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Research paperv

Influence of annealing temperature on structural and optical properties of SnS:Ag thin film for solar cell application

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Abstract

Thermal evaporation method have been used to prepared thin films from tin sulfide (SnS) doping with 20 nm particle size of silver (Ag) at room temperature, under pressure up to 1×10^{-7} mbar with rate of statement 0.5 nm. sec^{-1}. The SnS:Ag thin films deposited on glass substrate at different annealing temperature (as-deposited, 423, 473, 573 and 623 K) for 2 hours. The effect of annealing treatment on the structural and optical properties has been studied. From X- ray diffraction (XRD) examination, predominant peak (111) appears at annealing temperature 623 K, also the others as (101) and (002). Scherer's formula used to calculate the crystallite size that ranged from 3-7 nm. Using UV-Vis spectrophotometer to recording the transmittance spectra and then calculate the optical properties in the wavelength range 300-900 nm. The absorbance decreased with the increasing of annealing temperature, while the transmittance increased. The optical constants such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant, and absorption coefficient decreased with the increasing of annealing temperature. The energy band gap increased from 2.1 eV for the as-deposited film to 3.3 eV for the film annealed at 623 K.

Keywords: *SnS:Ag film, annealing temperature, optical properties, thermal evaporation, solar cell application*

1. Introduction

Tin sulfide (SnS) is a semiconductor, and very important, useful for technological application such as optoelectronic devices, photovoltaic and solar cells because of their attractive physical properties which can be controlled by varying the chemical alignment [1]. SnS is a p-type semiconductor whose electrical properties can be tailor-made by doping and physical variation [2]. SnS having direct optical band gap (E_g = 1.3 eV) and it is a IV-VI compound semiconductor material [3].

SnS is a very necessary because of its extraordinary absorption coefficient (10^5) [4], apposite band gap for solar cells, and richness in nature [5], therefore it's have been used as absorber layers in thin film solar cells to transform solar emission to electricity[4]. There are many methods to prepare thin films from tin sulfide such as electro deposition [6], spray pyrolysis[7], pulsed laser deposition (PLD) [8], sputtering [9], vacuum evaporation [10], photo electrochemical (PEC) [11], and chemical bath deposition (CBD) [12]. SnS in an orthorhombic double-layered construction with lattice factors of a = 0.385, b = 1.142 and c = 0.438 nm. SnS is much less toxic, cost effective and is stable in slight acidic media associated to additional semiconductor compounds [13]. In this work, thermal evaporation method used to prepare thin films from SnS doped with Ag nanoparticle and study the effect of annealing temperature on structural and optical properties.

2. Experimental details

Using a thermal evaporation technique (Edward C-306), thin films have been prepared from tin sulfide (SnS) that doped with 0.006 wt.% of silver (20 nm particle size and purity of 99.9%), at room temperature (RT) under pressure up to 1×10^{-7} mbar and rate of deposition 0.5 nm. sec^{-1}. The SnS:Ag thin films deposited on glass substrate and annealed at different temperatures (as-deposited, 423, 473, 573 and 623 K) for 2 hours. the films thicknesses were kept constant at thickness of 125 nm that measured using Lambda Limf-10. The structure was examined using X-ray diffraction (SHIMADZU X-ray diffracts meter system (XRD-6000) system) with a Source CuK_α and radiation of wavelength λ = 1.5406 Å. UV-Visible spectrophotometer ((Shimadzu UV- 1650 PC) made by Phillips, (Japanese company)) in the range of wavelength 300-900 nm.

3. Results and Discussion

3.1 X-ray diffraction analysis

Using X-ray diffraction (XRD) to characterize the structure of SnS:Ag films that prepared with thickness of 125 nm, which records the intensity as a function of Bragg's angle were; Source CuK_α with emission of wavelength λ = 1.5406 Å, Objective: Cu, Current = 30 mA, Voltage = 40 kV, Scanning speed = 0.25 deg/min and the X-ray scans are implemented between 2θ values of 15º and 55º. Figure (1) shows the X-ray diffraction (XRD) spectra for as-deposited and annealed SnS:Ag thin films at different temperatures. From the figure, it seems the prepared films are amorphous until to 573K , and then the peaks are appear at annealing temperature 623 K. From XRD spectra of the film annealed at 623 K, a predominant peak (111) was appear at 2Ө = 31.71º, and further medium intensity peaks at 2Ө = 30.60º, 45.72º relate to the (101), (002). The diffraction peaks are recognized to SnS taken from the Joint Committee of Powder Diffraction Standard (JCPDS: 39-0354) [14]. This indicates that the particles are SnS with a strong (111) reflection plane. The favored location of the particle is due to the circumstance that the growing method is controlled by nucleation. The results are in agreement with the finding of other researches [15,16,17]. The crystallite size were calculated from Scherer's formula [18]:

