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RESEARCH ARTICLE

Effect of Tin concentration on Structural Morphological and optical properties of $Cd_{1-x}Sn_xS$ thin films

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Abstract

$Cd_{1-x}Sn_xS(0\leq x \leq 1)$ thin films have been prepared on glass substrates at 300°C substrate temperature by the chemical spray pyrolysis(CSP) method using an aqueous solution with varying tin concentrations. The hickness of the films have been measured to be (400±5)nm. The films have been characterized to evaluate the structure ,morphology, transmittance and optical energy band gab. X-ray diffraction(XRD) studies show that the films are polycrystalline with hexagonal and orthorhombic structures. The grain size of the films was found decreased with increasing tin concentration values. The optical band gab energies and types of optical transition and absorption of the films have been determined from the optical transmittance spectra. The optical absorption studies in the wavelength range 200-1100 nm show that band gap energy values of the films decrease from (2.41 to1.9)eV as the Sn concentration increases.

INTRODUCTION:

There has been considerable interest in the field of transparent semiconducting materials such as CdS, SnS .etc. for use in a variety of applications ,including architectural windows ,solar cells ,heat reflectors ,light transparent electrodes ,thin-films photovoltaic devices and many other optoelectronic devices[1] .CdS and SnS are both promising materials for solar cells. CdS, which belongs to II-VI compound semiconductors[2,3],It is an n-type semiconductor with a direct band gap of(2.4Ev), CdS is used as a window materials for heterojunction thin films solar cells [4,5,6,7,8]. It has also application in light-emitting diodes(LED) ,gas detectors photovoltaic cells, nonlinear optics , and thin film transistors [7,9,10].SnS is one of the Tin chalcogenide layered semiconductors in group IV-VI ,SnS, SnSe are promising material for solar energy conversion [11, 12] .SnS films are highly suitable for many application in a number of solid state devices ,such as photovoltaic ,photo - electrochemical(PEC),photoconductive cells ,and intercalation battery systems[13,14] . In addition, SnS thin films have large optical absorption coefficient(> 10^4 cm^-

^{1})[13,14,15] It is p-type window layer heterojunction devices[16,17, 18].SnS materials have an optical energy gap for direct transitions of (1.6 eV) .Various methods employed for deposition CdS and SnS films are chemical bath deposition[19,20],chemical vapour deposition[1], electrochemical deposition[21-23] ,rf sputtering ,vacuum evaporation[1] and spray pyrolysis method[24,25].Amongst all the deposition methods ,spray pyrolysis(SP) method is a simple ,convenient and low-cost method for large area deposition of many binary, ternary and quaternary semiconducting films with varying anion and cation concentrations .It is noted that so far there are a few reports in the literature on the physical properties of $Cd_{1-x}Sn_xS$ semiconductor films . In the present work , $Cd_{1-x}Sn_xS$ thin films were deposited by chemical spray pyrolysis technique at different composition of (x) .The effect of tin concentration on the structural , morphological and optical properties of these films was studied and discussed

2 Experimental details.

$Cd_{1-x}Sn_xS$ semiconductor films were prepared on glass substrates at 300°c substrate temperature by the CSP method using aqueous solutions. The spray solution consisted of(by volume) 0.05M cadmium chloride($CdCl_2.H_2O$), thiourea (H_2NCSNH_2) and 0.05 tin chloride($SnCl_2.2H_2O$) solutions. The composition of $Cd_{1-x}Sn_xS$ films changed from pure CdS to pure SnS (x= 0 ,0.3 ,0.5 ,0.7 ,1). The glass substrates soaked in chromic acid , cleaned in isopropyl alcohol ,rinsed in distilled water at each step and dried in air. The chemical spray-head-to-substrate distance was fixed approximately at 30 cm .Nitrogen was used as the carrier gas during spraying . The glass substrates were heated by an electrical heater and control of substrate temperature was done by using thermocouple type chromel -alumel .
Films thickness was determined by a multiple beam interferometry (Fizeau fringes in reflection) . The films were characterized by X-ray diffraction technique using (Philips X-ray diffractometer) with CuK radiation with wavelength (1.5406)A$^{\circ}$. A(UV-160A UV-visible recording) spectrophotometer supplied by Japanese company (Shimadzu) was used to record the optical absorbance and transmittance spectra of $CdSn_XS_{1-X}$ thin films at wavelength range (480-1100) nm .Surface morphology of the films were studied by using (CSPM AA3000) Atomic Force Microscope (AFM) supply by Angstrom Company .

