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INFLUENCE OF HEAT TREATMENT ON SOME PHYSICAL PROPERTIES OF $Zn_{0.9}Sn_{0.1}S$ THIN FILMS

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Tri-compound $Zn_{0.9}Sn_{0.1}S$ thin films were prepared from the binary compound of them with high purity. Thin $Zn_{0.9}Sn_{0.1}S$ films of thickness 300±5 nm was grown onto heat glass substrate at 413K under high vacuum and rate deposition of 1.6 nm/sec using thermal evaporation method. The effect of heat treatment at various temperatures (T_a=373,423,473, and 523 K) on the structural, morphological and optical properties of prepared films were investigated. X-ray diffraction data showed that all prepared thin films (as deposited and annealed) are polycrystalline and hexagonal structure with (002) orientation, also a small peak of orthorhombic structure of SnS compound was appeared. The surface of $Zn_{0.9}Sn_{0.1}S$ thin film was examined by atomic force microscope which confirmed that prepared thin films are polycrystalline in nature. The study of optical properties revealed an increase of direct optical energy gap after heat treatment. Also it was found that the optical constants were affected by annealing temperature.

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AFM measurement, optical properties.

1. Introduction

The characterization of zinc sulphide (ZnS) and tin sulphide (SnS) which prepared by different techniques have attracted considerable attention due to their potential applications[1].Zinc sulphide is one of the II-VI groups with a wide and direct bang gap near UV region, and ithas a high refractive index (2.27) at 1μm with high transmittance in the visible range[2,3]. ZnS has n-type conductivity, and it can crystallize in two forms: a hexagonal form with wurtzite structure (E_g=3.79-3.93 eV) and a cubic form with sphalerite structure (E_g=3.6 eV), also, ZnS becomes very appealing because it has low toxicities in comparison with the other semiconductors[2,4].

In recent years the polycrystalline and nano zinc sulphide thin films have much attention because it can be used as window in heterojunction photovoltaic diodes [5-7], due to decrease in the optical energy band gap, the window absorption losses and amends the short-circuit current of the solar cell, also it used as a light emitting diode[8],dielectric filter, and a reflector [9]. On the other hand, tin sulfide is an IV-VI binary semiconductor compound [10], which showing different phases, such as: SnS, SnS_2, Sn_3S_4, andSn_2S_3[11].

The constituent elements of tin sulfide are Sn and S which abundant and are less toxic in nature compared with GaAs, CdTe and InP, and it is stable in slight acidic media [12].

The optical properties of tin mono sulfide(SnS) depend on the prepared technique, but most studies found that the value of direct optical energy gap varies from (1.2-1.5 eV),and the

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value of indirect optical energy gap varies from (1.0-1.2 eV) [13], high absorption coefficient with p-type conductivity, and its orthorhombic crystalline structure [10,14], so tin sulfide has been used as absorber layer for photovoltaic application. Also it's used for near-infrared detector [15] and photovoltaic materials with high conversion efficiency [16].

This paper studies the influence of annealing temperature on the structural, morphological, and optical properties of $Zn_{0.9}Sn_{0.1}S$ films were grown on to glass slides using vacuum evaporation technique.

2. Experimental procedure

The tri-compound $Zn_{0.9}Sn_{0.1}S$ were prepared by adding 10% ratio SnS to the 90% ZnS compound. The $Zn_{0.9}Sn_{0.1}S$ thin films with thickness of 300 nm were fabricated by thermal evaporation method under (10^{-5}mbar) on to corning glass substrate at kept temperature (T_s=413K) with 1.6 nm/sec deposition rate. The prepared films were treated in air at different temperatures (T_a= RT, 373, 423, 473, and 523 K) for 60 min.

The structural of as deposited (RT) and annealed$Zn_{0.9}Sn_{0.1}S$ samples were obtained using X-ray diffractometer (XRD) using Cu K_α radiation (λ=1.541Å).

