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Influence of Annealing Temperatures on the Optical Properties of Chemically Deposited Antimony Trisulphide Thin Films

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Abstract: Thin films of antimony trisulphide (Sb_2S_3) were successfully grown on soda-lime glass substrates using the solution growth technique. The deposition time was varied between 1 h to 5 h and the other deposition variables were kept constant. The as-deposited layers were then subjected to post deposition heat treatments, with annealing temperatures in the range 100 ºC to 300 ºC. The effect of the post deposition annealing on the optical properties of the films were investigated. The optical characterisation was done using a UV spectrophotometer to investigate the absorbance, and transmittance versus wavelength measurements, to enable the determination of some important optical constants such as the optical absorption coefficient, energy bandgap, extinction coefficient, and the optical density. The value of the energy bandgap was 2.15 eV for the as-deposited layers, and decreased with annealing temperatures. The extinction coefficient was in the range 0.21 – 1.3, and the optical density was between 0.02 to 0.18.

Keywords: Energy bandgap, Extinction coefficient, Annealing, Optical constants.

1 Introduction

Nanotechnology has gradually penetrated different research field in recent times. In the optoelectronics industry, nanotechnology has been extensively utilised in fabrication of various devices. In this regard, considerable attention has been directed towards the preparation and characterisation of thin films of metal chalcogenides for different applications. Antimony trisulphide (Sb_2S_3) is a V–VI semiconductor compound. It has been reported that antimony trisulphide has been successfully utilised in solar cells as absorber/window layers due its excellent opto-electronic properties [1-5], and is a semiconductor with high photosensitivity and high thermoelectric power [6-7], and has been utilised as target materials for television cameras [8], in microwave devices [9], and switching devices [10]. The photoconductivity of antimony trisulphide thin films has been reported by different research groups [11-12]. In the literature, it has been established that antimony trisulphide can be grown using different deposition techniques and these includes; successive ionic layer adsorption and reaction SILAR [13-14], spray pyrolysis [15-17], flash evaporation [18], solvothermal routes [19], thermal/vacuum evaporation [20-31], sol-gel method [32], chemical bath deposition [11-12, 33], electro-deposition [34], hydrothermal treatment [35], and Radio frequency sputtering technique [36]. In the present study, chemical bath deposition was utilised because of the ease and versatility of the method in growing high quality thin films. Antimony trisulphide is abundant and more environmentally friendly compared to the other cadmium- based chalcogenides mostly employed in the fabrication of some optoelectronic devices such as in solar cells and other electronic applications. Most recently, the use of antimony trisulphide in dye sensitised solar cells (DSSC) [37], nanowire solar cells [38], and in semiconductor solid state solar cells have been reported [39-40]. It has been established that Sb_2S_3-sensitized solar cells exhibit solar conversion efficiencies > 6 % [41]. The effect of post deposition annealing has been reported by other research groups [23] and it has

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been observed that the microstructural, optical, and electrical properties of antimony trisulphide thin films can be greatly modified using such process.

The major aim of the present study is to grow antimony trisulphide thin films by using a low cost deposition technique, and to characterise the layers using standard characterisation technique in order to optimise certain useful parameters needed for optimum use of the films and thus, establish their suitability for applications in optoelectronic and photonic industry.

2 Subjects and Methods

2.1 Substrate preparation

Substrate cleaning is a critical step in thin film deposition. In this study, the initial step was to clean the soda-lime glasses used as substrate with detergent and then degreased with acetone. The sodalime glasses were further cleaned ultrasonically to make the substrates completely dirt-free.

2.2 Source preparation

The antimony trichloride ($SbCl_3$) used as source materials were procured from Guangdong Guanghua Sci-Tech Co Ltd, China, sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) and acetone that was obtained from BDH Chemical Ltd, UK through local suppliers. The source materials all had percentage purity ≥ 99.0 %. To prepare the source solution, a 2.0 g of the $SbCl_3$ was dissolved in a 10 ml of acetone in a beaker. Inside the beaker, a 125 ml of $Na_2S_2O_3$ 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 in the acidic range (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 synthetic foam.

2.3 Film thickness measurements

Film thickness is one of the fundamental and critical parameters that determines the behavior of most semiconductor thin film materials. In this study, the film thickness was calculated using the gravimetric method or double weight method as discussed in the literature [1, 42-43], thus the formula (equation 1) was utilised. This formula 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;

$$t = \frac{m_1 - m_0}{\rho S} \tag{1}$$

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 ($\rho = 6.20$ gm/cm^3 for Sb_2S_3).

