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pH Dependent Optical Properties of Chemically Deposited Sb_2S_3 Thin Films

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Abstract: In this study, thin films of antimony trisulphide (Sb_2S_3) were successfully grown on soda-lime glass substrates using the chemical bath deposition method. The pH of the bath was varied between 1.59 and 2.24 and the other deposition variables were kept constant. The change in the pH was made possible by varying the Sb: S (antimony: tin) ratios in the solution bath. The as-deposited layers were then subjected to post deposition heat treatments, with annealing temperatures kept at 200 ^oC. The influence of the variation in pH and that 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 study the absorbance, and transmittance versus wavelength measurements, to enable the determination of some important optical constants such as the optical absorption coefficient (α), energy bandgap (E_g), extinction coefficient (k), optical density (ρ_d) and the dielectric constants. The energy band gap was obtained to be direct, with values in the range suitable for use in optoelectronic and photonic devices.

Keywords: pH, Annealing, Photonic devices, Optical properties.

1 Introduction

Antimony trisulphide (Sb_2S_3) is a V–VI semiconductor compound, and has gained considerable attention recently in the fabrication of various optoelectronics, photonic devices, and in the nanotechnology industry. Deposition and characterisation of thin films of metal chalcogenides for different applications has been widely reported in the literature. Sb_2S_3 is a semiconductor compound that exhibits high photosensitivity and high thermoelectric power [1-2]. In the literature, it has been widely reported that antimony trisulphide can be successfully utilized in solar cells as absorber/window layers due to the excellent opto-electronic properties [3-7] of this compound. Antimony tri-sulphide is reported to have been used as target materials for television cameras [8], in microwave devices [9], switching devices [10], and radio labeling for clinical applications [11]. Also the photoconductivity of antimony trisulphide thin films has been reported by different authors [12-13].

Post deposition heat treatment of thin films is known to introduce significant modifications in the structural, electrical, and solid state properties of the films. The effect of post deposition annealing of Sb_2S_3 thin films has been reported in the literature [14-15]. According to the literature, the optical energy bandgap of antimony sulphide is reported to be in the range of 1.12 eV to 2.5 eV, implying that it covers the visible and near infrared range of the solar spectrum [1,12,16-18]. Current reports in the literature indicate that antimony trisulphide can be grown using different deposition techniques and these techniques are; chemical bath deposition [1,12-13,19-20], flash evaporation [21], solvothermal routes [22], spray pyrolysis [23-25], sol-gel method [26], radio frequency sputtering technique [27], electro-deposition [28], hydrothermal treatment [29], thermal/vacuum evaporation [30-39], and successive ionic layer adsorption and reaction SILAR [40-41]. Chemical bath deposition method has proved to be cost effective in growing high quality thin films. Research in thin films is currently geared towards harnessing the potentials of more environmentally safe materials. Antimony tri-sulphide thin films 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 photonic devices. Solar cells based on antimony trisulphide thin films has been reported in the literature [42-46].

In the literature, the effect of pH on the properties of antimony sulphide is rarely investigated. The major aim of the present study is to grow antimony trisulphide thin films by using a low cost deposition technique, investigate the effect of pH on the properties of the layers through

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standard characterization technique. This will enable the optimization of useful conditions/variables needed for optimum use of the films for applications in optoelectronic and photonic devices.

2 Subjects and Methods

2.1 Substrate preparation

The substrates used were soda lime glasses that were procured from local suppliers (Conraws Limited, Enugu, Nigeria). The soda-lime glass substrates were thoroughly cleaned with detergent and then degreased with acetone. The sodalime glasses were further cleaned ultrasonically to make the substrates completely dirt-free. The glass substrate were then dried in Nitrogen before use.

2.2 Source preparation

The source materials (antimony trichloride ($SbCl_3$)) used, were procured from Guangdong Guanghua Sci-Tech Co Ltd, China, while sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) and acetone were obtained from BDH Chemical Ltd, UK through local suppliers. The source materials all had percentage purity ≥ 99.0 %. Different concentrations (0.05 M -0.25 M) of antimony trichloride were prepared by dissolving the appropriate amount of the solute in the solvent using basic equations for obtaining concentration as contained in the literature [47]. The concentration of the sodium thiosulphate was fixed at 0.25 M. A 50 ml of the solution from each of the respective concentrations of the antimony trichloride was added into a 50 ml of sodium thiosulphate in 5 separate beakers. The pH of the respective solutions after the addition were found to be in the range 1.59 to 2.24. Inside each beaker, 5 clean glass slides were then immersed and held vertically with a synthetic foam. The films were removed after 45 h and rinsed with distilled water.

2.3 Film thickness measurements

The film thickness was calculated using the gravimetric method or double weight method as contained in the literature [20, 48], thus the formula (equation 1) was used.

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

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 (ρ = 6.20 gm/cm^3 for Sb_2S_3).

