

INFLUENCE OF DIP TIME ON THE OPTICAL AND SOLID STATE PROPERTIES OF AS-GROWN Sb_2S_3 THIN FILMS

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Antimony sulphide thin film was deposited on glass substrate using the chemical bath deposition technique at room temperature. Sb_2Cl_3 dissolved in acetone and $\text{Na}_2\text{S}_2\text{O}_3$ were taken as the source of antimony and sulphur respectively. From the absorption and transmission spectra determined using Unico UV-2102 PC spectrophotometer, the band gap energy was found in the 1.60 to 2.30eV range. The result shows that dip time influences both the optical properties and band-gap energy of the films. XRD analysis revealed that the crystallinity of the as-grown Sb_2S_3 thin films were enhanced by longer dip time.

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1. Introduction

Chemical bath deposition (CBD) is an attractive pathway for deposition of thin films of metals or semiconductors. The CBD process is a very simple, cost effective and economically reproducible technique that can be applied in large area deposition at low temperature [1-4]. The technique involves controlled release of metal ions (M^{2+}) and sulphide (S^{2-}) or selenide (Se^{2-}) ions in an aqueous bath in which the substrates are immersed. In this process, the release of metal ions (m^{2+}) is controlled by using a suitable complexing agent. The deposition begins with nucleation phase followed by growth phase in which the thickness of films increases with duration up to the terminal phase where film depletion into constituent ions occurs after a certain time.

With an optical band gap in the range of 1.06eV to 1.88eV in crystals and in polycrystalline thin films with $\text{V}_2\text{-V1}_3$ composition [5-6], the sulphides and selenides of antimony are good absorber materials for photovoltaic application. The use of Sb_2S_3 thin films in Schottky barriers solar cells of Pt- Sb_2S_3 and n- Sb_2S_3 /P-Ge structures with conversion efficiencies of 5.5 and 7.3% respectively can be found in literature [7, 8]. Sb_2S_3 has also found application in other devices such as television cameras, microwave, switching and optoelectronic [9].

Various researches have shown a downward trend in the optical band gap of Sb_2S_3 thin film when annealed in air [5, 10] and in nitrogen [11]. The formation of ternary compound by annealing chemically deposited Sb_2S_3 -CuS thin films has also been reported [12]. In the present research, we report on the influence of dip time (deposition time) on the optical properties and band gap energy of as-grown thin films of Sb_2S_3 using solution growth technique (also known as chemical bath deposition).

2. Experimental details

2.1 Preparation of Sb_2S_3 thin films

Sb_2S_3 thin films were deposited on clean glass slides by chemical bath deposition (CBD) [10]. 1.3g of SbCl_3 were dissolved in 5ml of acetone, followed by addition of 25ml, 1M $\text{Na}_2\text{S}_2\text{O}_3$. The mixture was made up to 50ml with addition of distilled H_2O . 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: Q1 (1hr), Q2 (1.5hrs), Q3 (2.5hrs) and Q4 (3hrs).

2.2 Characterization

The structure of the films was studied with optical microscope and Philips PW 1500 XRD. The band gaps of the films were determined by using the absorbance and transmittance measurement from Unico-UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000nm

3. Results and discussions

3.1 Structure and surface morphology

X-ray diffraction analysis was carried out on chemical bath deposited Sb_2S_3 thin films. The samples were grounded to below 100 mesh in an agate mortar and then loaded into a 2.5cm diameter circular cavity holder and ran on an MD 10 mini diffractometer. $CuK\alpha$ was selected by a diffracted beam monochromator. The thin films were scanned continuously between 0 to 75 at a step size of 0.03 and at a time per step of 0.15sec. Phase identification was then made from an analysis of intensity of peak versus 2θ .