2.4 Optical characterisation and post-deposition heat treatments

The transmittance, and absorbance vs wavelength measurements for the as-deposited and annealed layers was done using a Unico–UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 400 nm to 1200 nm. The as-deposited films were annealed in a furnace. The annealing time was fixed at 1 h and the annealing temperature was varied between 100 ^{o}C to 300 ^{o}C.

3 Results

Physical observations of the films show that they were typically amber-reddish in colour, and got slightly darkened on annealing. Fig. I gives a typical absorbance versus wavelength plots for the as-deposited and annealed antimony trisulphide thin films. The behaviour exhibited in Fig. 1 is typical for the variation of absorbance with wavelength studies for antimony trisulphide thin films as such trends are commonly observed in the literature [43]. The effect of annealing on the absorbance is manifested in the shifting of the steep portion of the plots to flatter and higher values compared to the as-deposited form (Fig. 1). Fig. 2 gives a typical transmittance versus wavelength plots for the as-deposited and annealed antimony trisulphide thin films. The transmittance exhibited clear interference pattern for the as-deposited film and also at lower annealing temperature (100 ^{o}C).

However, the value of the transmittance decreased at higher annealing temperatures. Decrease in transmittance caused by a post deposition heat treatments have been reported by other authors in the literature [44-46]. The decrease in the transmittance values can be attributed to the precipitation of the Sb excess and the high absorption coefficient of Sb in the spectral region under investigation at those annealing temperatures.

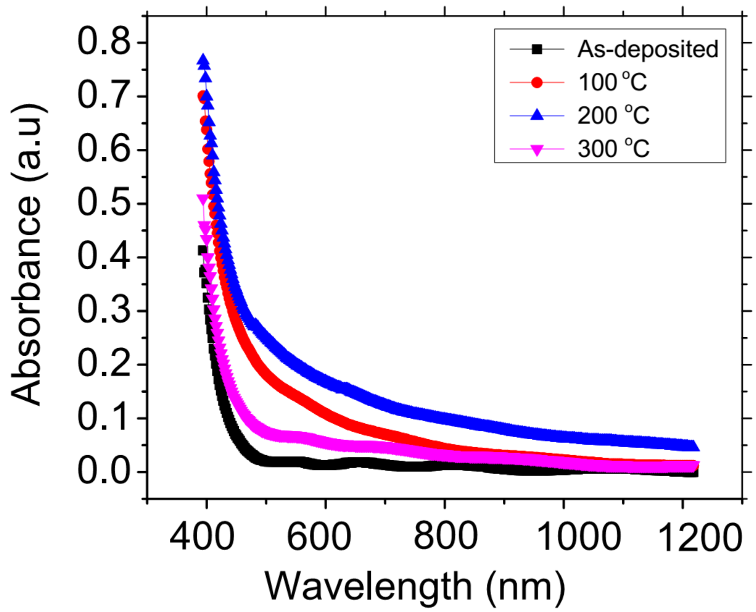

Figure. 1 Absorbance vs. Wavelength spectrum of Sb_2S_3 thin films at different annealing temperatures.

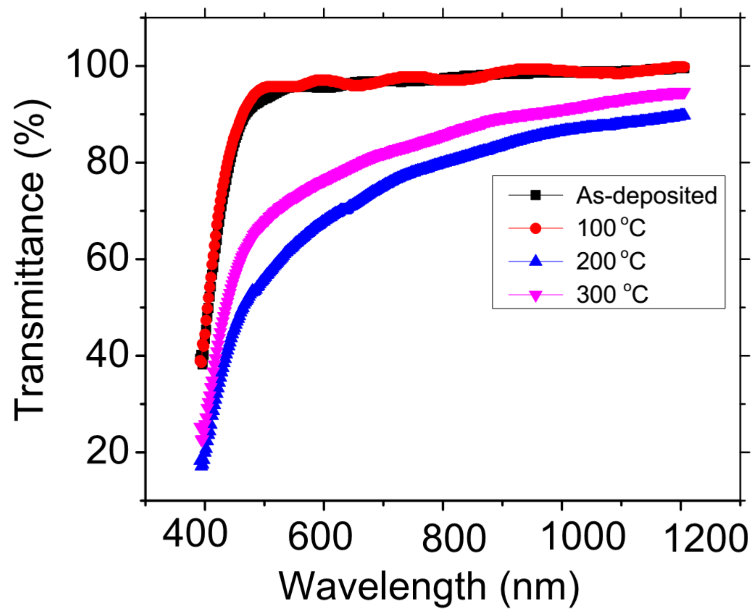

Figure. 2 Transmittance vs. Wavelength spectrum of Sb_2S_3 thin films at different annealing temperatures.