3.Results and discussions

3.1 Structural characterization

The structural properties of the $Cd_{1-x}Sn_xS$ films have been investigated by XRD patterns. The XRD patterns of the samples at different concentration of Sn are given in Fig .1. The spectra have been obtained by scanning angle 2Ө in the range from 20° to 60°.The existence of multiple diffraction peaks ,and sulphide phases in the diffraction patterns indicates the polycrystalline nature of the $Cd_{1-x}Sn_xS$ sample. It is seen that crystallinity of the CdS films is better than that of the other films .It should be noted that the XRD patterns exhibit clear dependence on Sn concentration. The CdS film has been crystallized in a hexagonal(JCPDS Card no:96-101-1055) with the preferential orientation of(002) as shown in Fig .1. The intensity of the peak corresponding to the CdS phase decreases as SnS concentration increases as shown in Fig .1. The SnS phase becomes dominant with lower Cd content .The SnS film has been crystallized in an orthorhombic structure (JCPDS Card no: 96-900-8296) with the preferential orientation of (021) as shown in Fig .1. The grain size (D_{hkl}) of $Cd_{1-x}Sn_xS$ thin films where x equal (0 , 0.3 , 0.5,0.7 & 1) deposited by chemical spray pyrolysis method on glass substrate at R.T with thickness (400) nm are evaluated for the preferred planes [hkl] using the scherrer 's formula[26]

$D_{hkl}=K\text{ג}/ß_{2\Theta}$ COS Θ …….(1)

With k=0.94 ,where Θ is the Bragg's angle ,ג is the wavelength of X-ray used , $ß_{2\Theta}$ is the width of the peak at the half of the maximum peak intensity

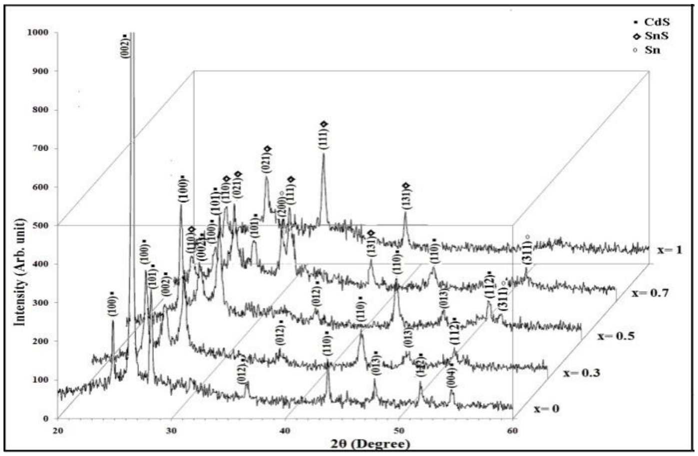
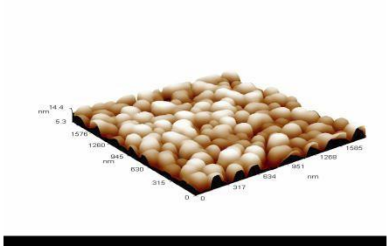
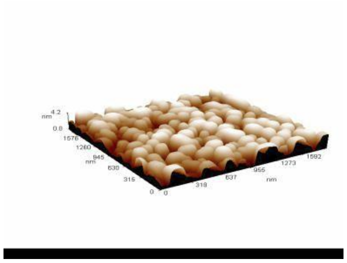


