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Optical Properties and Structural Characterizations of Sb_2S_3 Thin Films Deposited by Chemical Bath Deposition Technique

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Abstract

Thin films of Sb_2S_3were deposited on glass substrates at 300 K by chemical bath deposition (CBD) technique and annealed at various temperatures. The absorption coefficient α was determined using the absorbance and transmission measurements from a Unico UV-2102 PC spectrophotometer, at normal incidence of light in the wavelength range 200–1000 nm, and the structural characterization were done using XRD and photomicrograph. The films have high absorption, greater than 90%, in the UV region but with moderate transmittance of greater than 50% for as-deposited, and poor transmittance of less than 45% for the annealed throughout the entire spectrum. Plots of $(\alpha hv)^2$ against hv showed that the material has a direct band gap around 2.20 eV at 300 K, 1.70 eV at 453 K, and 1.60 eV at 473 K. The high absorbance of the films made them good materials for large area selective coatings for photothermal conversion of solar energy.

1. Introduction

Antimony trisulfide, Sb_2S_3, has found applications in various devices [1] such as television cameras, microwave, switching and optoelectronic. The use of Sb_2S_3 thin films in solar cell structures with conversion efficiencies of 5.5 and 7.3%, respectively, has been reported [2, 3].

In view of the various potential applications, several methods of depositions [1, 2, 4–22] have been employed to prepare Sb_2S_3 thin films, such as chemical bath deposition in non-aqueous and aqueous media, spray pyrolysis, flash evaporation and vacuum evaporation.

From the methods used for the preparation of Sb_2S_3 thin films, the chemical bath deposition method is often preferred because it offers large possibilities to modify the deposition condition so as to obtain films with determined structure and physical properties [9–22, 23].

Annealing of the films after deposition in air, changes the optical properties of the deposited thin films because of the changes in their structures [24, 25].

The objective of this paper was to study the effect of annealing in air on the structural and optical properties of Sb_2S_3thin films.

1.1. Deposition Of Sb_2s_3 Thin Films

11.51 g of $SbCl_3$was dissolved in 50 ml acetone. 5 ml of this solution was placed in a 50 ml beaker, to which 12 ml of 1.0 M sodium thiosulphate and 33 ml of distilled water were added. The resulting solution was stirred for a few seconds with a glass rod stirrer. A glass slide was inserted in the reaction bath, and held vertically in a synthetic foam cover. This process was repeated for different dip time with various reaction baths. The chemical equations for the bath described can be written as

$$2SbCl_3 + 3Na_2S_2O_3 \rightarrow Sb_2(S_2O_3)_3 + 6NaCl$$

$$Sb_2(S_2O_3)_3 + 6H_2O \rightarrow Sb_2S_3 + 3H_2SO_4 + 3H_3O^+$$

According to Nair et al [2], the dissociation of the soluble $Sb_2(S_2O_3)_3$ releases Sb^{3+} ions while the hydrolysis of thiosulfate releases S^{2-} ions. The growth mechanism of the Sb_2S_3 is an ion-by-ion condensation:

$$Sb_2(S_2O_3)_3 \leftrightarrow 2Sb^{3+} + 3S_2O_3^{2-}$$

$$S_2O_3^{2-} + H_2O \leftrightarrow SO_4^{2-} + S^{2-} + 2H^+$$

The antimony ions, together with the sulphide ions produced in the bath, condense at the substrate surface forming Sb_2S_3 thin film [2]:

$$2Sb^{3+} + 3S^{2-} \rightarrow Sb_2S_3 \downarrow$$

1.2. Observation Made In Depositing Antimony Sulfide (Sb_2s_3)

In preparing the reaction bath for the above thin films compound, it was observed that addition of sodium thiosulphate in a solution of antimony chloride ($SbCl_3$)/acetone, changed from colourless solution to milky colour. After thorough stirring and addition of distilled water, a gradual colour change was observed, with the colour changing from light orange to deep orange colour. The pH of the solution in the reaction bath is in acidic medium.

For the deposited thin films on glass substrates, the colours varied from light orange (deposited thin film for 4 hrs) to deep orange colour (deposited for 20 hrs). It was observed that the film deposited on both sides of the glass substrates.

1.3. Optical and Solid State Characterization

The optical and solid state characterizations performed on the films grown on this work were the absorbance A, the transmittance T, and the Band gap E_g of the films.

The absorbance/transmittance characterization was carried out using a UNICO UV-2102 PC Spectrophotometer in the ultraviolet and visible regions of the electromagnetic spectrum. The absorbance and transmittance were read from the machine while band gap values were determined using the absorption spectra method.