$D = 0.9\lambda / \beta \cos\theta$ (1)

where λ is the X-ray wavelength (Å) , β is the full width at half maximum intensity (FWHM) (radian), θ is Bragg's diffraction angle of the XRD peak (degree).

The crystallite size of peaks (101), (111) and (002) was 3.5, 3.0 and 7.0 nm respectively. The values of crystallite size refer to the quantization confinement effect. Our results are in good agreement with that reported by A. Bushra et. al [17].

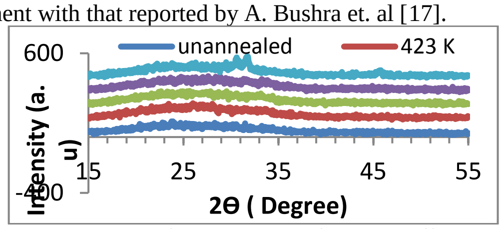

Fig.(1): XRD patterns of SnS:Ag thin films at different annealing temperature**.**

3.2 Optical measurements

Using spectrophotometer (Shimadzu UV- 1650 PC) made by Phillips, (Japanese company) to record the transmittance spectra of SnS:Ag thin films in the wavelength range 300-900 nm and various annealing temperature as shown in Figure (2). The transmittance of the films increased with the increase of annealing temperature. The film annealed at 623K showed a maximum transmittance of ~95% at a wavelength of 640-900 nm. The increased optical transmittance is associated to the improved in crystallinity when increase in the temperature as seen in XRD pattern of the films, which is in accordance with the findings of researcher [13,20].

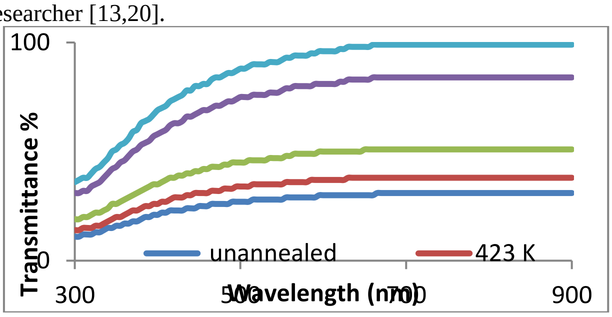

Fig.(2): The transmittance as a function of wavelength for SnS:Ag thin films at different annealing temperature.

The absorption is the percentage between absorbed light intensity (I_A) by material and the incident intensity of light (I_o) [20]:

$$A = \frac{I_A}{I_o} \quad (2)$$

Figure (3) shows the absorbance of SnS:Ag thin films that decreased with the increasing of annealing temperature. The result is in accordance with the findings of researcher [20].

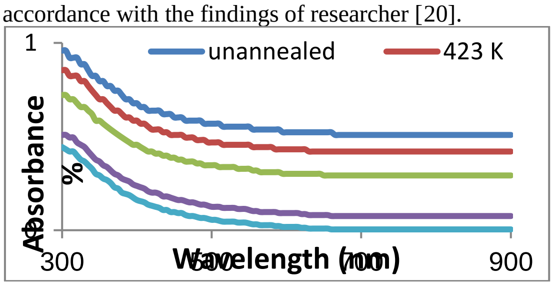

Fig.(3): The absorbance as a function of wavelength for SnS:Ag thin films at different annealing temperature.

By using the following equation to find the absorption coefficient (α) of SnS:Ag [21]:

$$\alpha = 2.303A/d \quad (3)$$

where (d) is the film thickness and (A) is the absorbance of film. Figure (4) shows the variation of α with the wavelength. The absorption coefficient are decreased with the increasing of wavelength and annealing temperature. The values of absorption coefficient are greater than (10^4 cm^{-1}), which refer to the direct transitions.