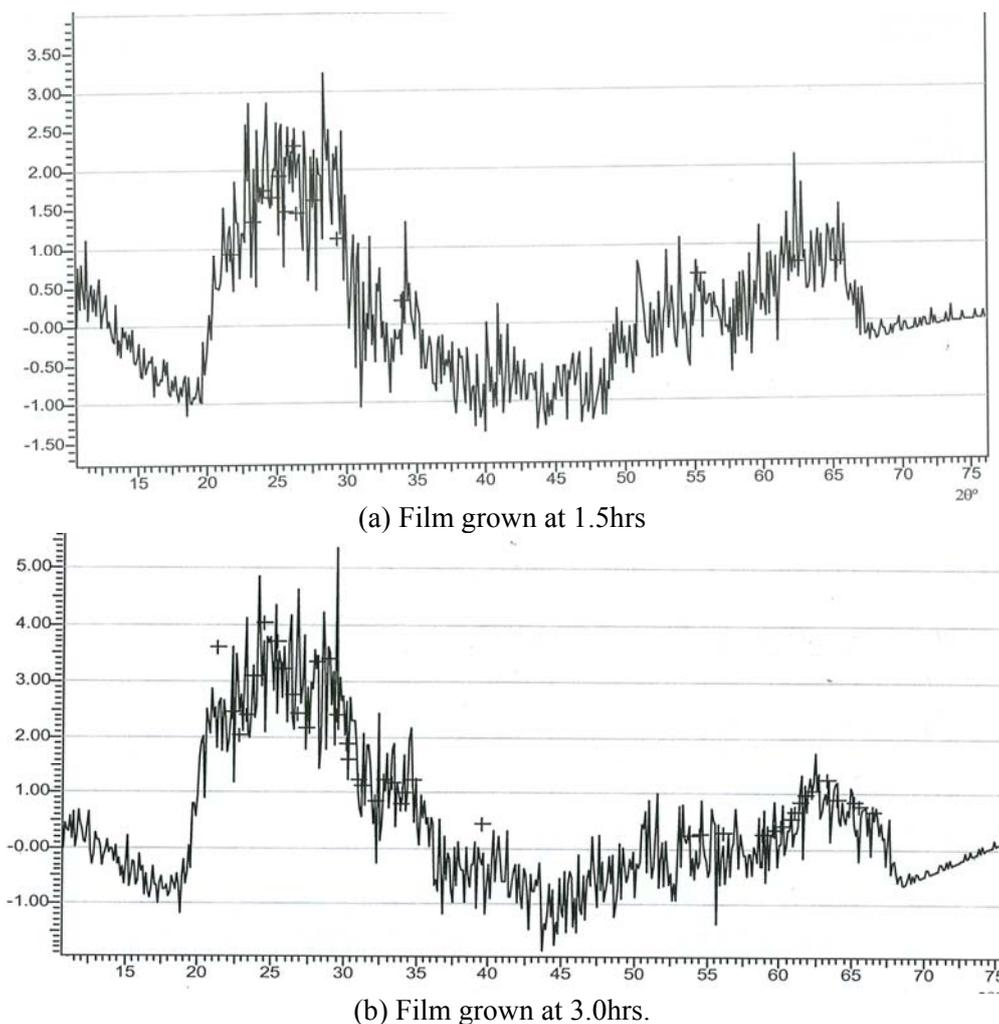


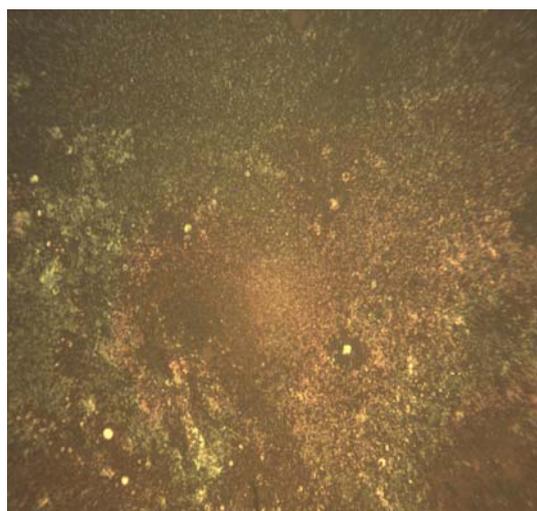
Fig.1. XRD pattern for Sb_2S_3 thin films

Typical diffraction pattern of Q2(1.5hrs) and Q4(3.0hrs.) are shown in figure 1. It has been reported that XRD peaks are not observed in the case of as-deposited Sb_2S_3 thin films [11, 15]. In our own case, the XRD patterns of the film deposited at 3hours displayed very few (rather than complete absence of) identifiable peaks. This observation has also been reported [16]. This is an indication that the as-grown Sb_2S_3 thin films are of poor crystallinity. Table 1 shows the inter-planer spacing, d , in comparison with the standard JCPDS-6-0474 for the film grown at a dip time of 3hrs.

