

COPPER-DOPED TIN SULPHIDE THIN FILM FOR SOLAR CELL MATERIAL

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ABSTRACT

The increasing human population has caused the demand for energy in society to escalate. The least dependency on fossil fuels and global concern are the drive factors for mankind to focus on green technology, especially in renewable energy. Many scientists believe that the sun is a suitable source to overcome the energy crisis by a way out that could harvest the solar energy. In this regard, photovoltaics (PV) or solar cell technology is considered to be a right option. However, the efficiency of the device is mainly concerned with the appropriate choice of the material. This study focuses on to search for a suitable thin-film solar cell (TFSC) material for absorber layer. Recently, tin sulphide (SnS) is proposed as a promising material for absorber layer. In this work, thermally evaporated thin films of SnS with different weight percentage of copper as a dopant has been deposited onto a glass substrate and then annealed in a vacuum environment. The effect of Cu-doping on the physical properties is determined using x-ray diffraction while the optical properties are analyzed using ultraviolet-visible-near infrared spectroscopy.

Keywords: Thin film; Tin Sulphide; SnS absorber layer; Solar cell; thermal evaporation;

INTRODUCTION

To-date, solar energy is considered one of the most copious, bottomless and clean source of the renewable energy. However to harvest the solar power, one of the finest ways is to use solar cell or photovoltaic (PV) technology. In these days, although, copper indium gallium diselenide (Cu(In,Ga)Se₂ (CIGS) and cadmium telluride (CdTe) are intensively used as talented absorber materials in the thin film solar cell system owing to the fact of their appreciable conversion competence, the rareness of the Ga, In, and the toxicity of the Cd demands for non-toxic, economical and highly efficient substitute materials [1, 2].

Recently, in a variety of studies, tin sulphide (SnS) has been reported a promising alternative solar cell absorber layer material. It belongs to group IV-VI semiconductor

and is reported with an orthorhombic crystal structure. Its particular potential is its direct energy gap (E_g) values (1.2-1.5) eV nearly equal to the best energy gap value (1.5 eV) required for solar devices, and the indirect band gap energy ranging from 1.0-1.2 eV [3]. Similarly, the value of its absorption coefficient (α) is reported greater than 10^4 cm^{-1} and light conversion efficiency higher than 24 % theoretically [4]. Additionally, the constituent elements of the SnS are abundantly available and non-toxic. Therefore, SnS can be said one of the best alternate candidates to CdTe and CIGS.

A potential thin film absorber layer material, ought to owe low electrical resistivity and high absorption. Although SnS have shown good characteristics, to further enhance the value of its absorption coefficient and lowering the resistivity, doping with metals like Ag, Sb, etc is considered appropriate [4, 5]. In this research, we are going to prepare tin sulphide thin films to investigate its potential as absorber layer with copper doping using thermal evaporation method. The performance of this layer is determined by characterizing the structural and optical properties.

EXPERIMENTAL

The deposition of the as-deposited and Cu-doped SnS thin films was done on a glass substrate using Edward E306 Vacuum Evaporator system under-optimized deposition conditions. The source materials (SnS powder & Cu) of the purity 99.99 % and 99.5 % were evaporated with different weight percentage (wt%) from a molybdenum crucible boat by applying a constant voltage of 30 V and current of 50 A. In order to deposit the Cu:SnS thin films of 300 nm thickness, a vacuum of 1×10^{-5} torr is maintained, while keeping the distance 10 cm between the substrate and source, and speed of deposition rate at 0.2 nm/s. While to monitor the thickness and deposition rate of the films, a quartz oscillator is used just placing below the substrate holder. Then to optimize the crystallinity as well as morphology, and to disperse copper concentration evenly in the obtained films, film samples were annealed for 120min at 200°C. The copper-doped (Cu:SnS) thin films were prepared with 0 wt. %, 5 wt. % and 10 wt. %. This percentage concentration of the copper doping was controlled using digital analytical balance.