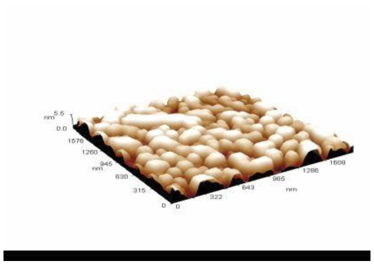
Fig.1. XRD patterns of the $Cd_{1-x}Sn_xS$ thin films: CdS ,$Cd_{0.7}Sn_{0.3}S$, $Cd_{0.5}Sn_{0.5}S$, $Cd_{0.3}Sn_{0.7}S$, SnS

Atomic force microscopic (AFM) allows us to get microscopic information on the surface structure and to plot topographies representing the surface relief. This technique offers digital images which allow quantitative measurements of surface features, such as root mean square roughness, Rq, or average roughness Ra, and the analysis of images from different perspectives, including three-dimensional simulation [27]. AFM images of the $Cd_{1-x}Sn_xS$ films are shown in Figs. 2 for two and three dimensions . It can be observed that the films exhibit a polycrystalline nature membranes are interrelated (conformation granules), convergent , spherical shape, and can attribute spherical shape to fixed speed of growth .The grain size and the average diameter of $Cd_{1-x}Sn_xS$ films are listed in table (I) .

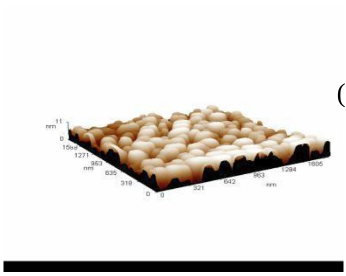


(a)x=0

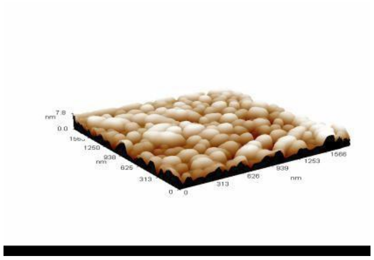




©x=0.5



(d)x=0.7



(e)x=1

Fig.2. AFM micrographs of (a)CdS , (b)$Cd_{0.7}Sn_{0.3}S$ (c) $Cd_{0.5}Sn_{0.5}S$ (d)$Cd_{0.3}Sn_{0.7}S$ (e)SnS films.

Table I: Variation of grain size and average diameter of $CdxSn_{1-x}S$ thin films with thickness of 400 nm

Film	Grainsize(nm)	Avg.Diameter(nm)
CdS	38.12	112.06
Cd0.7Sn 0.3S	12.57	105.09
Cd0.5Sn 0.5S	15.36	112.08
Cd0.3Sn 0.7S	17.44	117.03
SnS	15.51	99.59

The transmittance spectrum of $Cd_{1-x}Sn_xS$ thin films where x equal (0 , 0.3 , 0.5,0.7 & 1) are shown in Fig.(3). It is clear from the same figure that the transmittance decreases with increasing in Sn concentration and this is consider a wide range which can be useful in different application like optical filters . In addition the variation of the transmittance of $Cd_{1-x}Sn_xS$ thin films with the wavelength is very important because this variation will limit the transmitted wavelengths which play an important role in determination the category/type of the optical filters .