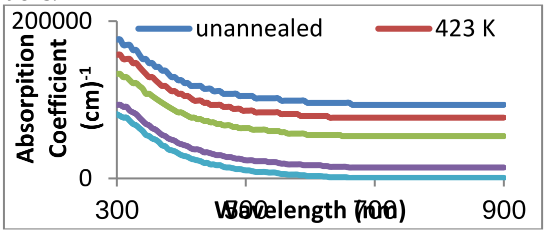

Fig.(4): The absorption coefficient spectra as a function of wavelength of SnS:Ag thin films at different annealing temperature.

The energy band gap (E_g) can determine using the following relation which is define as the interrupt of the plot of $(\alpha h\nu)^r$ as a function of the photon energy ($h\nu$) [22]:

$$(\alpha h\nu)^r = B(h\nu - E_g) \quad (4)$$

where B is a constant and r = 2 or 1/2 for a direct allowed transition and indirect allowed transition respectively, however, it is can be determined by extrapolating the linear portion.

A graph between $(\alpha h\upsilon)^2$ and $h\upsilon$ is schemed, and the straight line of the graph is extrapolated to energy axis to give direct energy band gap (E_g). Figure (5) shows that the optical band gap increased with increasing of annealing temperature from 2 eV for as-deposited film to 3.22 eV for the film annealed at 623 K. This performance because with the increasing of the annealing temperature, Ag atoms are relaxed to be spread, and the Ag-doped can drop the band gap [25]. The values of energy gap refer to the quantization confinement effect. The energy band gap of the films is tabulated in Table (1).

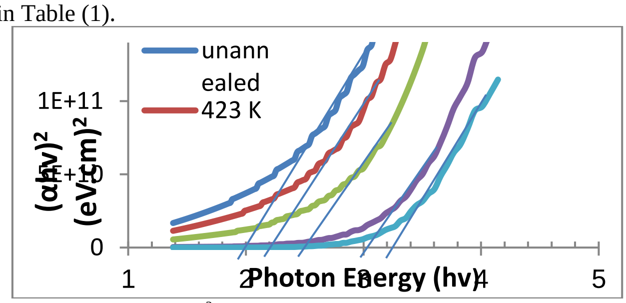

Fig.(5): A plots of $(\alpha h\nu)^2$ verses photon energy ($h\nu$) of SnS:Ag thin films at different annealing temperature.

Table (1) The optical energy gap of as deposited and SnS:Ag annealed films.

Annealing temperature (K)	E_g (eV)
As deposited	2.0
٤٢٣	2.2
٤٧٣	2.5
٥٧٣	3. 0
٦٢٣	3.22

Using the following relation to calculate the extinction coefficient of SnS:Ag thin film [24]:

$$k = \alpha\lambda/4\pi \quad (5)$$

where α is the absorption coefficient and λ is the wavelength. Figure (6) shows the variation of the extinction coefficient versus wavelength of the SnS:Ag thin films at different annealing temperatures. As a whole, with the increasing of annealing temperature, the extinction coefficient decreased. This performance is in agreement with the results of a researcher M. Devika [13].

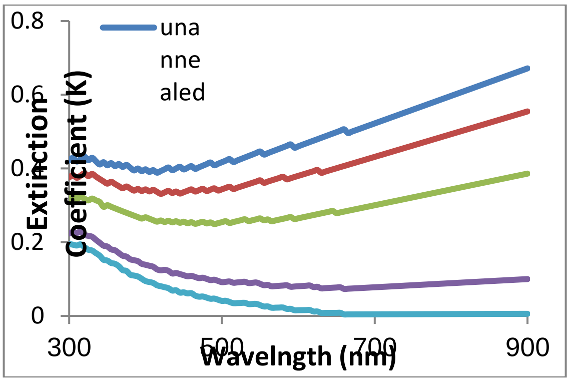

Fig.(٦): Variation of extinction coefficient with wavelength of SnS:Ag thin films at different annealing temperature.

From the following relation it can calculate the refractive index (n) of SnS:Ag thin film [20]:

$$n=\left(\frac{4R}{(R-1)^2}-k^2\right)^{1/2}+\frac{(R+1)}{(R-1)} \qquad (6)$$

where R is the reflectance. The variations of the refractive index versus wavelength for SnS:Ag thin films with different annealing temperature are presented in Figure (7). From the figure it can show that the refractive index (n) of SnS:Ag thin films increases with the increasing of annealing temperature until 473 K, while at 573 and 623 K annealing temperature, the refractive index decreased. which is in accordance with the findings of researcher M. Devika [13].

