

Effect of deposition time on the optical properties of antimony sulphide thin films grown by the solution growth technique

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ABSTRACT

Thin films of antimony sulphide (Sb_2S_3) were grown on soda-lime glass substrate using the solution growth technique. The deposition time was varied 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. From the optical characterisation done using a UV-spectrophotometer in the wavelength range of 400 nm to 1250 nm, it was observed that the optical constant; energy bandgap, extinction coefficient, and the optical density varied with the deposition time. The extinction coefficient was in the range 0.01 to 0.27 while the optical density varied from 0.01 to 0.34. The optical energy bandgap was in the range of 2.05 eV to 2.10 eV. These values strongly suggest the possible use of the films for optoelectronic applications especially as window layers in solar cell devices.

Keywords: deposition time, optical constants, window layers, solar cell devices

INTRODUCTION

It has been established that thin films is the best way to produce solar cells with increased efficiency at reduced cost due to reduced materials requirements amongst other favourable properties. However, there is need to understand the optoelectronic properties of a semiconductor material to enhance the knowledge of its use in device applications. In most photonic devices, their operation depends principally on the interaction of the photons with any or all of the intrinsic/extrinsic properties of the constituent materials of which the device is made of. This is a major indicator to how effectively and efficiently these constituent materials can usefully transmit (for window layer materials) or absorb (in the case of absorber materials) the photons. However, it is pertinent to note that the effectiveness and efficiency of these interactions can be seriously hampered by the presence of traps, recombination centers, interface effects, grain boundaries, voids, and other related defects. Research done by Jones et al [1], and by Mendis and Durose [2], indicate that the optoelectronic properties of materials can be affected by the presences of these defects since the measurable optoelectronic parameters will be affected. Antimony sulphide belongs to the chalcogenides group and it has been reported to exhibit the orthorhombic crystal structure [3], and a n-type electrical conductivity [4-5]. The constituent materials (Sb and S) are abundant and more environmentally acceptable compared to the Cadmium-related materials used in the fabrication of some advanced thin film solar cells. Antimony sulphide can be grown using low-cost and effective deposition technique. Some research groups have deposited thin films of Sb_2S_3 for various applications using different techniques such as; thermal evaporation [6], spray pyrolysis [7-8], Radio-frequency sputtering [9] successive ionic layer adsorption and reaction-SILAR [10], electrodeposition [11], and dip method [12]. In the literature, antimony sulphide has been used in several device applications such as; (i) target material for TV cameras [13-15], (ii) microwave devices [16], (iii) switching devices [17], (iv) decorative coatings

[18], and in various optoelectronic applications [19-20]. In this study, the optical properties of the antimony trisulphide are investigated with a view to understand and establish the suitability of the grown films for applications in various optoelectronic devices.

MATERIALS AND METHODS

The initial step was to clean the soda-lime glasses used as substrates. The substrates were thoroughly cleaned with detergent and then degreased with acetone. The sodalime glasses were then further subjected to an ultrasonic cleaning to make the substrates completely dirt-free. The source materials used were antimony trichloride (SbCl_3), sourced from Guangdong Guanghua Sci-Tech Co Ltd, China, sodium thiosulphate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and acetone that was procured from BDH Chemical Ltd, UK through local suppliers. The source materials all had impurity $\geq 99.0\%$. A 2.0g of the SbCl_3 was dissolved in a 10 ml of acetone in a beaker. Inside the beaker, a 125 ml of $\text{Na}_2\text{S}_2\text{O}_3$ was also added and the solution was then made up by adding distilled water. The system was left to stir for 10 min to ensure complete mixing using a magnetic stirrer. The initial pH of the solution was 4.93. The solution was then distributed into 5 separate beakers and 5 clean glass slides were then immersed into each beaker. The substrates were held vertically through a synthetic foam and allowed for the respective deposition time.