The structural analysis of the prepared thin films was performed using a Siemens X-ray diffraction (XRD). The transmittance measurements were done with "Shimadzu UV-3101PC spectrophotometer" using a light of the wavelength ranging from (400-1800)nm by incidenting it normally on the plane of the film surface.

RESULTS AND DISCUSSION

Structural properties

XRD pattern, as shown in Figure 1, gives confirmation of the polycrystalline nature of the as-deposited and annealed thin film samples. Figure 1 shows a strong peak in conjunction with few weaker peaks of the as-deposited thin films at $2\theta=31.8^\circ$. The estimated values of the d-spacing, assigned to these peaks concerning SnS data,

matching nicely with JCPDS (No. 00-39-354), reflects the orthorhombic crystal structure of the SnS as revealed in Figure 2(a). Moreover, in most of the as-deposited samples, SnS crystallites are found to be oriented along the (111) plane. Though with annealing the (111) peak position remains unchanged, the intensity of annealed thin films peaks is larger and sharper compared to as-deposited films. Moreover, the enlargement in the peak intensity is the obvious proof for the improvement of crystallinity with annealing temperature. Perhaps after annealing, layers are better oriented. Whereas for the as-deposited thin films, the pattern shows poor crystallinity comparatively [6]. Also, the as-deposited and annealed films show evidence of a bang between 15 and 40° because of the amorphous character of the glass substrate. Furthermore, obtained thin films were analyzed by averaging the calculated crystallite size of the each thin film (prior and post-annealing) by Scherrer's formula [7],

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

wherein Eq. 1, D represents the average grain size, λ is the "X-ray wavelength of Co K_{α} radiation" ($\lambda = 1.54 \text{ \AA}$), θ is the Bragg diffraction angle, and β is the "full width of the diffraction line at half of the maximum intensity". The estimated results from the Eq. 1 are listed in Table 1.

From the table 1, it can be seen that the size of the grain in annealed films is bigger than the as-deposited films. This effect, therefore, on the average grain size is attributed to the vacuum annealing temperature, since average grain size is growing up clearly with annealing temperature [8]. Besides, this effect may be credited to the relocation of atoms and corresponding re-crystallization of the thin films structures with annealing process [6]. It also can be seen further that the crystallite size is decreased as the dopant wt% increased for both films. This reduction in crystalline size is because of the lattice distortion caused by radius difference between the dopant and the replaced element. However, this is in contrary with Majumder et al and Gowri Manohari et al studies [9, 10], as in their study crystallite size of the film is reported to be increased with doping.

