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Investigation of Structural, Optical and Photovoltaic Properties of Sb2S3 Thin Films

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Abstract. Sb_2S_3 thin films were prepared on amorphous glass substrates by chemical bath deposition (CBD) at room temperature. The Sb_2S_3 thin films were characterized by x-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and UV-Vis spectroscopy. The XRD revealed that the as deposited Sb_2S_3 thin film has a different structure compared to annealed Sb_2S_3 thin film. As deposited Sb_2S_3 thin film showed amorphous structures while the Sb_2S_3 thin film became polycrystalline after annealing at 350 ^{0}C for 1h under N_2. The band gaps of the Sb_2S_3 thin films were compared using UV-Vis spectroscopy. The spectral response of the Sb_2S_3 thin film enhanced after the annealing process. The Sb_2S_3 thin films were subsequently used to make semiconductor-sensitized TiO_2 nanowire (NW) solar cells. The performances of the solar cells, with the short circuit current density and open circuit voltage, were investigated. Based on the optical and photovoltaic measurements, we consider that annealed Sb_2S_3 thin films can be promising materials for developing solar cell technologies.

***Keywords*:** Sb_2S_3 thin films, chemical bath deposition, semiconductor –sensitized solar cells

INTRODUCTION

Recently, much attention has been paid to the preparation and characterization of the group V-VI compounds due to their novel optical properties. The one of the most important metal chalcogenides group A_2^V B_3^{VI} is Sb_2S_3 with direct bandgap of ~ 1.78- 2.5 e V [1-5], has widely used as an important material in many different technological areas such as microwave devices, solar cells, various optoelectronics devices, and IR sensors because of their physical and chemical properties [6-15].

From the application view, sensitized solar cells with inorganic semiconductors are promising candidates for developing low-cost and high performance photovoltaic devices. The one of the most important part of structure of semiconductor -sensitized solar cells is sensitizer. The Sb_2S_3 thin films can be used as sensitizers due to their remarkable optical and electrical properties. For instance, Li et al.[16] investigated annealing effect on Sb_2S_3 – TiO_2 nanostructures for solar cells application in 2013. They concluded that the photovoltaic conversion efficiency for this structure increase from 0, 46% up to 1, 47% as a consequence of the annealing treatment.

Thin film or powders can be synthesized by several well-known methods. The CBD which is a simple and inexpensive method is considered as one of the most appropriate method [17]. In comparison other methods which require long time and extreme laboratory conditions, the thin films can be synthesized with simple laboratory equipments and within a few hours using the CBD method.

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In our present study, the synthesis of Sb_2S_3 thin films were prepared on amorphous glass substrates by chemical bath deposition (CBD) at room temperature, are reported. Structural, morphological, optical and photovoltaic properties of as-deposited and annealed Sb_2S_3 thin films have been investigated. The effect of annealing temperature on the optical and photovoltaic properties is discussed.

EXPERIMENTAL DETAILS

To synthesize Sb_2S_3 thin films at room temperature, commercial antimony chloride ($SbCl_3$) and sodium thiosulfate ($Na_2S_2O_3$. $5H_2O$) were used without any further purification. In a typical CBD method, 650 mg of $SbCl_3$ was dissolved in 10 ml of acetone in a clean beaker. 25 mL of 1 M aqueous solution of sodium thiosulfate was added into a solution containing $SbCl_3$. The total volume of mixture was made 100 mL by addition appropriate amount of deionized water. After obtaining a homogeneous mixture, 25 ml of the Sb_2S_3 solution was transferred to another clean beaker, then two glass microscope slides which were cleaned well with diluted hydrochloric acid, washed by double distilled water and dried, were vertically left into Sb_2S_3 solution for 45 minutes. Afterwards, the glass substrates were removed from the chemical bath, washed well with deionized water and dried in air. One of the glass substrates was annealed at 350 ^{0}C for 1 h under N_2.

X-ray diffraction (XRD) on a Rigaku x-ray diffractometer with Cu K_α (λ= 154,059 pm) radiation, Raman spectroscopy (DeltaNu ExamineR), and scanning electron microscopy (SEM) (JEOL JSM 5800) were used to analyze structural and morphological properties of Sb_2S_3 thin films, respectively. A Perkin Elmer Lamba 2 spectrometer was used to record UV-Vis absorption spectra to analyze optical properties of Sb_2S_3 thin films.