The absorptance and transmittance spectra of studied samples were obtained by (UV-160A) UV-visible recording spectrophotometer supplied by a Japanese company of type Shimadzu was in the range (400-1100 nm).

The Lambert relation was used to determine absorption coefficient (α)[13]:

$$\alpha=2.303\frac{A}{d} \tag{1}$$

where A is the absorption and d is the films thickness .

The incident photon energy (hυ) and α is related by the following relation[14]:

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

where β is proportional inversely with amorphousity and E_g is the optical band gap

Generally an optical constants (refractive index (n), extinction coefficient (k), and real and imaginary parts of dielectric constant (ε_r , ε_ι) are depend on the optical behavior of material.

The magnitude of n can be determined by using relation [15]:

$$n=\frac{1+R}{1-R}+[\frac{4R}{(1-R)^2}-k^2]^{1/2} \tag{3}$$

where R is the reflectance. The extinction coefficient can be determined from the equation [16]:

$$k=\frac{\alpha\lambda}{4\pi} \tag{4}$$

The two parts of dielectric constants were calculated from the relation[17]:

$$\varepsilon_r = n^2-k^2 \tag{5}$$

$$\varepsilon_i = 2nk \tag{6}$$

3. Results and discussion

Fig. (1) shows X-ray diffraction spectra for as deposited (RT) and annealed $Zn_{0.9}Sn_{0.1}S$ films at various annealing temperatures (373,423,473, and 523) K.

It is observed that all coated films are polycrystalline in nature and exhibited pointed peak at diffraction angle (2θ)equivalent to 28.66° which correspond to reflection from (002) plane of hexagonal structure. This proto type means that the (002) reflection is the mainly concentrated in the hexagonal phase, which means that the c-axis of the $Zn_{0.9}Sn_{0.1}S$ is vertical on the films plane.

Small peaks appeared in all patterns which corresponding to hexagonal and orthorhombic phase for ZnS and SnS compound respectively, as shown in Fig. (1) and Table (1).

There is a small shift to higher angle (22.66, 28.68, 28.66, 28.7, and 28.72°) for preferential plane (002) with increasing the annealing temperature from room temperature to 373, 423, 473, and 523 K, respectively. This is meaned that the high annealing temperature tend to increase the reaction between the ZnS and SnS to form the ternary compound $Zn_{0.9}Sn_{0.1}S$, where the ternary phase contain three basic peaks ,the first peak lies at 2θ equal to 29° which correspond to reflection from (111) plane for $Zn_{0.8}Sn_{0.2}S$ which found by Pawar et al[18].

It is obvious from figure (1) that the increase in annealing temperature leads to improve in the crystalline structure of studied thin films by noticing that dominate peak (002) become highest and more intense for the first two annealing temperatures and after that decreases as annealing temperature increasing . All these result are shown in Table (1).

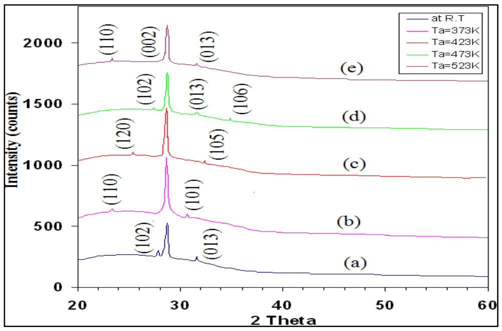


Fig. (1) X-ray diffraction spectra of $Zn_{0.9}Sn_{0.1}S$ thin films:
a- as deposited b- annealed at 373 K c- annealed at 423 K d- annealed at 473 K e- annealed at 523 K.

As deposited and heat treatment$Zn_{0.9}Sn_{0.1}S$ films at 523K were morphologically characterized using atomic force microscope (AFM) method.

The scan image of these thin films is shown in Fig. (2), which indicates that all thin films have high compactness, and the small grain size have uniform distribution. These facts confirm the result which obtained of XRD analysis, which refers the crystalline nature of these thin films.

