

Optical and structural properties of amorphous antimony sulphide thin films: Effect of dip time

M. D. Jeroh* and D. N. Okoli

Dept. of Physics, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria

ABSTRACT

Amorphous thin films of antimony sulphide were successfully deposited on glass substrates by chemical bath deposition technique. The structural and morphological characterizations were performed on the films by x-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively while the elemental composition of the films was obtained from energy dispersive analysis x-ray (EDAX) spectroscopy. Optical characterization of the films was done using an AVASPEC-2048 UV-VIS-NIR spectrophotometer in the wavelength range of 200-900nm. The effect of dip time on the optical, structural, elemental composition and morphological properties of the films was examined. It was observed that the direct band gap of the film decreased from 1.80eV to 1.50eV as dip time increases from 12hrs to 36hrs respectively.

Keywords: Antimony sulphide, dip time, direct band gap, thin film, glass substrates, chemical bath deposition, film thickness.

INTRODUCTION

Semiconductors over the years have gained wide usage in fabricating electronic devices. Since the invention of the transistor in 1947 by the American physicists; John Bardeen, Walter Brattain and William Shockley and the development of the integrated silicon chip in the 70s, semiconductor based devices have increasingly been of great use in our everyday lives. This trend is very much likely to continue due to man's insatiable need for advanced technological devices ranging from mp3 players, mobile cell phones, palmtops, laptop computers and presently, flat screen televisions (popularly known today as wall televisions) such as the liquid crystal display (LCD) and the light emitting diode (LED) respectively. Although silicon-based technology is by far the most advanced amongst semiconductor technology, there has been an increasing interest in the use of compound semiconductors such as GaAs, ZnO, CdTe, etc, which possesses electrical and optical properties that are absent in silicon. This, of course, has led to the increased study of binary and ternary semiconductor compounds for their possible applications in electronic and photovoltaic devices respectively. Sb_2S_3 is a V-VI binary semiconductor compound which can be represented by the chemical symbol $\text{A}^{\text{V}}\text{B}^{\text{VI}}$. Due to their high absorption coefficient, Sb_2S_3 thin films are good absorber materials in solar cells. These and other properties exhibited by this material make it a potential material for thin film deposition. Different methods have previously been employed to deposit thin films of Sb_2S_3 , some of which are chemical bath deposition [1-4], vacuum evaporation [5-7], spray pyrolysis [8-10], etc.

The effect of concentration on the structural properties of synthesized Sb_2S_3 bulk powder has been reported [11].

In this present work, chemical bath deposition was used to deposit thin films of Sb_2S_3 at different deposition time (12hrs, 24hrs and 36hrs). The effect of deposition time on the structural, elemental composition, morphological, optical properties and band gap energy of the deposited films were studied for possible photovoltaic applications.

MATERIALS AND METHODS

2.0. Experimental Details

The bath constituents for the deposition of Sb_2S_3 thin films were SbCl_3 , acetone, triethanolamine (TEA), $\text{Na}_2\text{S}_2\text{O}_3$ and distilled water respectively.

1.3g of SbCl_3 was dissolved in 5ml of acetone, 2ml of TEA, 5ml of 1M of $\text{Na}_2\text{S}_2\text{O}_3$ and 33ml of pure laboratory distilled water put in that order into a 50ml beaker. Three experimental setup were made with each containing a clean microscopic glass slide inserted vertically through a synthetic foam cover in which dip time was varied at 12hrs, 24hrs and 36hrs respectively. The deposition was allowed to proceed at room temperature. At the end of the dip time for each glass slide, the coated glass slide was removed, washed well with distilled water and allowed to dry in open air for 2hrs.

The structural property was studied by x-ray diffraction by means of an X'PERT PRO P'Analytical MPD x-ray diffractometer, the surface morphology of the films was studied by scanning electron microscopy at a magnification of 5.00kx while the composition of the films was studied by energy-dispersive analysis x-ray spectroscopy (EDAX). The optical transmittance and reflectance of the films were recorded on an AVASPEC-2048 UV-VIS-NIR spectrophotometer with an uncoated glass substrate as a reference frame. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

3.1. Thickness Variation

Fig. 1 show the thickness of the Sb_2S_3 thin films obtained at different dip time. From the figure, there is a gradual increase in the thickness of the film from $0.5\mu\text{m}$ to $0.75\mu\text{m}$ as dip time increases from 12hrs to 36hrs respectively.