2. Film Structures

X-ray diffraction (XRD) was used to determine the structure of the thin film samples in this work using a Philips PW1800 X-ray Diffractometer. The photomicrograph structures of the films grown in this work were studied with a Ortholux II photoscope.

3. Results and Discussions

The XRD patterns of the crystal nature of the thin films were studied using CuKα radiation source with wavelength 1.54056 Å. The scanning were done continuously between 0° and 70° at a step size of 0.03 and at time per step of 0.15 s on Sb_2S_3 thin films deposited onto glass at substrate temperatures 300 K and annealed to various temperatures.

The Sb_2S_3 thin film annealed in air for 2 hours at 453 K showed diffraction peaks, as shown in Figure 1. The diffraction peaks appeared at $2\theta = 25°, 36°, 37°$, and 41°, which correspond to diffraction from (310), (240), (231) and (331) planes for film annealed at 453 K. Other small peaks that appeared in the diffraction patterns of the annealed films indicate a partial oxidation of the samples, as it was to be expected [1].

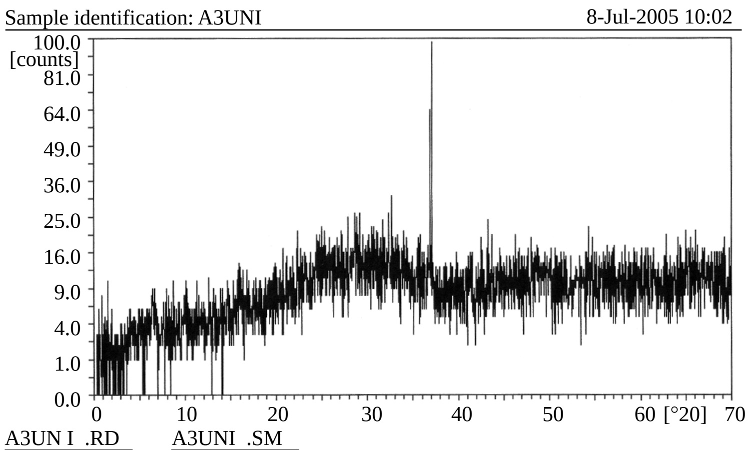

Figure 1. XRD for Sb_2S_3 thin Film annealed at 453 °C for 2 hours.

The photomicrographs are shown in Figure 2. The crystalline structure is clear in the micrograph of films.

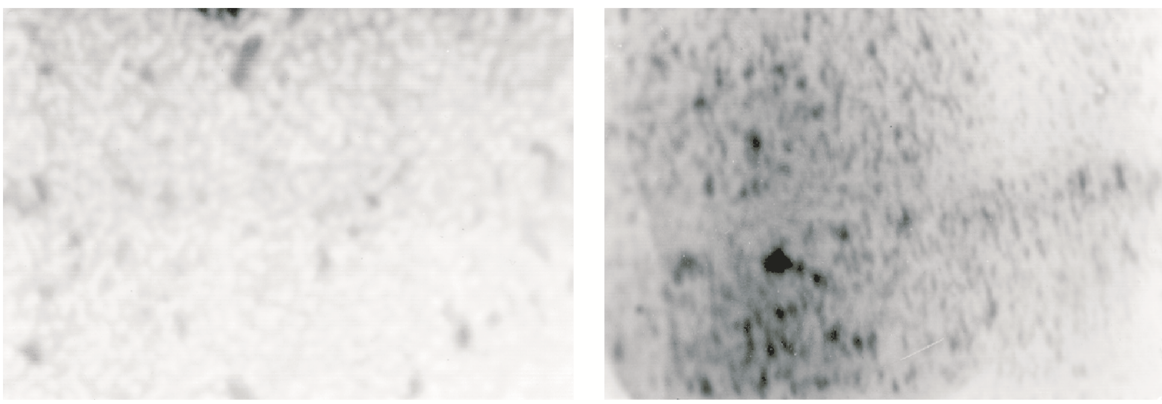

Figure 2. Optical micrograph Sb_2S_3 Thin Films.

The optical properties of the Sb_2S_3 thin films are also influenced by the heat treatment. The optical absorption spectra of Sb_2S_3 films deposited onto a glass substrate were studied in the range of wavelengths 200–1000 nm. The variation of absorbance A and transmission ($\%T$) with wavelength λ, before and after heat treatment, are shown in Figures 3 and 4, respectively. After the annealing, the films transmittance decreased, which is due to increase of the crystallite size and resulted in the lower transmittance of the heat-annealed films. The increased roughness of the annealed thin films contributed to the drastic decrease of optical transmittance [26]. The thickness of the film as obtained from optical measurements [23] showed 0.691 μm (473 K), 0.440 μm (453 K) and 0.327 μm (300 K). The film shows moderate absorbance (0.23–0.24) for as-deposited but poor absorbance (0.27–0.51) for annealed samples throughout visible-near infrared regions, hence the film has potential application in the fabrication of thin film materials for photovoltaic generation of electricity.