Table 1. The structure parameters of $Zn_{0.9}Sn_{0.1}S$ thin films

T_a (K)	$2\theta_{Exp.}$	$2\theta_{Stan.}$	$d_{Exp.}$	$d_{Stan.}$	I/I_o	hkl
RT	27.84	27.85 (hex. ZnS)	3.20	3.20	10	102
	28.66	28.58 (hex. ZnS)	3.11	3.12	100	002
	31.60	31.58 (orth. SnS)	2.82	2.83	8	013
373	23.20	23.02 (orth. SnS)	3.83	3.86	7	110
	28.68	28.58 (hex. ZnS)	3.11	3.12	100	002
	30.74	30.52 (hex. ZnS)	2.90	2.92	7	101
423	25.40	25.97 (orth. SnS)	3.50	3.43	7	120
	28.66	28.58 (hex. ZnS)	3.11	3.12	100	002
	32.44	32.41 (hex. ZnS)	2.75	2.76	6	105
473	27.44	27.33 (hex. ZnS)	3.24	3.26	10	102
	28.70	28.58 (hex. ZnS)	3.10	3.12	100	002
	31.58	31.58 (orth. SnS)	2.83	2.83	6	013
	34.86	34.33 (hex. ZnS)	2.57	2.61	7	106
523	23.24	23.02 (orth. SnS)	3.82	3.86	8	110
	28.72	28.58 (hex. ZnS)	3.10	3.12	100	002
	31.58	31.58 (orth. SnS)	2.83	2.83	7	013

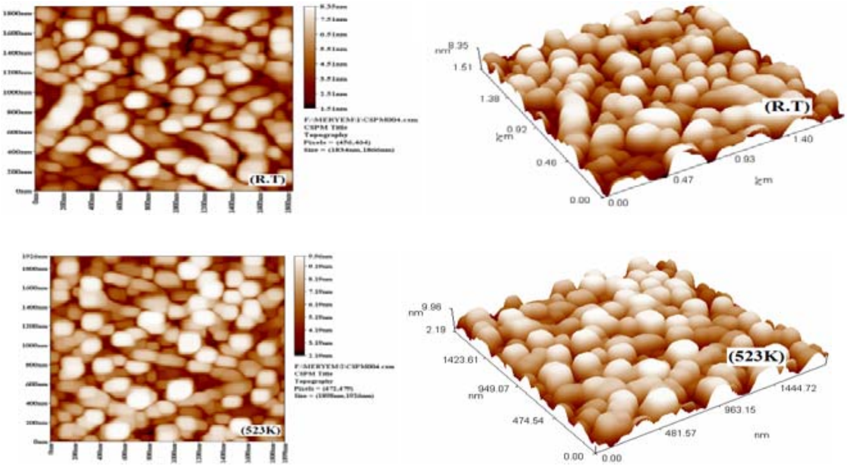


Fig.2 The two and three – dimensional representation of as deposited$Zn_{0.9}Sn_{0.1}S$ thin films and annealing films at (523K)

Table (2) summarized the value of grain size, surface roughness, and the values of root mean square (rms) were increased with the increasing of annealing temperature.

Table2.Grain size, surface roughness, and rms roughness of $Zn_{0.9}Sn_{0.1}S$ thin films: as deposited and annealed at 523K

T_a (K)	Grain size (nm)	Surface roughness (nm)	rms roughness(nm)
RT	88.27	1.52	1.77
523	100.06	1.58	1.86

Fig. (3) displays the variation of transmittance spectra for un-annealed and heat treatment $Zn_{0.9}Sn_{0.1}S$ films at various annealing temperatures (373, 423, 473, and523 K) as a function of wavelength (λ). From this figure it can observe that the fundamental absorption edges of the thin films shifts to wards shorter wavelength when the annealing temperature increases. Another noticeable remark from this graph is that the film deposited at room temperature has a lower transmittance as compared with heat treatment thin films at various temperatures. The value of optical band gap increases with increasing of annealing temperature. This behavior may be attributed to the reduction of density of the level existence close to the bands which can provide rising to band tailing, a sit was studied for other polycrystalline compounds.