2.4 Optical characterization and post-deposition heat treatments

The transmittance, and absorbance versus 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 280 nm to 1000 nm. The as-deposited films were annealed in a furnace. The annealing temperature and time was fixed at 200 ^oC and 1 h respectively.

3 Results

The physical observations of the as-deposited films indicate that they were typically fairly reddish in colour especially for films grown with pH range 1.73 to 2.06 and show amber-red at the other pH values. The effect of post deposition heat treatments on the physical observation is manifested in the slight darkening of the reddish colour.

Fig. 1 gives a typical transmittance versus wavelength plots for the as-deposited antimony trisulphide thin films. The behavior exhibited in Fig. 1, indicate that transmittance of the films strongly depend on the pH. The highest transmittance was obtained at the highest pH value (2.24). At this pH, the transmittance also exhibited some degree of interference effects. The existence of the interference pattern is an indication that the film grown at that pH is of uniform film thickness. As shown in Fig. 1, a slight interference pattern was also exhibited by the transmittance spectra of the films grown at pH range between 1.73 and 2.06. It is generally known that how well an optical coating performs is dependent upon different number of variables, which includes the number of layers, the film thickness, and the differences in refractive index at the layer interfaces. The transmission properties of light are predicted by wave theory and one of the consequences of the wave properties of light is that waves exhibit interference effects [49]. The effect and importance of interference phenomena in thin films has been widely reported in the literature [50-55]. The transmittance of thin films have been reported to be dependent on a variety of deposition variables which includes, film thickness, substrate distance, substrate types, concentration, substrate temperature, and annealing temperatures amongst others.

Olomi et al [56] noted that for non-metal thin film coating, the reflectance decreases as the film thickness increases because of increasing transmittance, but for metal thin film coating, transmittance decreases as the film thickness decreases due to increasing reflectance. A close look at the transmittance of the layers grown at the lower pH (1.59 - 1.73) and at the maximum pH value (2.24) as shown in Fig. 1, indicate that the transmittances exhibited a sharp fall near the fundamental absorption edge. Existence of a sharp fall in the fundamental absorption edge without the presence of shoulders usually indicate that there are no other phases present in the films, independent of the deposition technique. Similar behavior has been reported by other research groups in the literature [57-58]. However, at a pH value of 2.30, the transmittance spectrum exhibited a slight shift in the critical wavelength. It was also observed that at that pH (2.30), the fall near the fundamental absorption edge is not sharp, thus indicating the possibility of other phases.

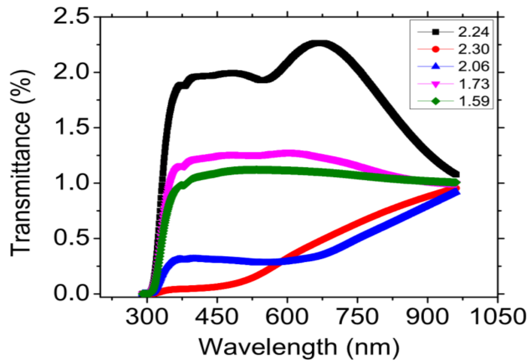

Figure 1: Transmittance vs. Wavelength spectrum of Sb_2S_3 thin films at different pH (as-deposited).

Fig. 2 gives a typical transmittance versus wavelength plots for the thin films of antimony trisulphide annealed at 200 ^oC. The effect of the post deposition annealing is manifested in reduced transmittance of the films compared to the as-deposited layers. In the literature, a reduction in the value of the transmittance induced by a post deposition heat treatments have been reported by other research groups [59-62]. The observed 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 discussion at those annealing temperatures investigated in this study. Ogah et al [62], investigated the effect of annealing on tin sulphide (SnS) thin films and observed similar effect, and noted that the main effect of the annealing treatment is to narrow the optical absorption edge toward that which corresponded to the energy bandgap of SnS (1.35 eV). The authors further associated this behavior (reduced transmittance after annealing) with an increase in grain size, densification of the layers, and a reduction in the presence of minority phases that were present in the films in the as-deposited form. From Fig. 2, it was clearly observed that the appearance of the interference pattern were more distinct in all the pH range that was investigated in the study, compared to the as-deposited form. The existence of the interference pattern in all the transmittances, indicates that the post deposition heat treatments resulted in better and increased uniform film thickness in the layers. Moreso, the presence of shoulders that was clearly manifested in the as deposited layers at the pH of 2.30, was found to disappear after the annealing treatments. The disappearance of the shoulders due to the annealing effect was caused by the re-evaporation of sulphur, arising from the difference in vapor pressure of Sb (antimony) and S (sulphur) respectively. The data that was sieved out from the transmittance and absorbance measurements were used to deduce important optical constants (not shown), such as the absorption coefficient α, energy bandgap E_g, extinction coefficients, k, and the optical density.