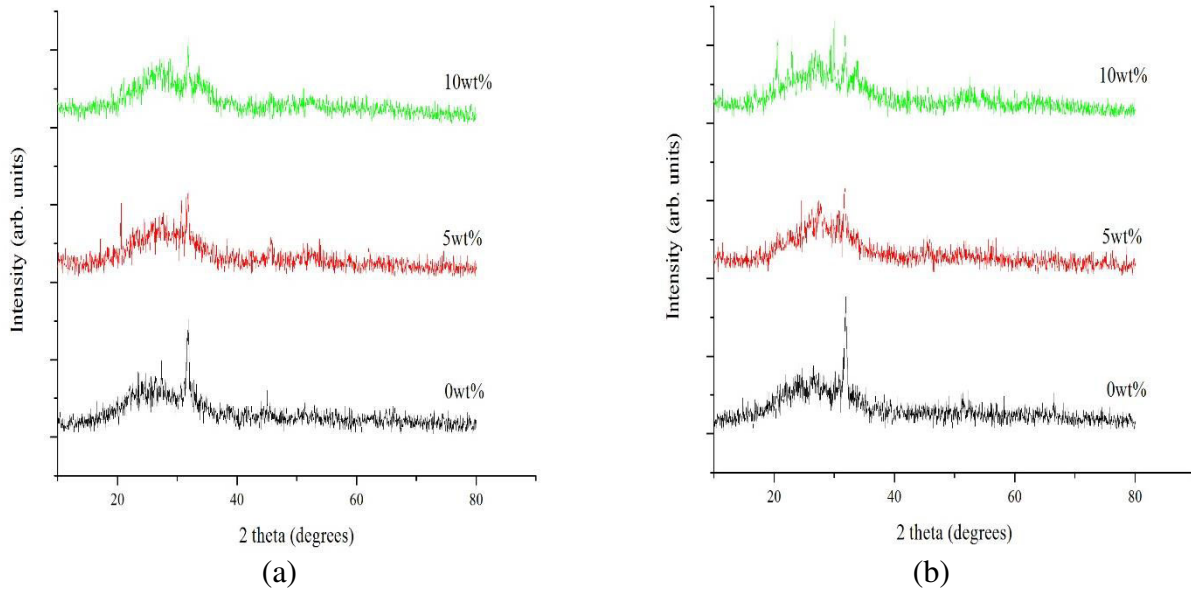


Figure 1. XRD pattern of (a) as-deposited (b) annealed thin films

Table 1: The average grain size of the Cu-doped SnS thin films predicted using Scherrer's formula

Cu doping (wt%)	Grain size, D (nm)	
	As deposit film	Annealed film
0	29	30
5	24	29
10	22	28

Optical properties

To study the optical properties, optical transmission spectra is measured in the wavelength range from 400–1800 nm and is displayed in Figure 2 in terms of % optical transmission for the as-deposited as well as annealed SnS films. From the figure, it can be noted that there is very low transmittance for the wavelength from 400 – 800 nm, highlighting the high absorbance of light in the thin films from visible spectrum to near infrared region. Similarly, we observed the improved interference pattern for the annealed thin films in the low absorption part, confirming the evenness and smoothness of the formed thin films alongside indicating smoothness at interfaces as well between air and thin film as well as thin film and glass [11, 12].

To determine the band gap energy of the as-deposited and annealed thin films, Tauc relation was used [13];

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where, α is used for the absorption coefficient, h is representing Plank's constant, ν is used for the incident light frequency, A is a constant, and n is used 1/2 for direct band gap and 2 for indirect transitions. The band gap energy values of the as-deposited and annealed thin SnS films, were determined from the plots drawn between $(\alpha h\nu)^2$ and $h\nu$. The straight portion of the vertical section of corresponding plots are extrapolated to the energy axis (x-axis). The x-axis intercept provides band gap energy for the relevant sample of the film. The calculated band gap energy values demonstrate the direct band gap nature of the SnS thin films. As a illustration, it can be seen in Figure 4 which is the representative graph of $(\alpha h\nu)^2$ vs $h\nu$ for annealed undoped SnS film for clarity on the estimated band gap energy. Where the obtained data for band gap energy values with different doping concentration is summarized in Table 2.

It can be seen from the Table 2, that the band gap value for the as-deposited and doped films decreased as the doping wt% is increased. This band gap decrease might be attributed to increasing in carrier concentration due to copper impurities [14], since the increase in doping concentration caused the increase in conductivity due to a higher concentration of carrier available for conduction [15].