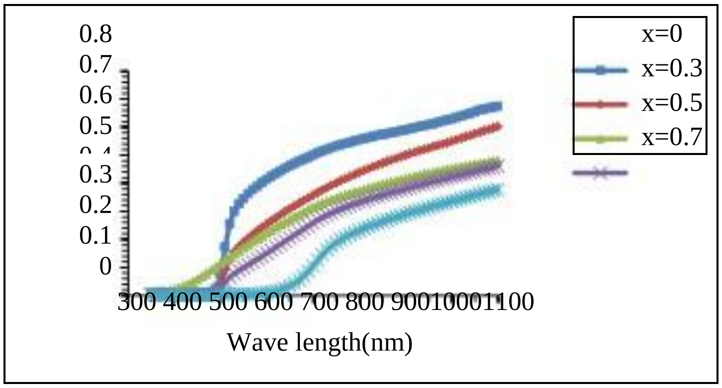


Fig .3. optical transmittance spectra of the $Cd_{1-x}Sn_xS$ thin films

The absorbance spectrums of $Cd_{1-x}Sn_xS$ thin films are shown in Fig. (4). It is clear that as the Sn concentration increases the absorbance of $Cd_{1-x}Sn_xS$ thin films is increased . This increasing in the absorbance is attributed to the decreasing of Cd concentration (Cadmium vacancies increase) which results in an increase of the depth of donor levels associated with these vacancies and these levels will be available for the photons to be absorbed therefore the absorbance of $Cd_{1-x}Sn_xS$ thin films will increase with increasing in Sn concentration . As well as from the same figure , it can be seen that the absorption edge shifts to the higher wavelengths corresponding to the red region as the Sn concentration increased and takes the values 550 nm , 555 nm , 580,610 nm and 770 nm for x equal 0 , 0.3 , 0.5, 0.7 and 1 respectively . From this shifting in the absorption edge to the red region it can be deduced that the energy gap of $Cd_{1-x}Sn_xS$ thin films will decrease with increasing in Sn concentration .

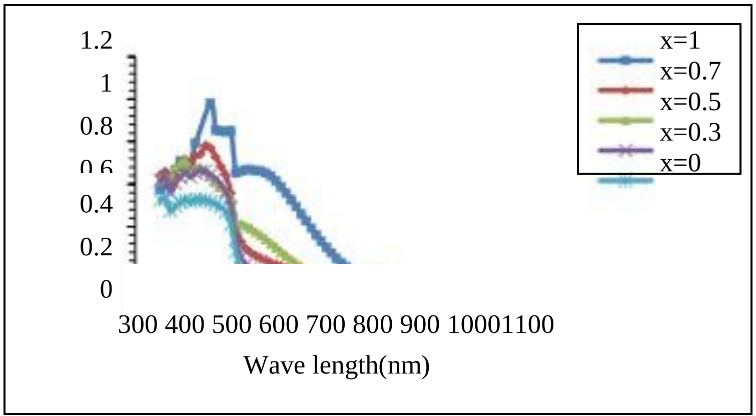


Fig.4.optical absorption spectra of the $Cd_{1-x}Sn_xS$ thin films.

The optical energy gap values (E_g) for $Cd_{1-x}Sn_xS$ thin films prepared by chemical spray pyrolysis(CSP) method have been determined from the region of the high absorption at the fundamental absorption edge of these films by using Tauc equation [28]:

( ) (2)

Where , is the absorption coefficient , is the incident photon energy in eV ,

is a constant depends on the nature of the material (properties of its valence and conduction band) [28] and is a constant depends on the nature of the transition between the top of the valence band and bottom of the conduction band [29] . This equation is used to find the type of the optical transition by plotting the relations $(\alpha h\upsilon)^2$, $(\alpha h\upsilon)^{2/3}$, $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^{1/3}$ versus photon energy ($h\upsilon$) and select the optimum linear part. It is found that the first relation yields linear dependence, which describes the allowed direct transition , then E_g was determined by the extrapolation of the portion at ($\alpha=0$) as shown in Fig.(5). It is clear that the optical energy gap for $Cd_{1-x}Sn_xS$ thin films decreases and shifts towards the red region as the Sn concentration in the films increased. This is attributed to the decreasing of Cd concentration (Cadmium vacancies increase) which results increase of the depth of donor levels associated with these vacancies which in turn causing a reduction in the optical energy gap for $Cd_{1-x}Sn_xS$ thin films . The optical energy gap values for Cd_{1-}xSnxS thin films were 2.4 eV , 2.3 eV , 2.25 eV,2.15eV and 1.95 eV for x equal (0 , 0.3 , 0.5,0.7 & 1) respectively . The obtained values of the optical energy gap match well with the reported values of CdS [30] and CdSn [31]