The data extracted from the transmittance and absorbance measurements were used to deduce important optical constants such as the absorption coefficient α, energy bandgap E_g, extinction coefficients, k, and the optical density.

Fig. 3 gives the typical plots of $(\alpha h\nu)^2$ vs $h\nu$ for the antimony trisulphide thin films at the different annealing temperatures. It is an established fact that the fundamental absorption, which corresponds to an electron excitation from the valence band to the conduction band, can be used to determine the nature and value of the optical energy band gap from the plots of $(\alpha h\nu)^2$ vs $h\nu$. This is mostly done by extrapolating the linear portion of the graph of $(\alpha h\nu)^2$ vs $h\nu$.

The energy bandgap was calculated using the relation [47-51],

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

Where B is an energy independent constant and n is an index that characterizes the optical absorption process. Usually, n = 0.5 for direct allowed transition, and 1.5 for direct forbidden transitions. The energy band gap was direct and was obtained to be 2.15 eV for the as-grown film while the annealed layers show energy bandgap in the range 1.80 eV to 1.90 eV. Versavel and Haber [36] reported on thin films of amorphous and crystalline antimony sulfide films grown by radio frequency sputtering technique and observed a strong absorption coefficients of 1.8×10^5 cm^{-1} at 450 nm and 7.5×10^4 cm^{-1} at 550 nm, with direct energy bandgaps of 2.24 eV for the amorphous case and 1.73 eV for the crystalline films. Other research groups have also reported energy bandgaps in the range 1.5 eV to 2.6 eV [22-23, 27-28, 42-45]. The decrease in the energy bandgap of the annealed layers is because an increase in the annealing temperatures could lead to a better crystal ordering due to a reduction in structural imperfections in the annealed layers compared to the as-deposited films. Decrease in energy band gap can also be caused by quantum size effects.

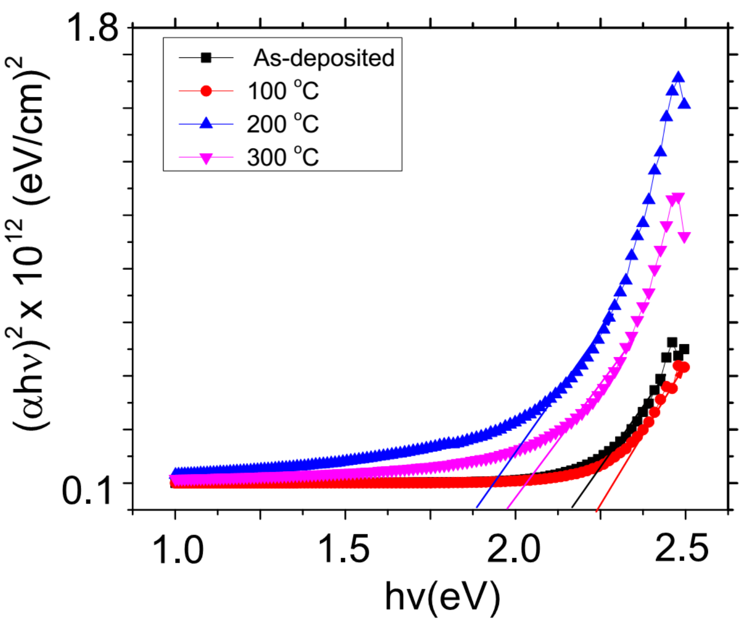

Figure. 3 Plots of $(\alpha h\nu)^2$ vs $h\nu$ of Sb_2S_3 thin films at different annealing temperatures.

Fig. 4 shows the variation of extinction coefficient values with wavelength at the different annealing temperatures. The extinction coefficient is related to the absorption coefficient and the wavelength under study. The extinction coefficient (k) was calculated from the relation defined as [47, 50]:

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

Where α is optical absorption coefficient and λ is the wavelength.

The extinction coefficient decreased with increasing wavelength. This could be attributed to the effect of reduced absorption at the higher wavelength (decreasing photon energies). From the analysis, it has been found that the values of the extinction coefficient was in the range 0.21 – 1.3, with the optimum values obtained for the plot of the films annealed at 200 °C. The values of the extinction coefficient of the films are within the range reported by other research groups [30].