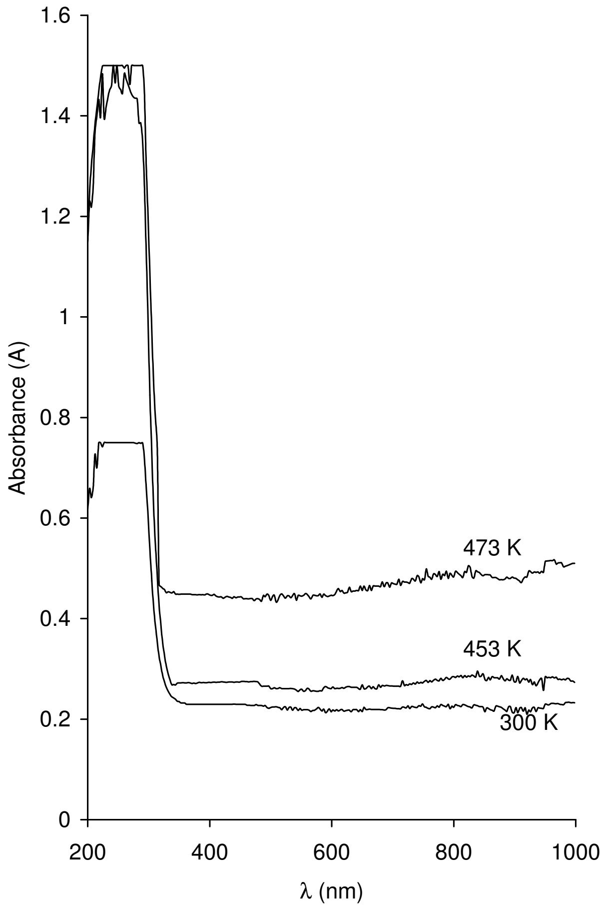

Figure 3. Absorbance (A) against wavelength (λ) for Sb_2S_3 Thin Film at Various Temperatures.

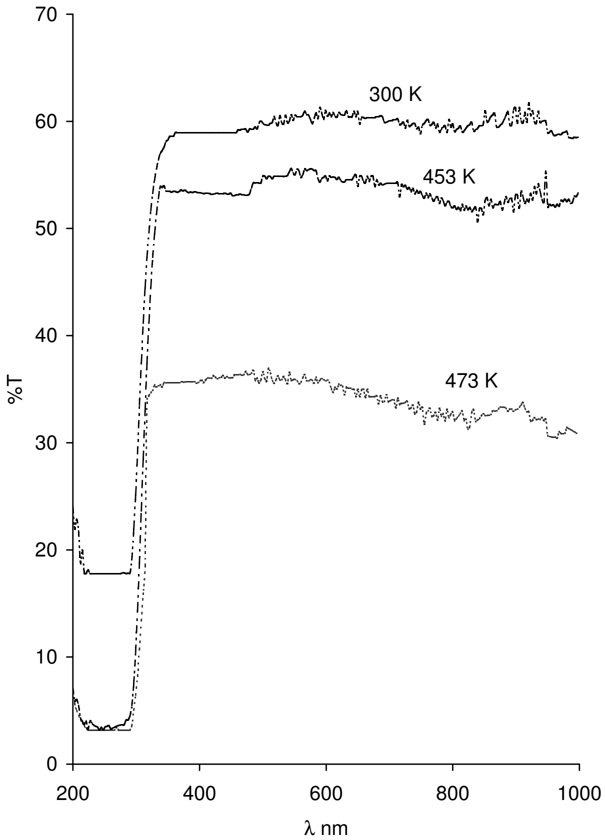

Figure 4. Transmittance (T) as function of wavelength (λ) for Sb_2S_3 Thin Film at Various Temperatures.

The dependence of the absorption coefficient α, on the photon energy is important in studying energy band structure and the type of transition of the electrons. The absorption coefficient, α, was estimated by the transmittance data as shown in Figure 5. In order to determine the optical band gap of the semiconductor the following dependence of α on the photon energy equation [1, 3] is used:

$$(\alpha hv) = B(hv - E_g)^n,$$

where B is a parameter that depends on the transmission probability, E_g is the band gap energy, α is the absorption coefficient and n is an index that can assume values of (1/2, 2) depending on the nature of the electronic transitions.