Film deposition using chemical bath deposition occurs through different process. It has been established that film deposition on a substrate occurs in two steps of nucleation and particle growth. Nucleation and film growth can be due to an inter-play of other processes such as: simple-ion cluster mechanism, simple hydroxide cluster mechanism, complex ion-by-ion decomposition mechanism, and the complex-cluster decomposition mechanism. The simple ion process could diffuse to the substrate to initiate nucleation and the nucleated layers then grow by adsorption of ions in the solution and or nucleation of new crystals. In the literature, some research groups noted that the formation of antimony sulphide in a thiosulphate bath is mostly by hydrolytic decomposition in an acidic media [4].

Film thickness is one of the most critical parameters that influence the behavior of thin films when used in making devices. For instance, it has been established that the film thickness of an absorber layer must be greater than $1/\alpha$ for such thin film to yield high solar conversion efficiency [21-22]. The film thickness was deduced using the gravimetric method or double weight method as discussed in the literature [4, 23], thus the formula (equation 1) was used to calculate the film thickness. This relation is based on the fact that the film thickness is equal to the perpendicular distance to the surface from a point on the boundary surface, through the film to the film/glass boundary and hence is related to the mass, area of the deposited film, and the bulk density of the constituent materials used for the deposition thus;

$$t = \frac{m_1 - m_0}{\rho S} \quad (1)$$

In equation 1, t is the film thickness, m_0 is the mass of an empty glass substrate, m_1 is the mass of the film that deposited on the glass substrate and covered an area S , and ρ is the bulk density of the antimony sulphide ($\rho = 6.20 \text{ gm/cm}^3$ for Sb_2S_3).

The optical characterisation (absorbance and transmittance spectroscopy) was done using a Unico –UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 400 nm to 1200 nm.

RESULTS AND DISCUSSION

Fig.1 gives the variation of the absorbance of the films with wavelength. 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). The critical wavelengths are the regions of strong absorption. It could be observed in Fig. 5 that there is a steep bend for films deposited between 1h to 3 h and 5h while the film deposited at 4 h exhibited a different behavior. This could be attributed to the difference in the film thickness (the film thickness was maximum at 4h). Similar behavior has been reported by other research groups [23-24].

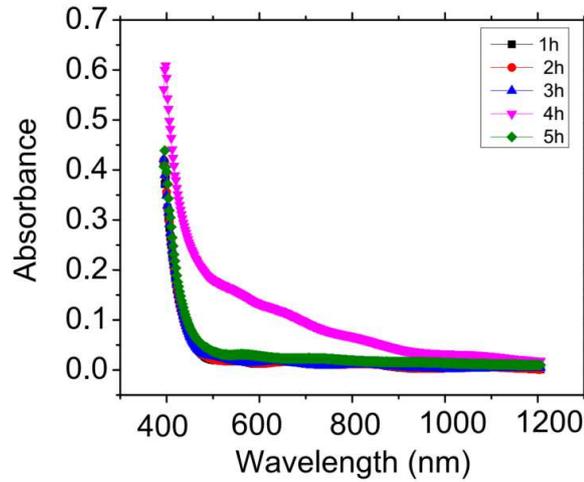


Fig. 1: Plot of absorbance vs wavelength

The variation of the transmittance with wavelength is presented in Fig. 2. The transmittances of the films were very high and exhibited interference patterns. The existence of the interference pattern is an indication that the film thickness is uniform and of good surface homogeneity. This behavior has been observed by other authors [3] and in other chalcogenides thin films (SnS) [25-26].