The broading in the optical energy band gap may be attributed to increase in the grain size which performs to decrease the flaw stats[19].Therefore the films treated at different temperature are the best for window applications.

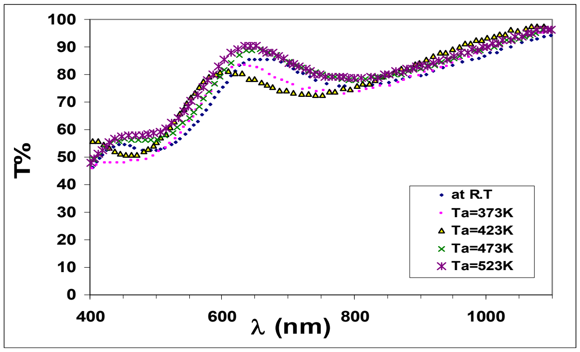


Fig.3. Transmittance vs. wavelength for as deposited and annealed $Zn_{0.9}Sn_{0.1}S$ thin films at different annealing temperatures.

By using equation (1), the absorption coefficient can determine from the region of high absorption at fundamental absorption edge of film. The relation between α and λ can observed in figure (4) .It is clear from this shape the absorption coefficient has a high value ($\alpha \geq 10^4 cm^{-1}$) which means the material has a direct band gap.

From Table (3), the value of α in general decreases from 1.71×10^4 to 1.18×10^4 cm^{-1} with increasing annealing temperature from RT to 523K at λ equal to 550 nm. This is attributed to an increase in transmittance (decrease in absorpttance) with increasing temperature as mentioned previously.

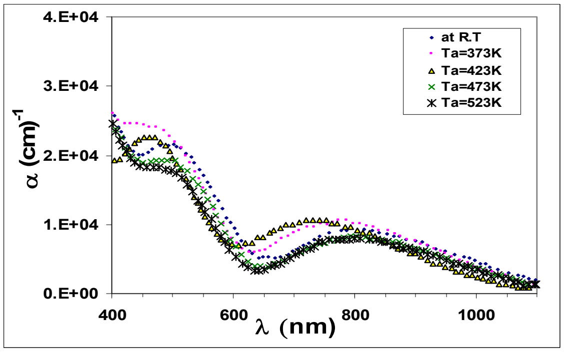
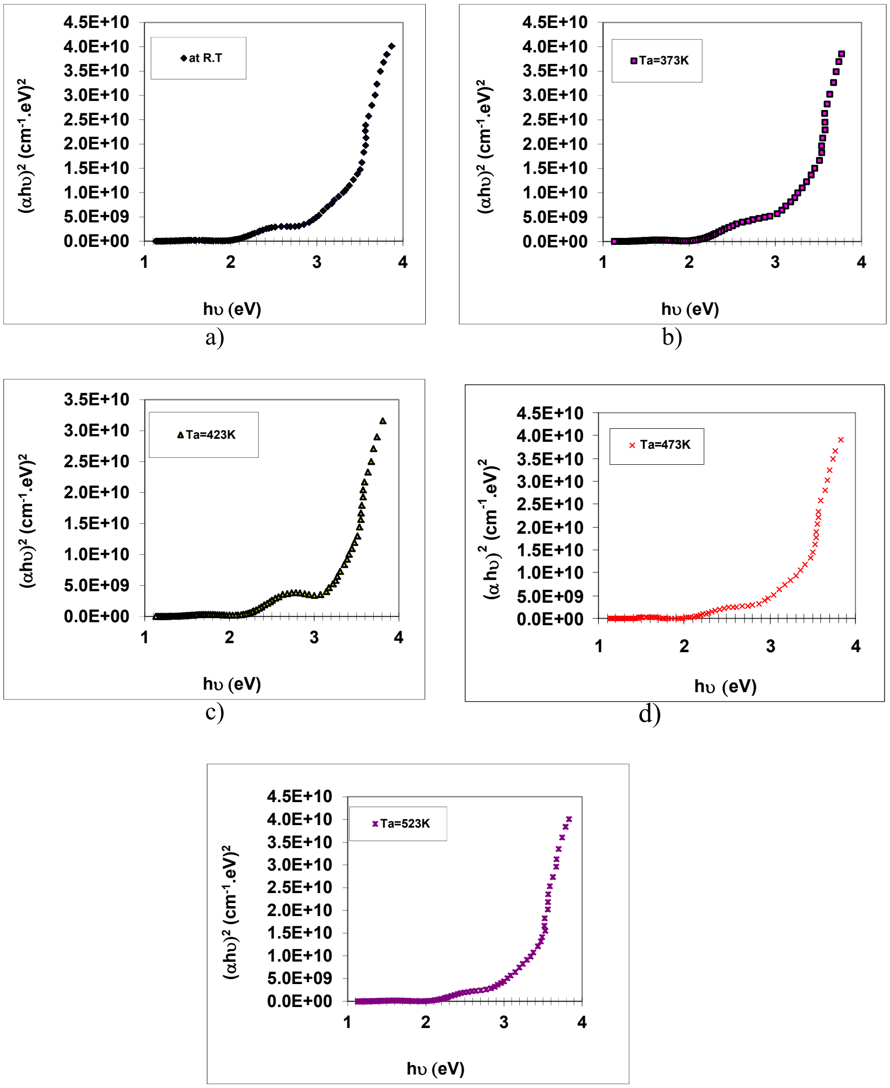