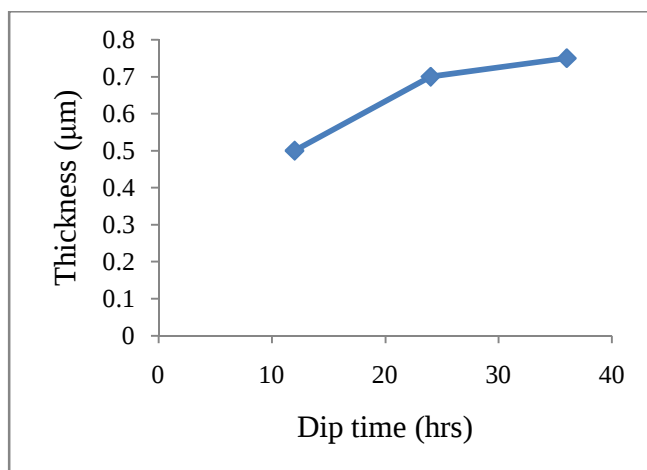


Fig. 1: Variation of thickness of Sb_2S_3 thin films with dip time.

3.2. Structural Characterization

XRD patterns of Sb_2S_3 thin films deposited at different dip time is displayed in fig. 2. A careful observation of the two films show that XRD peaks are not observed for the films under study. This is an indication that the films deposited in this work are amorphous. Thus, increasing the dip time did not have any effect on the structure of the film deposited at room temperature.

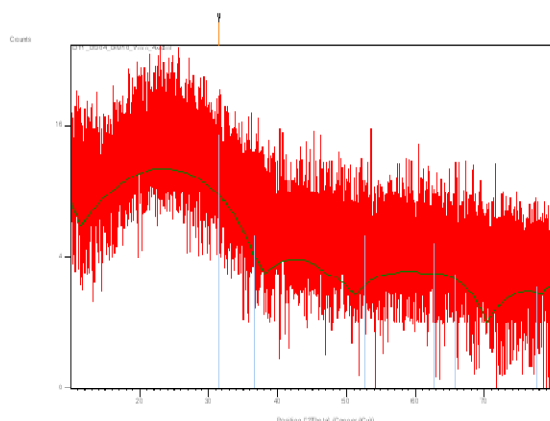


Fig. 2a: XRD spectra of as-deposited Sb_2S_3 thin films at 12hr dip time.

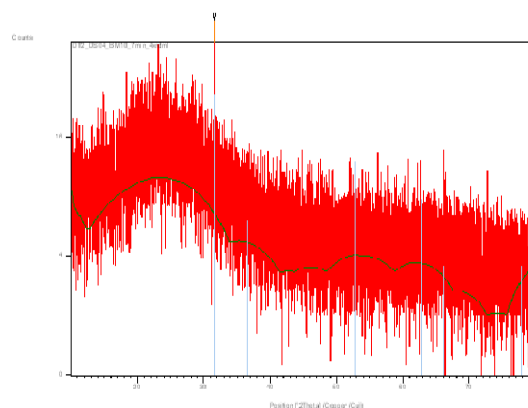


Fig. 2b: XRD spectra of as-deposited Sb_2S_3 thin films at 24hr dip time.

3.3. Surface Morphology Studies

The surface morphology of the films was obtained using a Carl-Zeiss MA-10 scanning electron microscope at a magnification of 5.00kx. The SEM micrographs are shown in figure 3. A close observation of fig. 3 indicates that the micrographs of Sb_2S_3 deposited at 12hr dip time show a cluster of spheres which are irregularly distributed over the surface of the film. A careful look at fig. 3b shows that there are fewer cluster of spheres in 3b which appear to be larger than those formed in fig. 3a. This, we believe is an indication of overgrowth of the particles which imply an increase in thickness of the films with increase in dip time. This result is in perfect agreement with the one earlier reported [12]. Figure 3 is shown below.

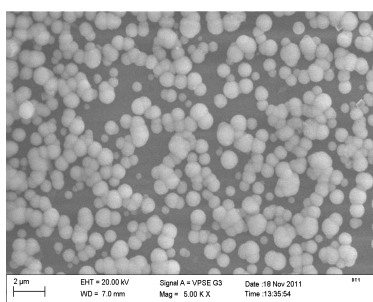


Fig. 3a: SEM micrograph of as-deposited Sb_2S_3 thin films deposited at 12hrs dip time.