The performances of fabricated Sb_2S_3 devices were tested under a light intensity of 100 mW/cm^2 from a 150 W Xenon arc lamp. For current density (J) – voltage (V) measurements, fluorine doped tin oxide (FTO, 13Ω.sq^{-2}) conductive glass substrates were used as the photo electrodes. The TiO_2 nanowires (NWs) were coated on the FTO substrates using the doctor blade method, then sintered at 450 ^{0}C for certain time. Sb_2S_3 thin films were grown on the TiO_2 NWs coated on the FTO substrates by CBD method at room temperature. One of the Sb_2S_3 thin films grown on the TiO_2 NWs coated on the FTO substrates was annealed at 350 ^{0}C for 1 h under N_2. Then, the obtained annealed and as-deposited Sb_2S_3 films grown on the TiO_2 NWs coated on the FTO substrates were secured against Cu_2S counter electrode containing a polysulfide electrolyte. Dai et al. [18] indicated the preparation of were Cu_2S counter electrode and polysulfide electrolyte.

RESULTS and DISCUSSIONS

Figure 1 demonstrates the XRD patterns of as-deposited and annealed Sb_2S_3 thin films deposited onto glass substrates by chemical bath deposition at room temperature. It can be clearly seen that the Sb_2S_3 thin film was obtained with a good crystalline structure when it was annealed at 350 ^{0}C for 1h while as- deposited Sb_2S_3 thin film showed amorphous structure. All diffraction peaks of annealed thin film prepared at room temperature can be well indexed as the orthorhombic phase structure of Sb_2S_3, which is consistent with the standard card (ICDD 00-001-0538).

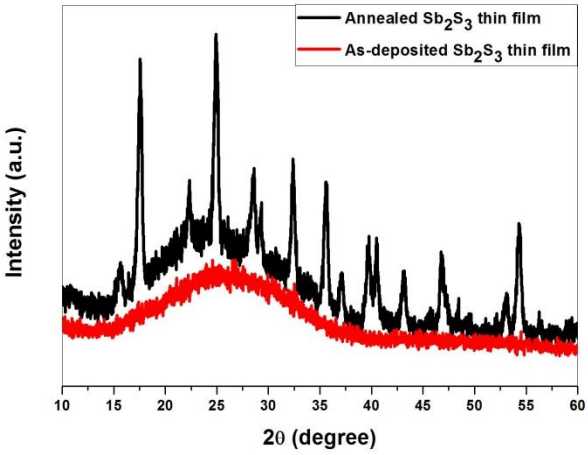

Figure 1. The XRD patterns of as- deposited Sb_2S_3 and annealed Sb_2S_3 thin films.

The diffraction peaks of annealed Sb_2S_3 thin film prepared at room temperature were used to

calculate d-values using by Bragg's law as given in Equation 1:

$$d = \lambda/2*\sin\theta \quad (1)$$

Where, d is the lattice spacing, λ is wavelength of the used x-ray, and θ is the Bragg's diffraction angle. Calculated d values were compared with standard d values, which are revealed in Table 1.

Table 1. Comparison of the standard "d" values and calculated "d" values of annealed Sb_2S_3 thin film.

2 θ (degree)	Calculated"d" values (Å)	Standard "d" Values (Å)	hkl
17.58	5.040	5.040	(1,2,0)
22.70	3.920	3.917	(2,2,0)
24.94	3.567	3.570	(1,3,0)
28.63	3.116	3.117	(2,1,1)
32.40	2.761	2.763	(2,2,1)
35.58	2.521	2.523	(4,2,0)
39.66	2.271	2.272	(0,4,1)
43.19	2.093	2.094	(5,2,0)
46.74	1.942	1.943	(5,0,1)
53.13	1.723	1.724	(5,3,1)
54.32	1.687	1.689	(3,60)

There is a good agreement between both of d values. Based on the Table 1, the Sb_2S_3 thin film was obtained as desired after it was annealed at 350 ^{0}C for 1 h under N_2.

The SEM image of annealed Sb_2S_3 thin film is shown in Figure 2a reveals that the shape of the grains is spherical. After annealing treatment, Sb_2S_3 thin film shows more uniform and higher grain size while the shape of the grain size of as – deposited Sb_2S_3, thin film prepared by Krishan et al. [15], is not clear. This is in a good agreement with our result obtained from XRD measurement.