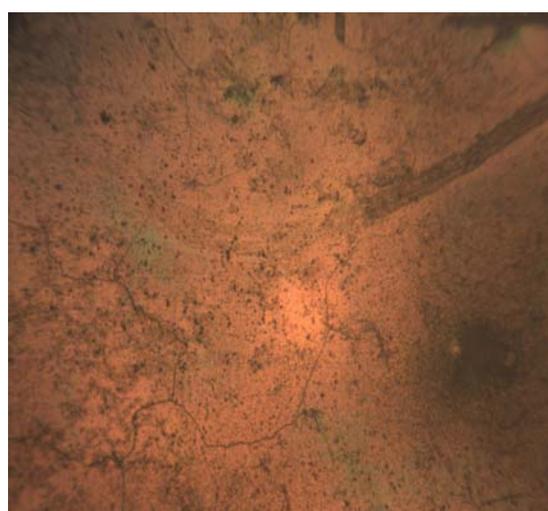
Table 1. Comparison of standard and observed 'd' values of Sb_2S_3 thin film at dip time of 3hrs

Standard 'd' values	Observed 'd' values	Reflection plane
3.632	3.643	101
3.458	3.463	111
3.178	3.189	021
3.053	3.030	211

The surface microstructure of the films were obtained by taking the photomicrographs of the films coated on the transparent glass slides with wide KPL-W10x/ 18 Zeiss Standard 14 photomicroscope with M₃₅ 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in figure 2. A close observation of the optical micrographs of Sb_2S_3 thin films show that the grains were uniformly distributed. The spread of the deposited film increased with dip time.



(a) Film grown at 1.50hrs dip time



(b) Film grown at 3.0hrs dip time

Fig. 2. Optical Micrograph of Sb_2S_3 thin film at different dip time.

3.2 Optical Studies

Fig 3 and 4 are plots of absorbance vs. wavelength and transmittance vs. wavelength for Sb_2S_3 thin films deposited at different dip time. Fig 3 shows a red shift in the absorbance of the films as dip time increases. The absorbance generally decreased with wavelength and has relatively low values in the IR region of the solar spectrum.

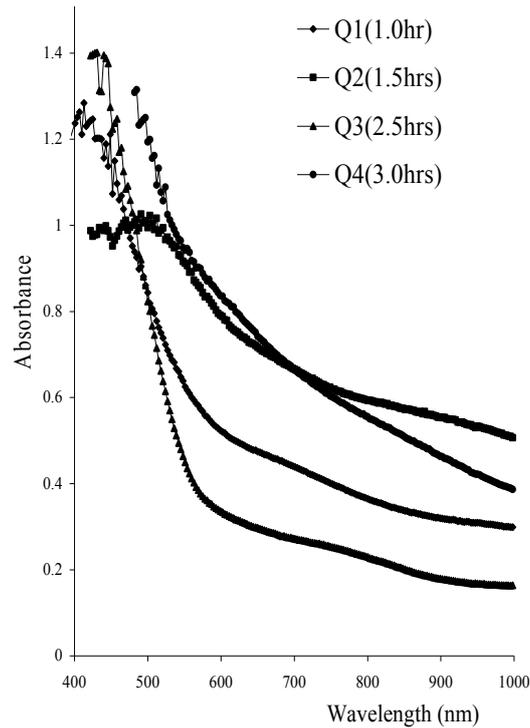


Fig. 3. Absorbance vs. wavelength for Sb_2S_3 thin films at various dip time.