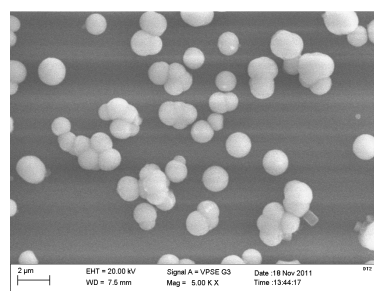


Fig. 3b: SEM micrograph of as-deposited Sb_2S_3 thin films deposited at 24hrs dip time.

3.4. Elemental Composition

The elemental composition and chemical states of the Sb_2S_3 thin films under study was analyzed by energy-dispersive analysis x-ray spectroscopy (EDAX).

The EDAX spectrum of the as-deposited Sb_2S_3 thin film is displayed in fig. 4 for two different dip time (12hrs and 24hrs) respectively.

The presence of Sb, S and Cl can be observed from figure 4. The atomic percentage of Sb increases from 1.39% to 5.15% as dip time increases from 12hrs to 24hrs respectively, while the atomic percentage of S also increases from 1.41% to 4.81% as dip time increases from 12hrs to 24hrs respectively. The results obtained in this research shows that the films are non-stoichiometric. From the results, we see that dip time has a considerable effect on the deposited films in that the atomic percentage of the film was seen to increase with dip time. We believe that this trend is likely going to continue at higher dip time. The O_2 peak detected from the EDAX spectrum is unavoidable in any chemically deposited thin film. This has previously been reported [13].

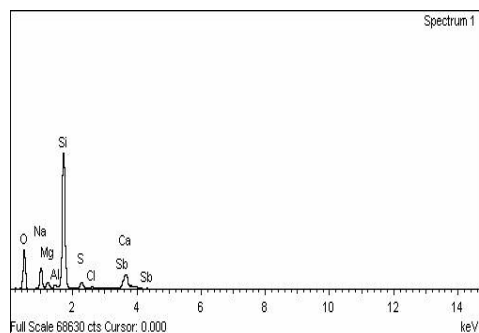


Fig. 4.1a: Energy-dispersive analysis spectrum of as-deposited Sb_2S_3 thin films deposited at 12hrs dip time.

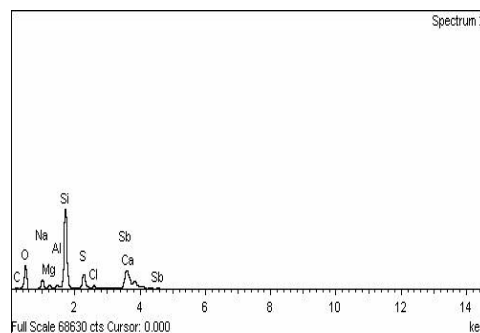


Fig. 4.2b: Energy-dispersive analysis spectrum of as-deposited Sb_2S_3 thin films deposited at 24hrs dip time.

The presence of Cl in the EDAX spectrum is due to the precursor SbCl_3 while the presence of Na is due to the starting material $\text{Na}_2\text{S}_2\text{O}_3$. The presence of Si and other elements present may have come from the glass slide used. The atomic percentage of Sb and S obtained at different dip time is shown in table 1 below.

Table 1: Atomic percentage of Sb and S at different dip time

Element	Dip Time (Hrs)	Atomic (%)
Sb	12	1.39
Sb	24	5.15
S	12	1.42
S	24	4.81

3.5. Optical Studies

The optical transmittance (T%) and the reflectance spectra (R%) of the films were recorded on an Avantes AVASPEC-2048 UV-VIS-NIR spectrophotometer with an uncoated glass substrate as a reference frame. Fig. 5a show the spectra transmission for Sb_2S_3 films deposited at different dip time interval. Transmittance spectra of the films increases as dip time increases. All the samples show poor transmission of solar radiation which indicates high absorbance of solar spectrum by the thin films as indicated in figure 4.3. A similar result has previously been reported [3] for as-deposited Sb_2S_3 thin films.