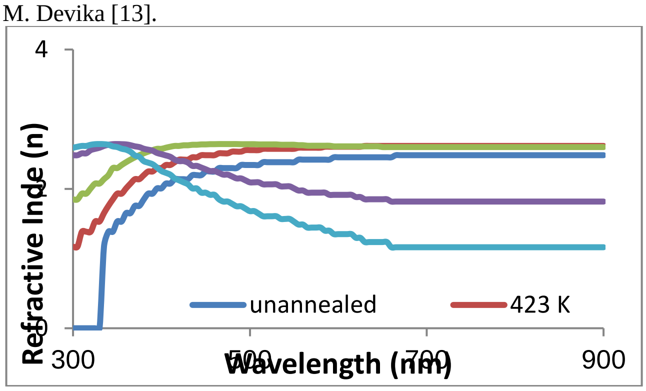

Fig.(7): Variation of refractive index with wavelength of SnS:Ag thin films at different annealing temperature.

The real (ε_1) and imaginary (ε_2) parts of dielectric constant can calculate by using the following relations [25]:

$$\varepsilon_1 = n^2 - k^2 \qquad (7)$$

$$\varepsilon_2 = 2nk \qquad (8)$$

The relationship between ε_1, ε_2 and wavelength are presented in Figures (8 and 9). From the figures (8,9) it is found that ε_1 increased with the increasing of annealing temperature at 473 K but with the increasing annealing temperature to 623 K the real dielectric constant decrease, while the imaginary dielectric constant deceased with the increasing of annealing temperature. The performance of ε_1 is like to that refractive index because of the smaller value of k^2 compared with n^2, while ε_2 is mainly depended on the k values according to the formulas (7, 8). This performance is in agreement with the results of a researcher M. Devika [13].

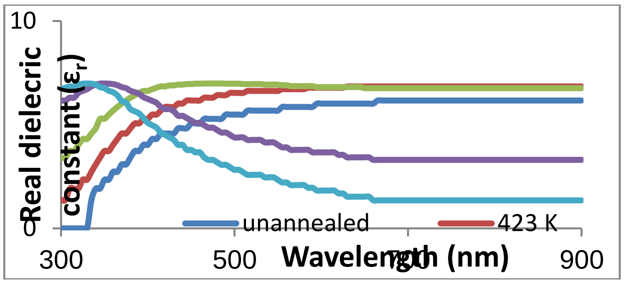

Fig.(8): Variation of ε_r with wavelength of SnS:Ag thin films at different annealing temperature.

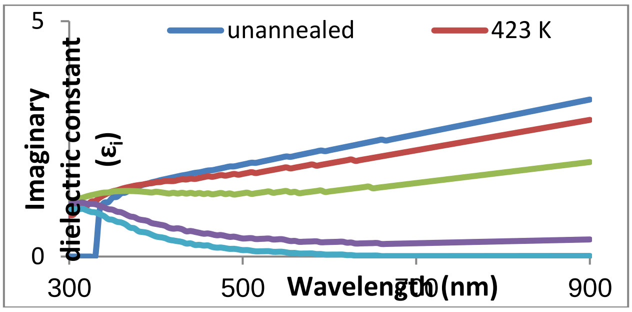

Fig.(٩) Variation of ε_i with wavelength of SnS:Ag thin films at different annealing temperature.

4.Conclusions

Thermal evaporation method have been used to prepared SnS:Ag thin films deposited on glass substrate, and then annealed at different annealing temperature (as-dposited,423, 473,573 and 623 K). The XRD pattern show that the prepared films are amorphous, and with increasing of annealing temperature, the polycrystalline structure is growth with predominant peak along (111) direction. The crystallite size are calculated from the resultant data of XRD to ranged from 3-7 nm, that refer to the quantum confinement. The optical properties of SnS:Ag thin films were investigated from the transmittance pattern. The transmittance increased with the increasing of annealing temperature, while the absorbance decreased. The energy band gap increased from 2.0 eV for as-deposited to 3.22 eV for the film annealed at 623 K, the values of energy gap refer to the quantum confinement. The optical constants such as absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant decreased with the increasing of annealing temperature. indications to increase care to the use of such materials in the design and fabrication of a solar cell.

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