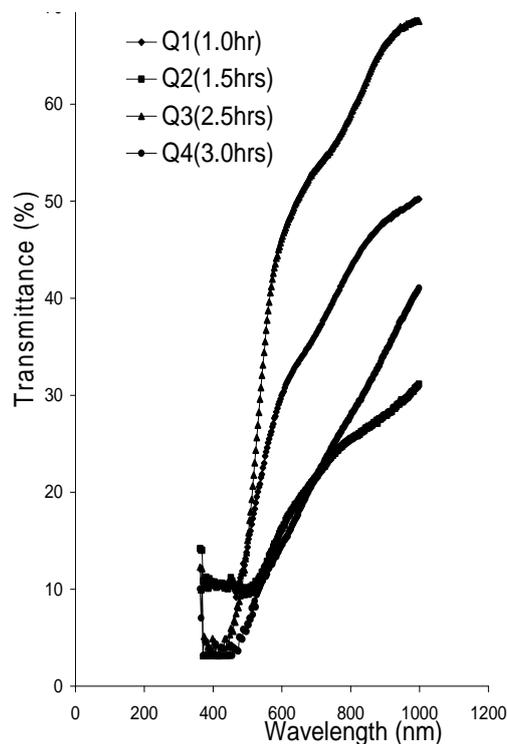


Fig. 4. Transmittance vs. wavelength for Sb_2S_3 thin films at various dip time.

Strong absorption was observed at wavelength range of 400-500nm. Hence the film has potential application in fabrication of solar cell.

The transmittance spectra displayed in fig 4 shows a downward trend in the transmittance of the films as dip time increases. The film deposited at a dip time of 1hr has the highest transmittance of ~ 70% at a wavelength of ~ 1000nm.

Fig 5 is a plot of reflectance as a function of wavelength for Sb_2S_3 thin films deposited in this work. The films show an average reflectance of 18% in the wavelength range of 550-950 nm.

Fig 6 shows that the refractive index of films deposited at longer dip time decreases uniformly with increasing photon energy in the VIS-NIR region.

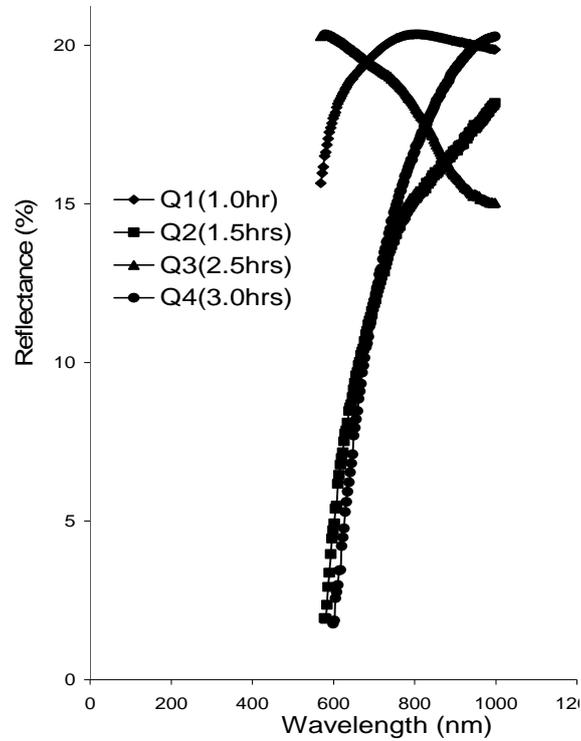


Fig. 5. Reflectance vs. wavelength for Sb_2S_3 thin films at various dip time.