Fig. 4. Absorption coefficient vs. wavelength for as deposited and annealed$Zn_{0.9}Sn_{0.1}S$ thin films at different annealing temperatures.

Fig.5(a, b, c, d, and e)displays the relation between $(\alpha h\nu)^2$ and photon energy (hν) for direct transitions of all prepared$Zn_{0.9}Sn_{0.1}S$ thin films.

The direct band gap (E_g) values are determined by using equation (2) and given in Table (3). The optical energy gap was found to increase from 3.20 eV to 3.35 eV with the increases of the annealing temperature from R.T to 523 K. This is related to eliminate the defect and decreasing the defect state in energy gap.



a)

b)

c)

d)

e)

Fig. (5) $(\alpha h\upsilon)^2$ with $(h\upsilon)$ for $Zn_{0.9}Sn_{0.1}S$ films at different annealing temperature.
a) RT (b) 373 K (c) 423 K (d) 473 K (e) 523 K

Fig. (6) shows the relation between refractive index (n) as function of λ for all samples at different annealing temperatures. From this graph and table (3) we noticed that the value of n in general decrease from (2.46-2.22) when temperature increases from (R.T-523) K at λ equal to 550 nm. This behavior associated with decrease in reflection which refractive index depends on it.

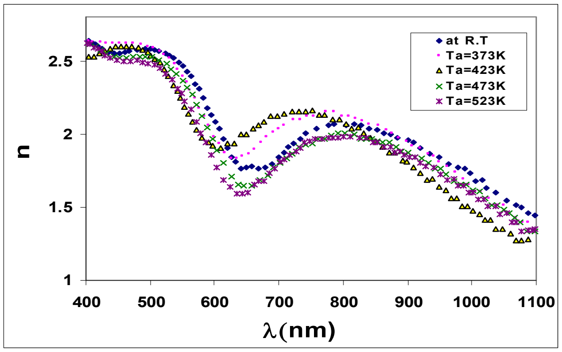


Fig. (6) The refractive index vs. the wavelength for as deposited and annealed $Zn_{0.9}Sn_{0.1}S$ thin films at different annealing temperatures

Fig. (7) represents the relation between extinction coefficient (k) as function of λ for as deposited and annealed thin films at different temperatures. One can conclude that the behavior of k is similar to behavior of α, because k is directly related to the absorption of light. The value of k in general decreases from to 0.07-0.05 when temperature increases from RT to 523K as shown in Table (3).