Fig. 5 shows the variation of the optical density with wavelength at different annealing temperatures. The behaviour of the change in the optical density with wavelength is relatively similar to that observed in the variation of the extinction coefficient. This is because of similar dependence of both parameters (extinction coefficient and optical density) on the optical absorption coefficient. The optical density was calculated using the relation [52-53];

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

In equation 4, α is the optical absorption coefficient and t is the film thickness

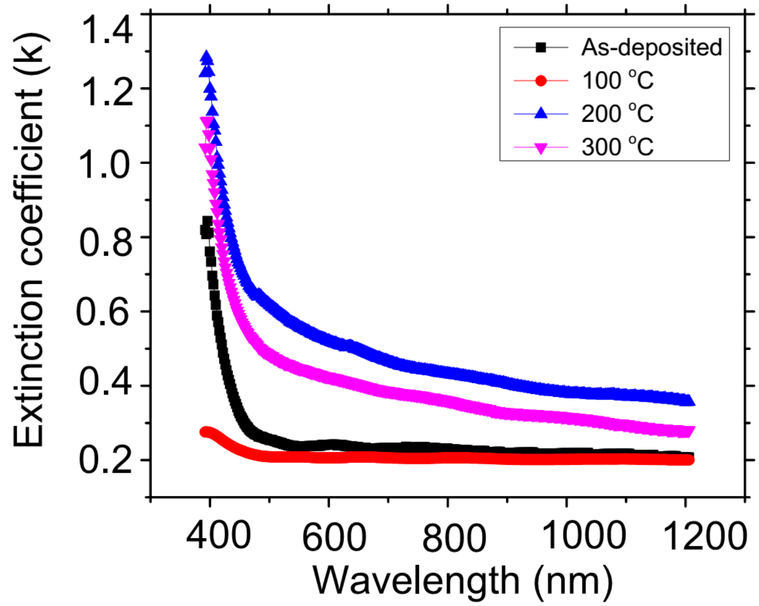

Figure. 4 Extinction coefficient (k) vs. wavelength (nm) at different annealing temperatures.

The values of the optical density was in the range 0.02 to 0.18, with the higher values obtained at the higher annealing temperatures. Variation of the optical densities with film thickness has been reported to be in the range 0.01-0.98 for antimony trisulphide thin films grown by the chemical bath deposition technique [42]. The lower values obtained in the present study was explained as due to the change in the crystal ordering due to the annealing effects.

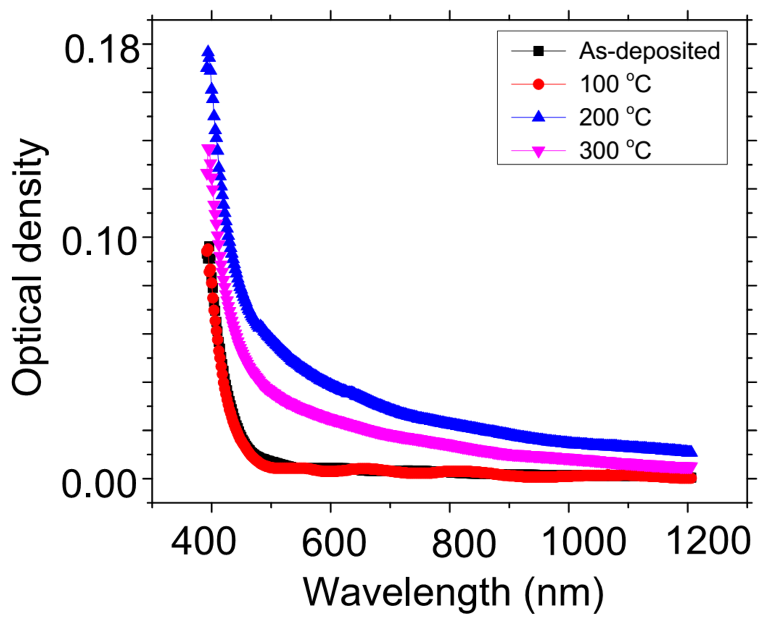

Figure. 5 Optical density vs. wavelength (nm) at different annealing temperatures.

4 Discussion

Sb_2S_3 thin films were grown using the solution growth technique and the optical properties were investigated. The optical constants were deduced using standard procedures from current literature. From the optical analysis, the energy band gap was in the range 1.80 eV to 2.15 eV, suitable for use as absorber layers in solar cell devices. Also from the optical analysis, it was observed that the values of the extinction coefficient was in the range 0.21 – 1.3, with the higher values obtained at higher annealing temperatures.

5 Conclusion

In this study the variation of the optical constants (optical absorption coefficient α, extinction coefficient k, and the optical density) at different annealing temperatures has been investigated. The values of the optical constants are within the range reported by other authors. The value of the energy bandgap was obtained in the range 1.80 eV to 1.90 eV (annealed layers), which suggest possible use of the layers as absorbers in solar cell devices, and 2.15 eV (as-deposited films), indicating the possibility of its use in optoelectronic and photonic devices. The values of the extinction coefficient and the optical density are in agreement with current reports in the literature.

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