For the direct allowed transitions, n has a value of 1/2 and, is plotted as Figure 6. From the intercept of the straight part of the curves with the hν-axis, the optical band gap of Sb_2S_3 films was estimated and the optical band gap obtained is around 2.20 eV (300 K), 1.70 eV (453 K) and 1.60 eV (473 K). This band gaps agree fairly with the reported values of Sb_2S_3 thin films [2, 27]. The film deposited in this work shows narrow band gap, as such, it could serve as good absorber layers for photocells.

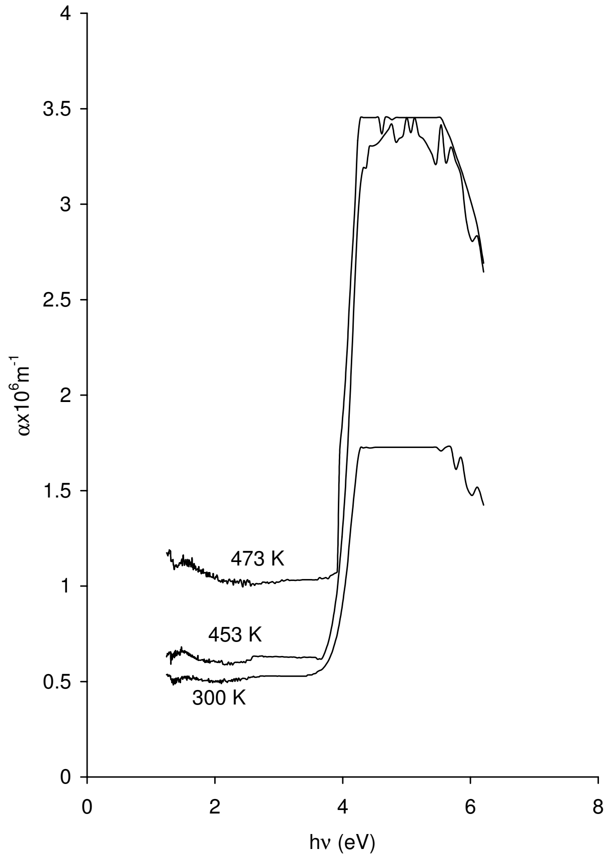

Figure 5. Plots of a as a function of Photon Energy (hn) for Sb_2S_3 Thin Film at Various Temperatures.

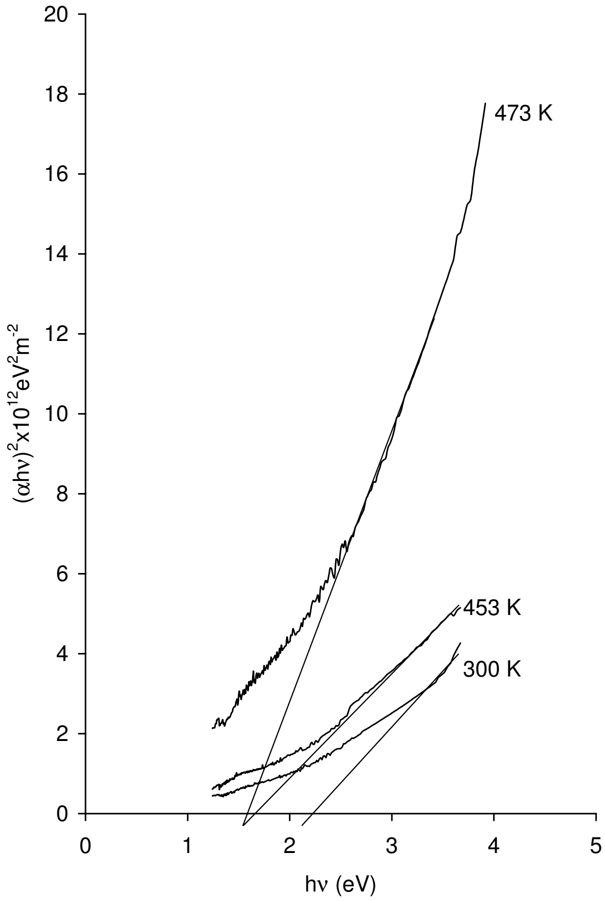

Figure 6. Plots of (ahn)2 as a function of Photon Energy (hn) for Sb_2S_3 Thin Film.

4. Conclusions

Sb_2S_3 thin film with thickness 0.327 μm (300 K) was deposited using the CBD method and annealed film resulted in thickness 0.440 μm (453 K) and 0.691 μm (473 K). These studied using spectrophotometer, XRD and optical microscopy. The direct optical transitions were observed to be present in the Sb_2S_3 thin films that were deposited which a slightly decreases from 2.20eV to 1.60eV due the annealing temperatures on the structural and optical properties. The moderate (0.23–0.24) and poor absorbance (0.27–0.51) exhibited by the film both for the as deposited and annealed in the solar spectrum respectively, could serve as solar absorbers for solar cell applications.

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