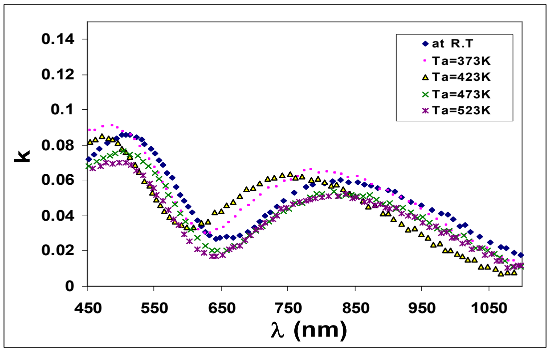
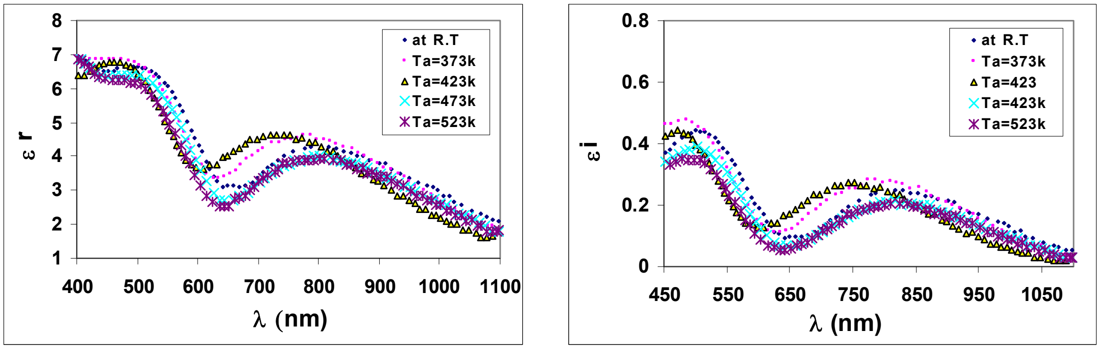


Fig. (7) The extinction coefficient vs. the wavelength for as deposited and annealed $Zn_{0.9}Sn_{0.1}S$ thin films at different annealing temperatures

Fig.8(a, and b) shows the variation of real (ε_r) and imaginary (ε_i) part of dielectric constants, which have the same behavior of n and k respectively. The values of ε_r and ε_I in general decrease from 6.05 to 4.93 and from 0.36 to 0.23 respectively when annealing temperatures increase.



a) *b)*

Fig. (8) a-ε_r b-ε_i vs. wavelength for as deposited and annealed $Zn_{0.9}Sn_{0.1}S$ thin films at different annealing temperatures.

Table(3) The optical constants of $Zn_{0.9}Sn_{0.1}S$ films at different annealing temperatures at λ=550 nm.

T_a (K)	E_g (eV)	α(cm^{-1}) *10^4	n	k	ε_r	ε_i
RT	3.20	1.71	2.46	0.07	6.05	0.36
373	3.24	1.53	2.39	0.06	5.72	0.32
423	3.30	1.11	2.18	0.05	4.77	0.21
473	3.32	1.47	2.36	0.06	5.60	0.30
523	3.35	1.18	2.22	0.05	4.93	0.23

4. Conclusions

The $Zn_{0.9}Sn_{0.1}S$ thin films have been prepared successfully onto heat glass substrate at 413K by vacuum evaporation method. All the prepared thin films are polycrystalline in nature which had a hexagonal structure with orientation in the [002] direction and a small peak of orthorhombic structure of SnS compound were appeared. Also AFM measurement confirm the fact that all thin films are polycrystalline, and from these measurement one can noticed that the grain size, surface roughness, and the root mean square values were increased with the increasing of heat treatment. The optical properties revealed that the absorption edge of thin films shift towards short wavelength after heat treatment. Therefore the films treated at various temperatures are the best for window layer in solar cell applications.

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