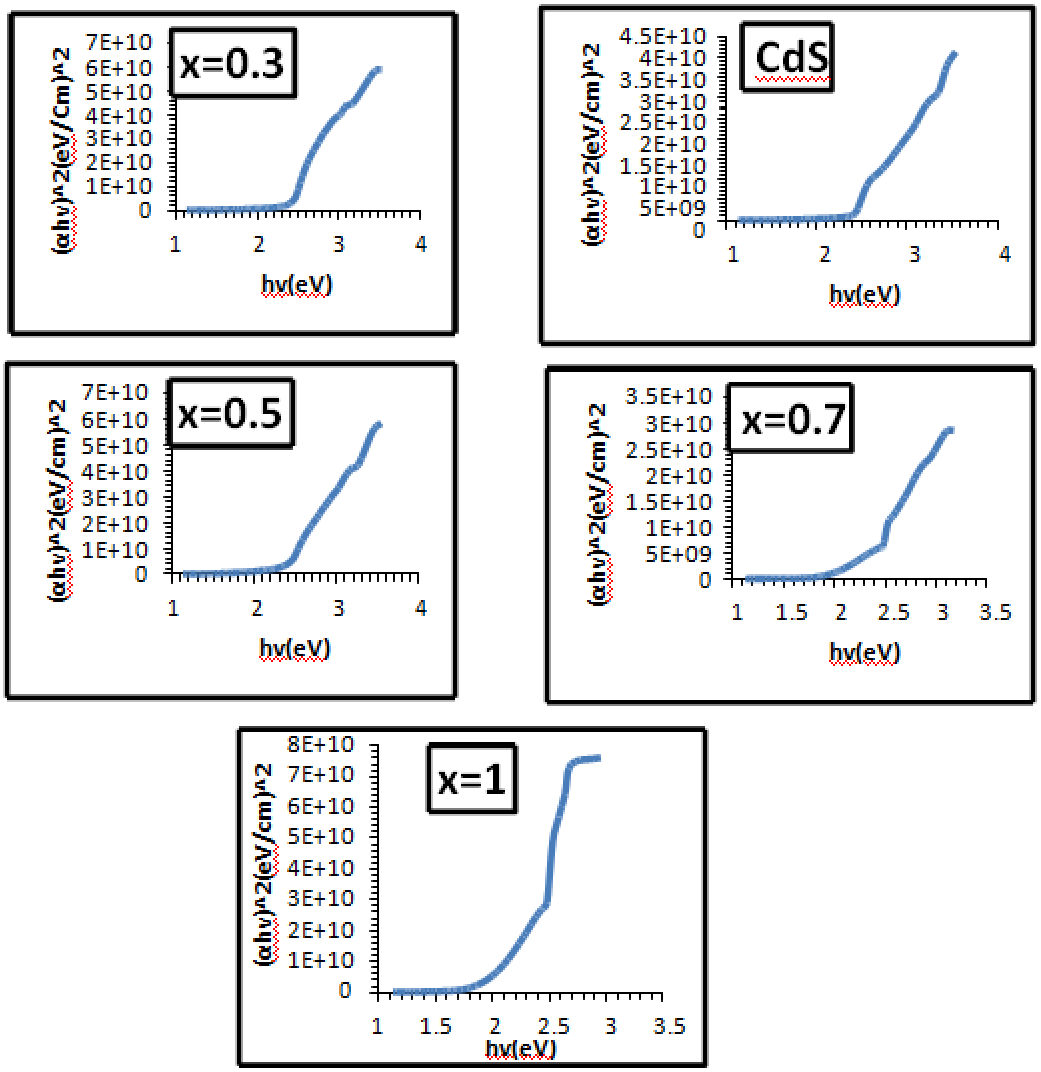


Fig .5. plots of$(\alpha h\nu)^2$ versus photon energy (hν) of the $Cd_{1-x}Sn_xS$ thin films .

