Lou; M Chen; X Wang; W Liu. *Chemistry of materials*, **2007**, 19(4), 872.

[14] G Ghosh; BP Varma. *Thin Solid Films*, **1979**, 60, 611.

[15] ZS El Mandouh; SN Salama. *J. Mater. Sci.,* **1990**, 25, 1715.

[16] Q Lu; H Zeng; Z Wang; X Cao; L Zhang. *Nanotechnology*, **2006,** 17, 2098.

[17] J Grigas; J Meshkauskas; A Orliukas. *Phys. Stat. Sol.,* **1976**, A 37, K39.

[18] MS Ablova; AA Andreev; TT Dedegkaev; BT Melekh; AB Pevtsov; NS Shendel; LN Shumilova. *Sov. Phys. Semicond*., **1976**, 10, 629.

[19] R Oomen; NJ Mathew; PU Rjalakasmi. *J. Ovonic Res.,* **2010**, 6(6), 259.

[20] J George; MK Radhakrishnan. *Solid State Commun*., **1980**, 33, 987.

[21] E Montrimas; A Pazera. *Thin Solid Films*, **1976**, 34, 65.

[22] PA Nwofe. *Adv. Appl. Sci. Res.,* **2015**, 6(3), 168.

[23] AU Ubale; VP Deshpande; YP Shinde; DP Gulwade. *Chalcogenide Letts.,* **2010**, 7(1), 101.

[24] DS Campbell. In: R. Nledermayer, H. Mayer (Ed.), Basic Problems in Thin Film Physics, Vandenhoeck and Ruprecht, Göttingen, 1966, p.113.

[25] PA Nwofe. PhD Thesis, Northumbria University, (Newcastle Upon Tyne, UK, **2013**).

[26] PA Nwofe; KTR Reddy; JK Tan; I Forbes; RW Miles. *Physics Procedia*, **2012**, 25, 150.

[27] Y Rodríguez-Lazcano; L Guerrero; O Gomez Daza; MTS Nair; PK Nair. *Superficies y Vacío*, **1999**, 9, 100.

[28] AA El-Shazly; MM El-Samanoudya; MAM Seyam; AH Ammar; EM Assim. *Eur. Phys. J. AP*, **2003**, 21, 225.

[29] S Srikanth; N Suriyanarayanan; S Prabahar; V Balasubramanian; D Kathirvel. *Adv. Appl. Sci. Res.,* **2011**, 2(1), 95.

[30] P.U. Asogwa, S.C. Ezugwu, F.I. Ezema, R.U. Osuji, *Chalcogenide Letts*., **2009**, 6(7), 287.

[31] F Aousgi; M Kanzari. *Energy Procedia,* **2011**, 10, 313.

[32] A Sinaoui; I Trabelsi; F Chaffar Akkar; F Aousgi; M Kanzari. *Int. J. Thin Fil. Sci. Tec*. **2014**, 3(1), 19.

[33] PE Agbo; FU Nweke; PA Nwofe; CN Ukwu. *International Journal of Science and Research,* **2014**, 3(11), 1832.

[34] JI Pankove. Optical Processes in Semiconductor, Prentice-Hall, Upper Saddle River, New Jersey, **1971**, pp. 36.

[35] PA Nwofe; KTR Reddy; JK Tan; I Forbes; RW Miles. *J. Phys: Conf. Ser.,* **2013**, 417, 012039.

[36] N Jessy Mathew; Rachel Oommen, P Usha Rajalakshmi; C SANJEEVIRAJA. *Chalcogenide Letts*, **2011**, 8(7), 441.

[37] N Jessy Mathew; Rachel Oommen; P Usha Rajalakshmi. *Chalcogenide Letts*, **2010**, 7(10), 701.

[38] C Cifuentes; M Botero; E Romero; C Calderón; G Gordillo. *Braz. J. Phys.* **2006**, 36, 1046.