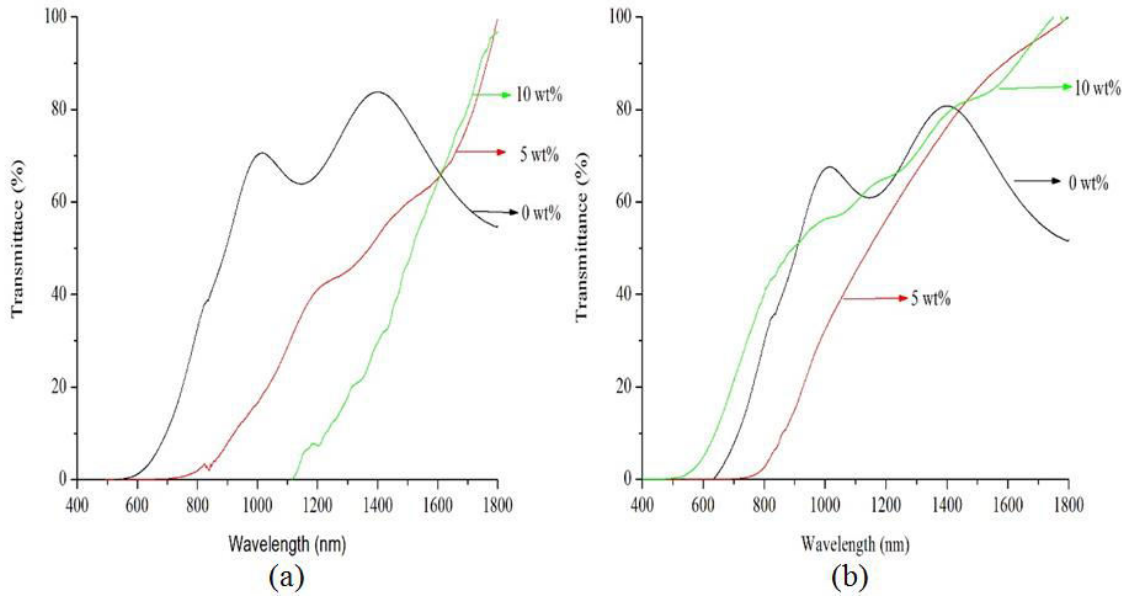


Figure 3: Transmission spectra of (a) as-deposited film (b) annealed film

However, our obtained results for the optical band gap are not in line with the Yue et al [8]. The decrease in the band gap energy after annealing may be caused by the lowering of inter-atomic spacing (amorphous $\rightarrow$ crystalline) and increasing grain size [16]. This study shows that on annealing, the films have larger grains. The large grain size gives the annealed samples a lower band-gap.

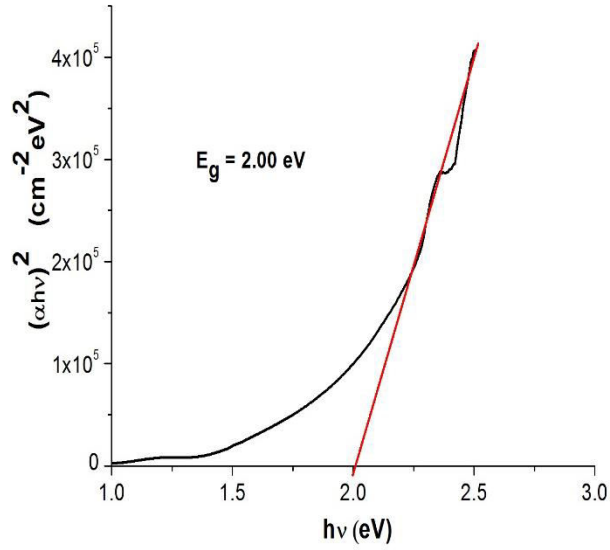


Figure 4: $(\alpha hv)^2$ vs $h\nu$ plot of annealed undoped SnS film

Table 2: Band gap energy, E_g of as-deposited and annealed film

Cu doping (wt%)	Band gap, E_g (eV)	
	As-deposited film	Annealed film
0	1.76	2.00
5	1.62	1.37
10	1.41	1.47

CONCLUSION

In this study, using thermal evaporation technique, copper doped tin sulfide thin films were prepared for the exploration of Cu-doping effect. Moreover, the influence of the annealing was examined on the physical properties of the pure and Cu-doped SnS films. From the XRD-analysis of the as-deposited as well as the annealed SnS (doped and undoped) thin films, it was found that the nature of the prepared thin films was polycrystalline in the (111) preferred orientation alongside showing in the enhancement of crystallinity upon annealing. The structural and optical properties was also varied with the Cu wt% doping. This study also showed that the optical properties of the Cu-doped SnS thin films are influenced by annealing treatments. From the results of this study, therefore, it is concluded that Cu-doped SnS thin films are promising material for the photovoltaic applications particularly as an absorber layer for the thin-film solar cells.

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