The refractive index ኘ of $Cd_{1-x}Sn_xS$ thin films have been determined by using the following equation [29]:

Where , R : is the reflectance of the films and k_o : is the extinction coefficient. The variation of the refractive index as a function of the wavelength for $Cd_{1-x}Sn_xS$ thin films is illustrated in Fig. (6). It is clear from this figure that the refractive index decreases with the increasing in the wavelength of the incident photon . Also it can be observed , that the refractive index of $Cd_{1-x}Sn_xS$ thin films increases with the increasing in the Sn concentration . This increasing is attributed to the decreasing in the grain size of the films with the increasing in the Sn concentration which interns causing an increment in the compactness of the films which in turns reduces the speed of light in the material of the thin film and then leads to an increasing in the refractive index. Where ( ) varies according to the grain size even if the crystalline structure is itself of the material

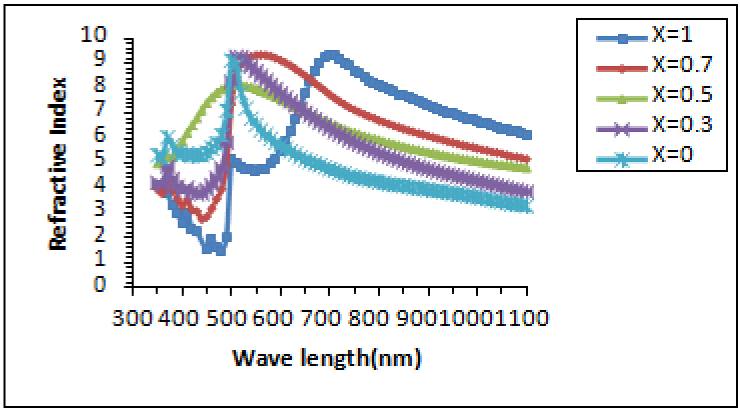


Fig.6. The variation of the refractive index as a function of the wavelength for $Cd_{1-x}Sn_xS$ thin films

The extinction coefficient ( ) have been determined by using the following equation

[29]:

Where : is the absorption coefficient and is the wavelength of the incident photon .

It is clear from this equation that depends on α and has a similar behavior to α . Fig. (7) illustrates the variation of the extinction coefficient of $Cd_{1-x}Sn_xS$ thin films with the wavelength for x equal (0 , 0.3 , 0.5.0.7 & 1). From this figure , it can be noted that varies slightly with the increasing in the wavelength corresponding to the reduction in the photons' energy and the decreasing in the absorption coefficient. Then increases highly at the absorption edge region and this increasing is attributed to the increasing of the absorption coefficient due to the direct electronic transitions thereafter reaches to its maximum value at the high absorption region corresponding to the increment in the photons' energy and the increasing in the absorption coefficient with the decreasing in the wavelength . In addition , it is clear from this figure that with the increasing in the Sn concentration the extinction coefficient increases . This is attributed to the increasing in the absorption coefficient due to the increasing of the depth of donor levels associated with tin vacancies and these levels will be available for the photons to be absorbed causing an increment in the absorbance and leads to increase in the absorption coefficient .Therefore will increase with the increasing in the Sn concentration since it has a similar behavior to α and depends on it .

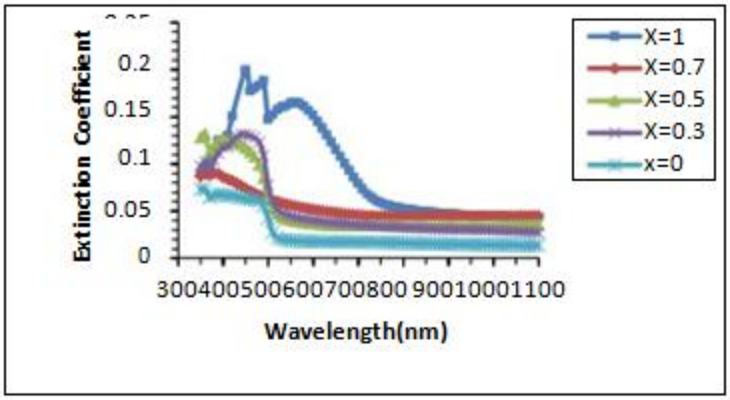


Fig.7. Extinction coefficient as a function of wavelength for $Cd_{1-x}Sn_xS$ thin films

The variation of the real (□$_r$) and imaginary (□$_i$) parts of the dielectric constant values versus wavelength for $Cd_{1-x}Sn_xS$ thin films deposited at R.T with different X are shown in Figs.(8,9)