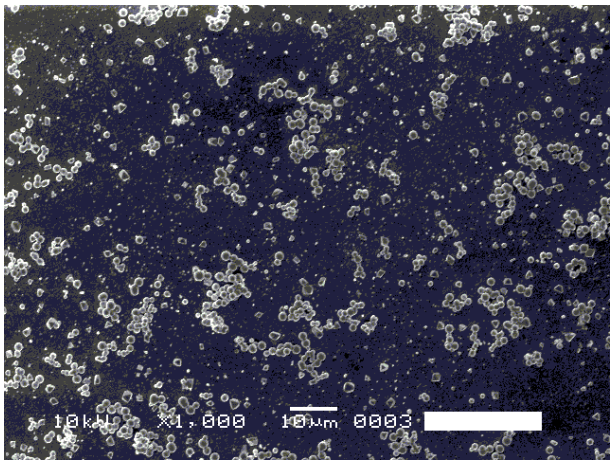

Figure 2a. SEM image of Sb_2S_3 thin film annealed at 350 ^{0}C for 1 h under N_2.

The energy dispersive x-ray (EDX) spectrum was used to confirm the elemental compositions of the Sb_2S_3 thin film. The peaks obtained from the EDX spectrum (shown in Figure 2b) are associated with S and Sb. This result is consistent with observation of Pan et al. [19]. They concluded that the peak located in low energy region is assigned to S K_α while three peaks located in higher energy regions are assigned to Sb L_α. Based on the EDX spectrum, the molar ratio of Sb/S found using the peak areas, 37.51/62.46, which is close to 2/3.

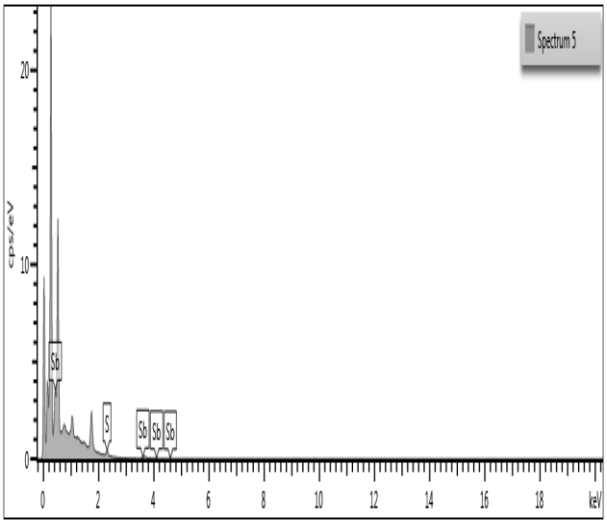

Figure 2b. EDX spectrum of Sb_2S_3 thin film (synthesized at room temperature) annealed at 350 ^{0}C for 1 h under N_2.

Figure 3 indicates the Raman spectra of Sb_2S_3 thin film annealed at 350 ^{0}C for 1 h under N_2. Two peaks at 115 cm^{-1} and 150 cm^{-1} were observed in the Raman spectra.

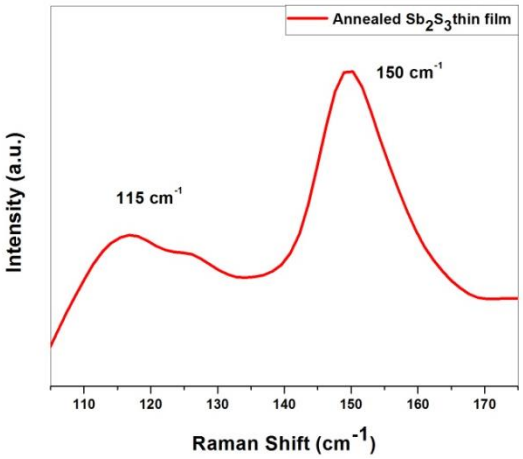

Figure 3. Raman spectra of Sb_2S_3 thin film annealed at 350 ^{0}C for 1 h under N_2.