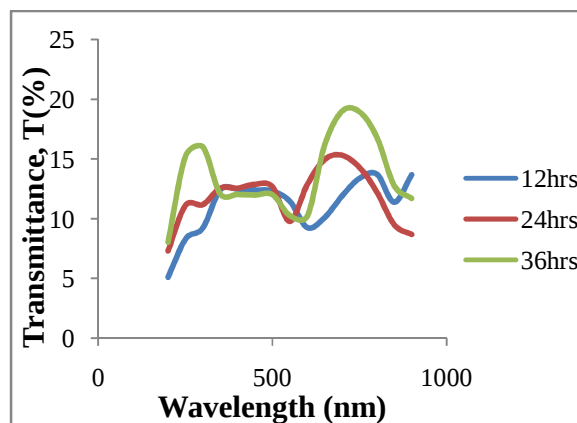


Fig. 5a: Transmittance curves for the Sb_2S_3 thin films deposited at different dip time.

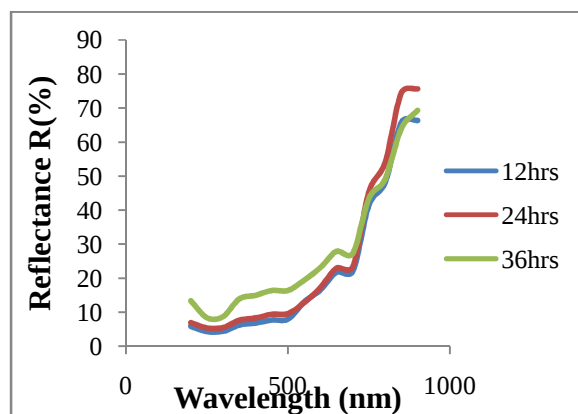


Fig. 5b: Reflection spectra of Sb_2S_3 thin films deposited at different dip time.

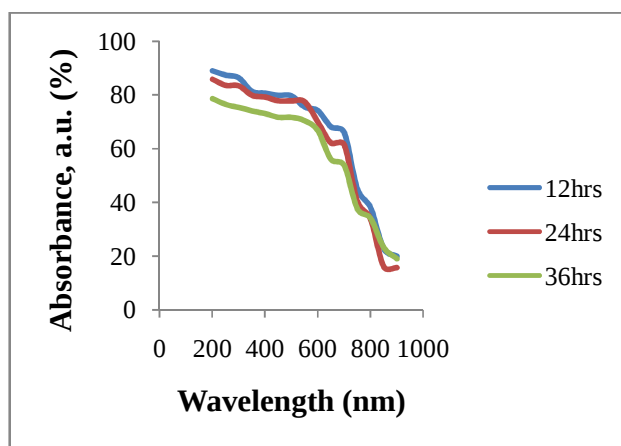


Fig. 5c: Absorbance curve for Sb_2S_3 thin films grown at different dip time.

The transmittance curves of the films deposited at different dip time show some observed interference pattern. This is due to the difference in refractive index of the film and the glass substrate used which results in multiple reflections as previously reported [6]. The interference pattern displayed by the transmittance curves show that the films grown in this research are homogeneous.

The reflectance curves for the as-deposited Sb_2S_3 thin films deposited at different dip time are displayed in figure 5b. All the samples show high reflectance in the IR region of the electromagnetic spectrum. A careful observation of fig. 5b shows that the reflectance of the film increases as wavelength increases with the highest reflectance value of about 75.61% at a wavelength of 900nm. The high reflectance exhibited by this material makes it useful in the manufacture of highly reflectance mirrors commonly found in desktop scanners, photocopy machines, astronomical telescope, car head lamps and halogen lamps.

The absorbance values for all the films were calculated from transmittance and reflectance values using the expression:

$$A + T + R = 1,$$

so that,

$$A = 1 - [T + R].$$

The absorbance curve of the Sb_2S_3 films grown at different dip time is shown in figure 5c.

A careful observation of fig 5 reveal that the absorbance curves of the samples show a downward trend as wavelength increases and decreases as dip time increases.

From a careful observation of the absorbance curve for all the samples, it is obvious that all the samples show very high absorbance in the wavelength range of 200-600nm corresponding to the UV-VIS region of the electromagnetic spectrum with the highest absorption of about 88.98%. The high absorbance exhibited by this material makes it a potential absorber in devices for photovoltaic conversion of solar energy.

3.6. Band Gap Analysis of The Sb_2S_3 Thin Films

The absorption coefficient was calculated from transmittance values using the expression:

$$\alpha = - \frac{[\ln T]}{t}$$

where, α = Absorption coefficient,

T = Transmittance values,

t = Thickness of the film.

The band gap can be estimated from tauc plot [14] using the relation:

$$\alpha h\nu = A(h\nu - E_g)^n,$$

where E_g is the band gap corresponding to a particular transition occurring in the film, A is a constant, ν is transition frequency and the exponent characterizes the nature of the band transition [14].