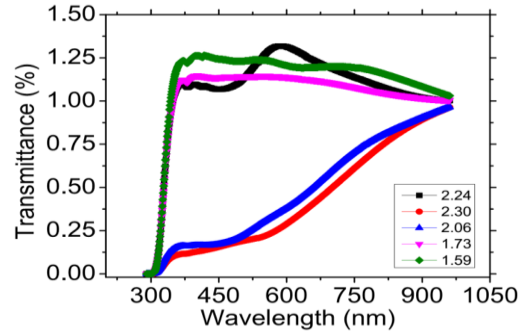

Figure 2: Transmittance vs. Wavelength spectrum of Sb_2S_3 thin films at different pH (after annealing at 200 ^oC).

Fig. 3 gives the variation of the absorbance with wavelength spectrum of Sb_2S_3 thin films at different pH (as-deposited). The absorbance spectrum of the as-grown films was recorded at different wavelengths, 280 – 1000 nm. As indicated in Fig. 3, all the films showed a sharp fall in their absorption at the fundamental absorption edge. The observed variation in the absorbance spectra as shown on Fig 3, was mainly attributed to the chemical composition and crystalline properties of the as-deposited Sb_2S_3 thin films at the different pH values. All the absorbance spectra (Fig. 3), exhibited a red shift towards longer wavelength at the different pH. The absorbance of the films generally decreased with wavelength and has relatively low values in the shorter photon energy region (longer wavelengths) of the solar spectrum. However, strong absorption was observed at wavelength range of 380-400 nm, indicating the potentials of the films for applications in photovoltaic solar cell devices. The wavelength range of strong absorption observed in this study is in agreement with that reported by other authors [1].

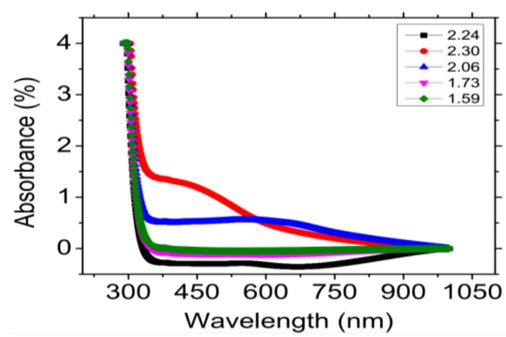

Figure 3: Absorbance vs. Wavelength spectrum of Sb_2S_3 thin films at different pH (as-deposited).

The variation of absorbance spectra with wavelength for Sb_2S_3 thin films has been widely reported in the literature, independent of the deposition methods [1,5,15,20].

Fig. 4 shows the influence of annealing on the variation of the absorbance spectra with wavelength for the different pH range. As shown in Fig. 4, the fall in the fundamental absorption edge exhibit an abrupt behavior. This also points to the fact that the annealed layers are relatively free of the secondary phases. The reduction of the secondary phases could lead to the value of the optical energy gap decreasing towards the lower values suitable for use of the layers as absorber materials in solar cell devices. It is also possible that this behavior was due to the fact that the post-deposition heat treatments resulted in the minimization of structural imperfections in the as deposited thin films. In the literature [20, 61-65], annealing effect has been reported as one of the major ways of; reducing interface state, increasing grain size, bandgap narrowing and other effects on the structural, morphological, optical, and electrical properties of thin films independent of the deposition techniques.

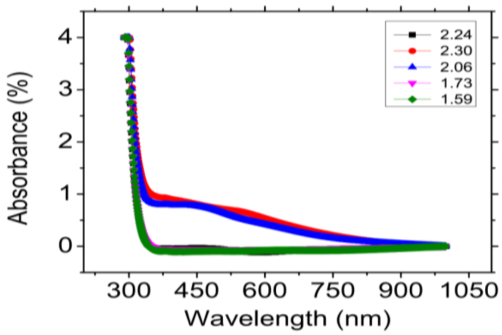

Figure. 4. Absorbance vs. Wavelength spectrum of Sb_2S_3 thin films at different pH (after annealing at 200 ºC).

4 Discussion

In the present investigation, Sb_2S_3 thin films were grown using the solution growth technique and the effect of different pH on the optical properties were studied. The optical constants were deduced using standard procedures from current literature. From the optical analysis, the transmittance and absorbance varied at different pH values. The layers annealed at 200 ºC were found to be free from secondary phases, indicating that the films are suitable for use in solar cell devices in lieu of the wavelength range at which the fundamental absorption edge occurred. Also from the transmittance spectra of the annealed layers, it was observed that presence of interference pattern was more visible, indicating that annealing at that temperature, led to increased uniformity in the film thickness.

5 Conclusion

In this study the effects of different pH on the properties of Sb_2S_3 thin films grown using the solution growth technique was investigated. The results show that the pH influenced the transmittance and absorbance spectra. Also the effect of the post deposition annealing on the transmittance and absorbance spectra of the films indicate that the properties of the films were significantly modified by the post deposition heat treatments. The range of wavelength at which the fundamental absorption edge were observed, points to the possible use of the films in optoelectronic and photonic applications.

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