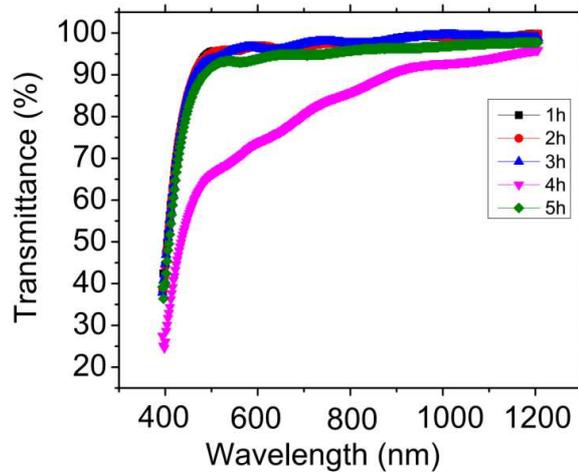


Fig. 2: Plot of transmittance vs wavelength

Fig. 3 gives the plots of $(\alpha h\nu)^2$ versus $h\nu$. The plots show that the films exhibited the classic “Urbach tails”. The Urbach tails is prominent for energies $< E_g$ instead of the graph showing $(\alpha h\nu)^2 = 0$ for energies $< E_g$. Such behaviour is commonly observed in polycrystalline thin films independent of the deposition techniques. The implication of the observed effect is that the long wavelength spectral response could be usefully utilised in making Sb_2S_3 -based devices. This behavior has been reported in the literature [27-29]. The energy bandgap was calculated using the relation given in the literature [26, 30-34] as;

$$\alpha = B(h\nu - E_g)^n \tag{2}$$

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

The energy band gap was deduced from the graph of $(\alpha h\nu)^2$ versus $h\nu$ (Fig. 3). Extrapolation of the intercepts on the $h\nu$ -axis gives the energy bandgap. In this study, it was observed that the plots are straight lines indicating that the transition is direct and allowed with the values of energy bandgap in the range 2.05 eV to 2.10 eV. In the literature [35- 36], energy band gap values in the range 1.58 eV to 2.43 eV has been reported by other authors for antimony sulphide thin films grown by the chemical deposition method and by the thermal evaporation technique. The values of the energy bandgap obtained in the present study, indicate that the films will find useful applications in solar cell devices as window layers.

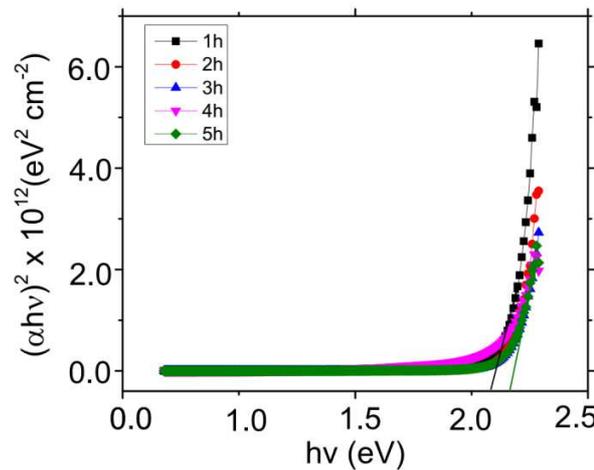


Fig. 3: Plots of $(\alpha h\nu)^2$ versus $h\nu$

It has been established that when light is incident on a thin film material, there is an interplay of reflection, transmission and absorption [30]. The absorption coefficient α , gives information on the extinction coefficient k , and is related as [30-31];

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

In equation 3, α is the optical absorption coefficient, λ is the wavelength, and π is a constant.

Fig. 4 gives the variation of the extinction coefficient with the wavelength. The evaluated extinction coefficient, k was in the range 0.01 to 0.27. From Fig. 4, it was observed that the extinction coefficient decreased gradually up to a “critical wavelength (around 498 nm to 505 nm)” for films grown between 1 h to 3 h and the film grown in 5h. The decrease was less steep for films grown at a deposition time of 4 h. The decrease of extinction coefficient with wavelength has been reported by other authors in the literature [22, 25].

Fig. 5 shows the variation of the optical density ρ_{opt} , with the wavelength. The optical density is related to the film thickness and the optical absorption coefficient. The optical density was calculated using the formula contained in the literature [37] as;

$$\rho_{opt} = \alpha t \tag{4}$$

In equation 4, α retains its meaning and t is the film thickness. The result show that the evaluated optical density was in the range 0.01– 0.34. The films grown at a deposition time of 1h exhibited higher values of the optical

density as shown in Fig. 5. This was due to the higher values of the optical absorption coefficient at the lower deposition time.