The direct band gap energy for the as-deposited Sb_2S_3 thin films was obtained from the plot of $(\alpha h\nu)^2$ versus the photon energy, $h\nu$, for different dip time and extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$ as shown in figure 6 (a-c). The band gap energy obtained in this research lie between 1.50eV to 1.80eV as shown in figure 6 (a-c). From the figures, it is observed that the band gap energy decreased from 1.80eV to 1.50eV as dip time increases from 12hrs to 36hrs respectively.

As previously reported [15], one of the requirements for an ideal absorber solar cell material is that it must have a direct band gap in the range of 0.7eV to 2.0eV. Since the values (1.50-1.80eV) obtained in this research fall within this range (0.7eV to 2.0eV), we can conveniently say that this material can serve as a good absorber for solid-state solar cell (SSSC). Figure 6 (a-c) are shown below.

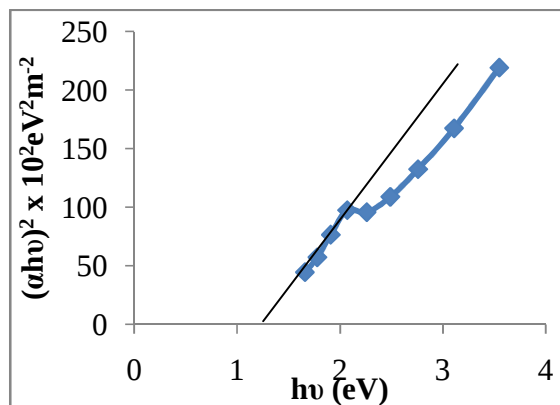


Fig. 6a: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Sb_2S_3 thin films at 12hrs dip time.

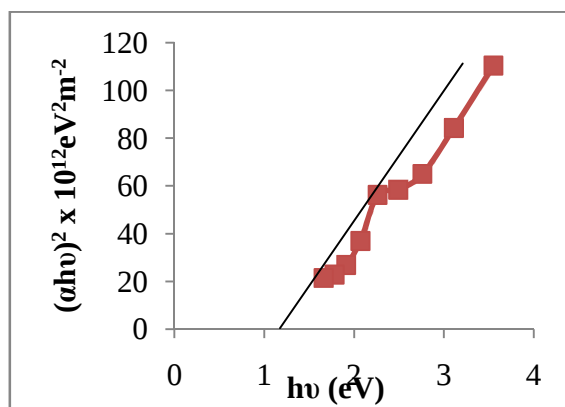


Fig. 6b: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Sb_2S_3 thin films at 24hrs dip time

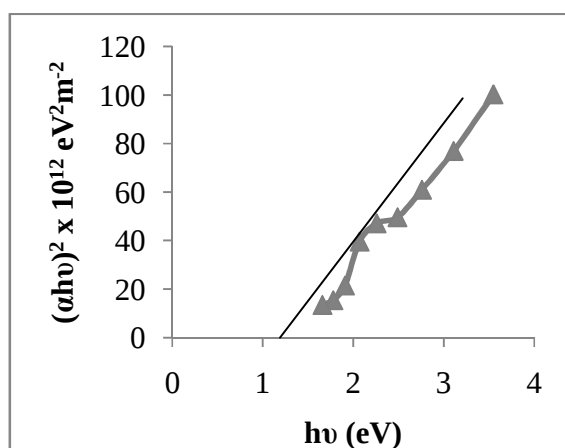


Fig. 6c: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Sb_2S_3 thin films at 36hrs dip time.

CONCLUSION

Thin films of antimony sulphide were successfully deposited on glass substrates at different dip time and characterized accordingly. The effect of dip time on the optical, structural, elemental composition and morphological properties was examined. It was discovered from our results that dip time has a considerable effect on the thickness, optical, elemental composition and morphological properties of the films. The band gap energy was observed to decrease from 1.80eV to 1.50eV as dip time increases from 12hrs to 36hrs. However, our results show that dip time has no effect on the structural property of the films deposited at room temperature, as all the films were seen to be amorphous in nature. Results from our research show that antimony sulphide can serve as good absorber material for the photovoltaic conversion of solar energy. Due to the high reflectance exhibited by the material, we also conclude that this material could be useful for the manufacture of highly reflectance mirror commonly found in desktop scanners, photocopy machines, astronomical telescope, car head lamps and halogen lamps.

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