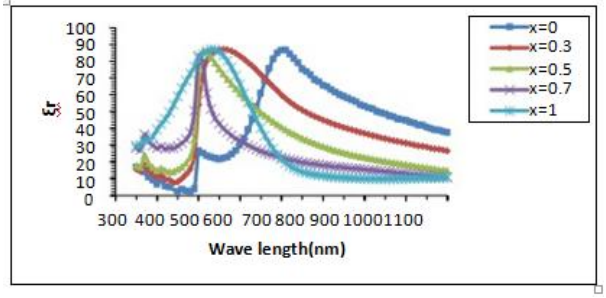


Fig.8. extinction coefficient of $Cd_{1-x}Sn_xS$ films with different x content.

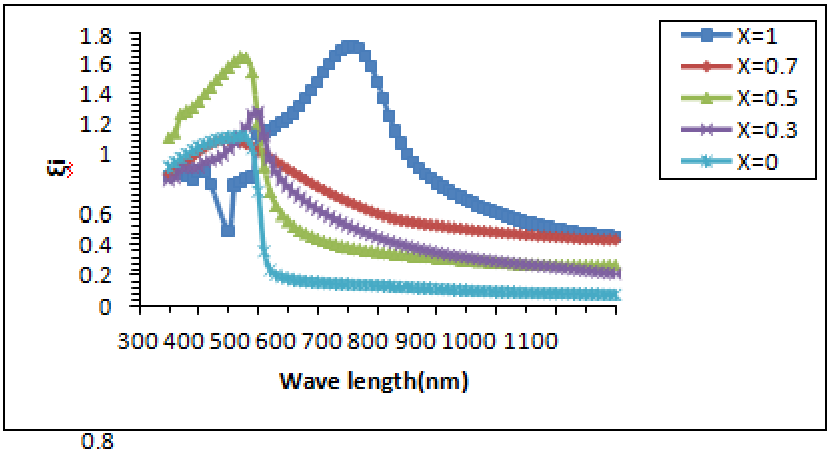


Fig.9.optical dielectric constant(ξ i)of the $Cd_{1-x}Sn_xS$ thin films.

The optical properties parameters including optical energy gab (E_g) , absorption coefficient (α) and optical constants which include refractive index(n) , extinction coefficient (k) , real (ε_r) and imaginary part (ε_i) of the dielectric constant at the wavelength equal to (690) nm for $Cd_{1-x}Sn_xS$ thin films where x equal (0,0.3 , 0.5 ,0.7 & 1) deposited by the chemical spray pyrolysis method on glass substrate at R.T with thickness (400)nm are listed in table (II) .

Table II : The optical parameters of $Cd_{1-x}Sn_xS$ thin films at (λ= 690) nm

x	Band aps Eg(eV)	T	α(cm)^-1	k	ξr	ξi	n	Abs
0	2.41	0.0858	3169.504	0.0401	24.57	0.340	4.821	0.077
0.3	2.34	0.2468	8500.229	0.0526	23.24	0.494	6.504	0.114

0.5	2.3	0.3047	6613.928	0.0764	42.30	0.614	6.691	0.126
0.7	2.1	0.3471	8743.483	0.0561	62.48	1.053	7.904	0.151
1	1.9	0.4916	15844.93	0.1146	84.84	2.007	9.211	0.275

It is clear from this table , that the optical energy gab decreases with the increasing in the Sn concentration whereas the other parameters increase with the increasing in the Sn concentration .

4. Conclusion

$Cd_{1-x}Sn_xS$ semiconductor films have been prepared by the chemical spray pyrolysis method at 300°C substrate temperature .XRD patterns of the films exhibit clear dependence on Sn concentration .SEM micrographs of the films show that the films have a polycrystalline nature membranes are interrelated (conformation granules)and convergent and spherical shape, and can attribute spherical shape to fixed speed of growth .

Optical studied indicates that $Cd_{1-x}Sn_xS$ thin films exhibit direct band gap which is

strongly depends on the Se concentration almost cover the entire visible spectral that makes these films are suitable for optoelectronic devices especially for solar cell and optical filters .

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