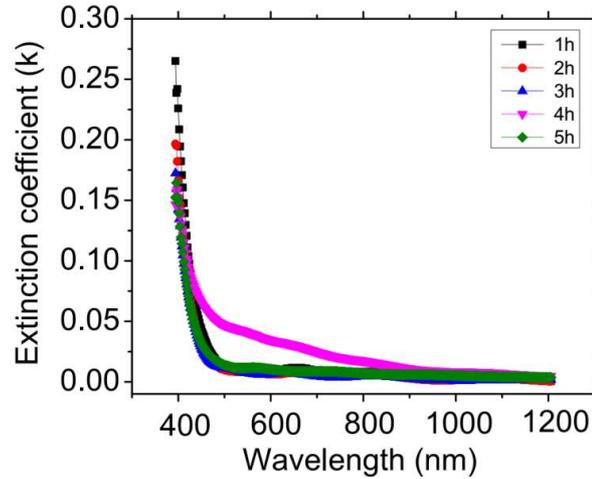


Fig. 4: Plot of extinction coefficient vs wavelength

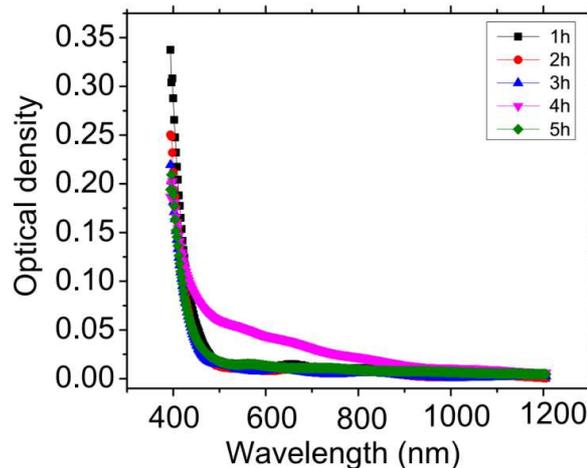


Fig. 5: Plot of optical density vs wavelength

CONCLUSION

Thin films of antimony trisulphide (Sb_2S_3) has been successfully grown using the solution growth technique. The films were then characterized using optical spectroscopy to investigate the optical properties. The transmittances of the films were $> 50\%$. The results show that the energy bandgap of the films were in the range suitable for application as window layers in solar cell devices. The evaluated optical constants such as the extinction coefficient and the optical density were observed to decrease with increasing wavelength.

REFERENCES

- [1] Mendis BG, Duros K, *Ultramicroscopy*, **2012**, 119, 82.
- [2] Jones PL, Cotton DR, Moore D, *Thin Solid Films*, **1982**, 88, 163.
- [3] Megharaoui-Meherzi H, Ben Nasr T, Kamoun N, Dachraoui M, *Physica B*, **2010**, 405, 3101.
- [4] Abd-El-rahman KF, Darwish AAA, *Curr. Appl Phys*, **2011**, 11, 1265.
- [5] Curran JS, Philippe R, Fourth EC Photovoltaic Solar Energy Conference, 1982 – Springer.