This result is consistent with result obtained by Watanable et al. [20] who explained that the maximum band at 150 cm^{-1} can be assigned to the vibration Sb-Sb bonds in S_2Sb- SbS_2 structural units whereas the band at 115 cm^{-1} can be associated with the vibration modes of SbS_3 pyramids, which are main building units of the film. The reason of the sharp intensity of the band at 150 cm^{-1} could be due to the increase in grain size of the Sb_2S_3 thin film annealed at 350 ^{0}C for 1 h under N_2. Minceva-Sukarova et al. [21] reported that the degree of sharpness reveals the crystalline nature of the Sb_2S_3 thin film after annealing treatment which is in a good agreement with our XRD result.

The band structures of as- deposited and annealed Sb_2S_3 thin films prepared by chemical bath deposition method at room temperature were studied using UV-Vis spectroscopy. The aim of the optical studies of the thin films in this study is to make comparison between as- deposited and annealed Sb_2S_3 thin films and to show how band gap of the Sb_2S_3thin film changes after it was annealed at 350 ^{0}C for 1h under N_2. The optical absorption spectra of as-deposited and annealed Sb_2S_3 thin films prepared at room temperature is shown in Figure 4.

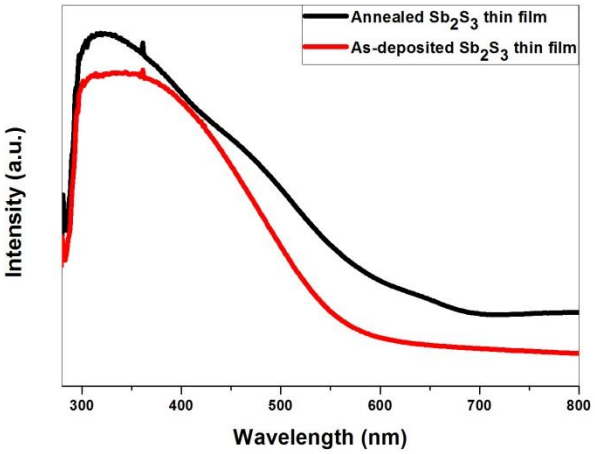

Figure 4. The UV-visible absorption spectra of as- deposited Sb_2S_3 and annealed Sb_2S_3 thin films.

Based on optical absorption spectra shown in Figure 4, two effects of annealing were observed on the optical properties. The first of them is that the absorption edge (~700 nm) of the Sb_2S_3 thin film annealed at 350 ^{0}C for 1 h under N_2 is red shifted compare to as- deposited Sb_2S_3 thin film (~579 nm). Owing to annealing treatment, the increase in the grain size causes the red shifted. The calculation of the band gap for as-deposited and annealed Sb_2S_3 thin films deposited onto glass substrates by chemical bath deposition at room temperature was done by using the relation is given in Equation 2.

$$\alpha h\upsilon = C(h\upsilon - E_g)^{1/2} \quad (2)$$

where α is absoprtion coefficient, $h\upsilon$ is photon energy, and E_g is energy gap. The $(\alpha h\upsilon)^2$ versus $h\upsilon$ for as-deposited and annealed Sb_2S_3 thin films, is shown in Figure 5, were plotted using the data obtained from Figure 4,

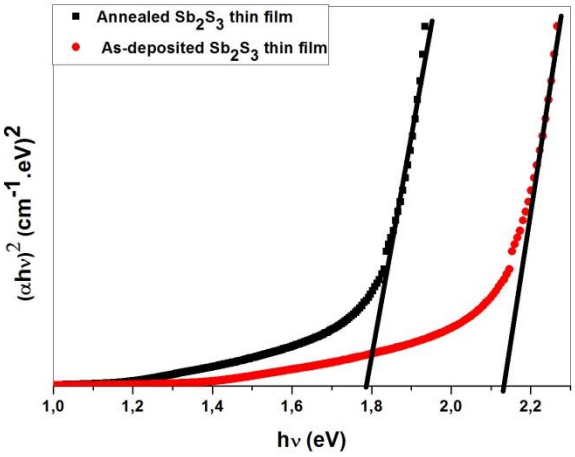

Figure 5. Determination of the optical band gap for as-deposited and annealed Sb_2S_3 thin films using $(\alpha h\upsilon)^2$ vs $h\upsilon$ plot.