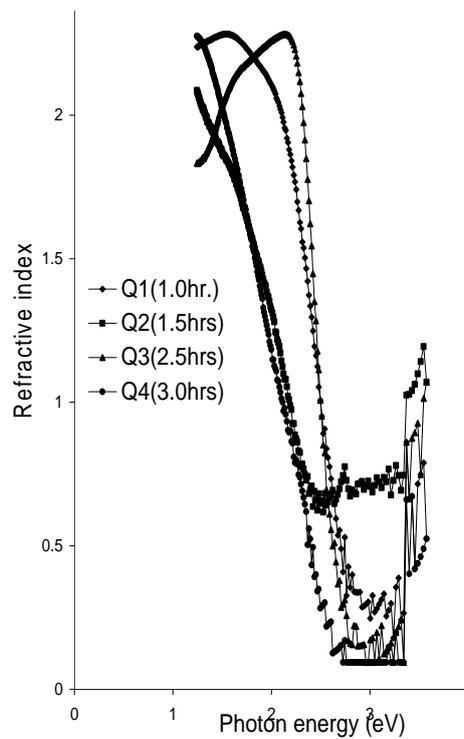


Fig. 5. Refractive index vs. photon energy for Sb_2S_3 thin films at various dip time.

However, the film deposited at a dip time of 1 hour show an increase in refractive index as photon energy increases up to a critical value, at which it begins to decrease with increase in photon energy. The highest observed refractive index of 2.28 was observed at photon energy of 1.54eV for sample Q2 (1.5 hrs.) and 2.12ev for sample Q1 (1hr.).

The optical band gap E_g was calculated using Tauc's plot $((\alpha h\nu)^2$ vs. $h\nu$) [13] as shown in Fig.7. The value of α is determined from transmittance spectra. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents E_g , which is determined by extrapolation. The values obtain for Sb_2S_3 thin film lie in the range of 1.60 – 2.30eV. A close observation of figure 7 shows that the energy gap decreased from 2.30 to 1.60eV as dip time increased from 1hr to 3hrs. This trend is different from that observed in CdS and CdNiS thin films reported elsewhere [4, 17]. However the decrease in the band-gap energy with dip time recorded in this work may be attributed to the change in the films thickness with time. This has the potential to lower the band-gap energy as revealed in the $(\alpha h\nu)^2$ vs. $h\nu$ plot of figure 7

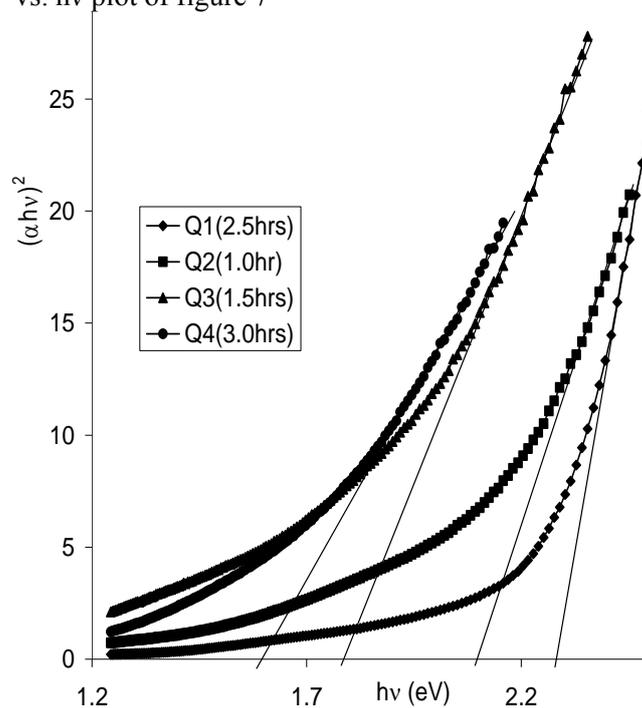


Fig. 7. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for Sb_2S_3 thin films at various dip time.

4. Conclusions

Thin films of Sb_2S_3 were deposited using the CBD method. The films were studied using X-ray diffraction, spectrophotometry and optical microscopy. XRD analysis revealed that the crystallinity of the as-grown Sb_2S_3 thin films were enhanced by suitable dip time. Dip time also influences the optical properties and the band-gap energy of the film. Band-gap energy decreased with increasing dip time. The values of the band-gap energy (1.60 – 2.30eV) are in the required range for solar cell fabrication. Thin films with band gap energy lower than 1.90eV are used as absorber materials in solar cell architecture while those with higher band gap energy can be used as window layers. The results from this work indicate that the requirement for absorber or window materials for solar cell application can simply be meant by choosing the appropriate deposition time during the preparatory stage of Sb_2S_3 thin film.

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