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- [6] El-Shaazy AE, Seyam MAM, El-Samanoudy MM, Ammar AH, Assim EM, *Appl. Surf. Sci.*, **2002**, 189, 129.
- [7] Rajpure KY, Bhosale CH, Lokhande CD, *Thin Solid Films*, **1997**, 311,114.
- [8] Rajpure KY, Lokhande CD, Bhosale CH, *Mater. Chem. Phys.*, **1997**, 51, 252.
- [9] Versavel MY, Haber JA, *Thin Solid Films*, **2007**, 515(18), 7171.
- [10] Sankpal BR, Pathan HM, Lokhande CD, *J. Mater. Sci. Lett.*, **1999**, 18, 1453.
- [11] Yesugade NS, Lokhande CD, Bhosale CH, *Thin Solid Films*, **1995**, 263, 145.
- [12] Nayak BB, Acharya HN, Choudhuri TK, Mitra GB, *Thin Solid Films*, **1982**, 92, 309.
- [13] Ghosh G, Varma BP, *Thin Solid Films*, **1979**, 60, 611.
- [14] El Mandouh ZS, Salama SN, *J. Mater. Sci.*, **1990**, 25, 1715.
- [15] Lu Q, Zeng H, Wang Z, Cao X, Zhang L, *Nanotechnology*, **2006**, 17, 2098.
- [16] Grigas J, Meshkauskas J, Orliukas A, *Phys. Stat. Sol.*, **1976**, A 37, K39.
- [17] Ablova MS, Andreev AA, Dedegkaev TT, Melekh BT, Pevtsov AB, Shendel NS, Shumilova LN, *Sov. Phys. Semicond.*, **1976**, 10, 629.
- [18] Oomen R, Mathew NJ, Rjalakasmi PU, *J. Ovonic Res.*, **2010**, 6(6), 259.
- [19] George J, Radhakrishnan MK, *Solid State Commun.*, **1980**, 33, 987.
- [20] Montrimas E, Pazera A, *Thin Solid Films*, **1976**, 34, 65.
- [21] Fahrenbuch AL, Bube RH, *Fundamentals of Solar Cells*, Academic Press, New York, **1983**, pp. 332.
- [22] Nwofe PA, Ph.D. Thesis, Northumbria University, (Newcastle Upon Tyne, UK, **2013**).
- [23] Ubale AU, Deshpande VP, Shinde YP, Gulwade DP, *Chalcogenide Letts.*, **2010**, 7(1), 101.
- [24] Asogwa PU, Ezugwu SC, Ezema FI, Osuji RU, *Chalcogenide Letts.*, **2009**, 6(7), 287.
- [25] Akkari A, Guasch C, Castagne M, Kamoun-Turki N, *J. Mater. Sci.*, **2011**, 46, 6285.
- [26] Nwofe PA, Reddy KTR, Sreedevi G, Tan JK, Miles RW, *Jpn. J. Appl. Phys.*, **2012**, 51, 10NC36.
- [27] Malaquias J, Fernandes PA, Salomé PMP, da Cunha AF, *Thin Solid Films*, **2011**, 519, 7416.
- [28] Nwofe PA, Reddy KTR, Miles RW, *J. Renewable & Sustainable Energy*, **2013**, 5, 011204.
- [29] Gosh B, Roy R, Chowdhury S, Banerjee P, Das S, *Appl. Surf. Sci.* **2010**, 256, 4328.
- [30] Pankove JI, *Optical Processes in Semiconductor*, Prentice-Hall, New Jersey, **1971**, pp. 36.
- [31] Nwofe PA, Reddy KTR, Tan JK, Miles RW, *Physics Procedia*, **2012**, 25, 150-157.
- [32] Agbo PE, Nweke FU, Nwofe PA, Ukwu CN, *International Journal of Science and Research*, **2014**, 6(11), 1832.
- [33] Agbo PE, Nweke FU, Nwofe PA, Ukwu CN, *International Journal of Advanced Research*, **2014**, 2(10), 353.
- [34] Agbo PE, Nwofe PA, *Int. J. Thin. Fil. Sci. Tech.* **2015**, 4(1), 9.
- [35] Jessy Mathew Rachel Oommen N, Usha Rajalakshmi P, *Chalcogenide Letts*, **2010**, 7(10), 701.
- [36] Rodríguez-Lazcano Y, Guerrero L, Gomez Daza O, Nair MTS, Nair PK, *Superficies y Vacío*, **1999**, 9, 100.
- [37] Cifuentes C, Botero M, Romero E, Calderón C, Gordillo G, *Braz. J. Phys.* **2006**, 36, 1046.