Using above plot, it was found that the band gap of annealed Sb_2S_3 thin films prepared at room temperature is around 1.77 e V (~700 nm) while the band gap of as- deposited Sb_2S_3 thin films prepared at room temperature is around 2.14 e V (~579 nm). It can be clearly seen that the band gap of annealed Sb_2S_3 thin film decreases after annealing treatment. Another effect of the annealing is to enhance the absorption spectral response of Sb_2S_3 thin film. So that annealed Sb_2S_3 thin film will have wide absorption windows. Because of this effect, it can be said that annealed Sb_2S_3 thin films prepared by chemical bath deposition at room temperature can be used effectively as sensitizers in solar cell technologies.

Figure 6 indicates the current density (J) versus voltage (V) of the as deposited and annealed Sb_2S_3 semiconductor-sensitized solar cells which prepared at room temperature, examined under 100 mW/cm^2 light intensity.

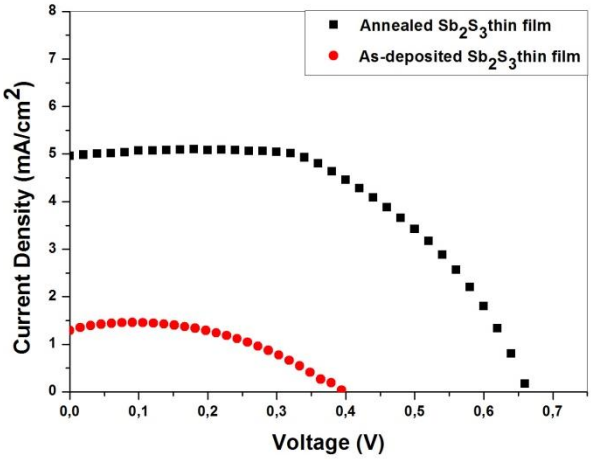

Figure 6. J-V plots of as-deposited and annealed Sb_2S_3 semiconductor-sensitized solar cell synthesized at room temperature.

It is important to note that there is a significant improvement in the performance of the annealed Sb_2S_3 semiconductor-sensitized solar cells prepared at room temperature compare to as-deposited Sb_2S_3 semiconductor-sensitized solar cell. The power conversion efficiencies (shown in Table 2) were found 1, 78% and 0, 24% for annealed and as-deposited Sb_2S_3 thin films prepared at room temperature, respectively.

Table 2. Comparison of V_{OC}, J_{SC}, and η of annealed and as-deposited Sb_2S_3 semiconductor-sensitized solar cells prepared at room temperature.

Samples	Open circuit voltage (V_{OC}) (V)	Short circuit current density (J_{SC}) (mA/cm^2)	Power conversion efficiency (η %)
Annealed Sb_2S_3 (room temperature)	0,66	4,83	1,78
As-deposited Sb_2S_3 (room temperature)	0,4	1,3	0,24

The reasons of this improvement could be arrayed [16];

The annealed Sb_2S_3 thin film has the enhanced spectral response compare to as-deposited films (shown in Figure 4). This enhancement will improve the current density. (2) The grain size of the Sb_2S_3 thin film increases after annealing process (shown in Figure 1). The increment in the grain size will reduce the particle to particle

hopping of the photo-induced carrier. (3) Annealed Sb_2S_3 thin film has a high crystal quality (shown in Figure 1). The improvement in the crystalline will reduce the recombination of photo-excited carriers and this effect will increase the power conversion efficiency. (4) One of the important factors to enhance the efficiency is the contact between working electrodes and nano-structured semiconductor sensitizers. The contact between Sb_2S_3 thin film and TiO_2 NW becomes good due to annealing effect. This good contact can block the interfacial recombination of the injected transfer from NWs to polysulfide electrolytes. Correspondingly, it will improve the performance of the annealed Sb_2S_3 semiconductor-sensitized solar cells.

CONCLUSIONS

In this study, we report the structural, optical and photovoltaic properties of as-deposited and annealed Sb_2S_3 thin films prepared by chemical bath deposition at room temperature. Desired Sb_2S_3 thin films prepared at room temperature were successfully obtained when the thin film was annealed at 350 ^{0}Cfor 1h under N_2. As deposited Sb_2S_3 thin film showed amorphous structures while the Sb_2S_3 thin film became polycrystalline after annealing at 350 ^{0}C for 1h under N_2. The band gaps of the Sb_2S_3 thin films were compared using UV-Vis spectroscopy. The spectral response of the Sb_2S_3 thin film enhanced after annealing process. Based on the optical and photovoltaic measurements, we consider that annealed Sb_2S_3 thin films can be promising materials for developing solar cell technologies.

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