Inter-Band Transitions and Urbach Tails of Chlorine Doped Tin Monosulfide

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Abstract

Thin films of SnS and chlorine doped SnS were prepared utilizing chemical spray pyrolysis.

The electronic transition was found to be direct and indirect for all the samples under investigation. The Urbach tail values were increased as the doping percentage increase while the energy gap takes the behavior of reverse. The single oscillator model proposed by Wimple and Didomoico were applied to the obtained sample which certainly obey single oscillator model.

الانتقالات الحزمية وذيول اورباخ لأغشية كبريتيد القصدير المشوبة بالفلور

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الخلاصة

حضرت أغشية رقيقة من كبريتيد القصدير وكبريتيد القصدير المشوب بالكلور باستخدام التحلل الكيميائي الحراري.

لقد وجد بان الانتقالات الالكترونية هي من النوع المباشر وغير المباشر ولكافة النماذج قيد الدراسة.

ان قيم ذيول اورباخ تزداد بازدياد نسبة التشويب بينما تسلك فجوة الطاقة سلوك عكسي, طبق نموذج المتذبذب الاحادي المقترح من قبل Wemple ,Didomenico على كافة النماذج المحضرة, لقد وجد بان كافة النتائج تتفق وبشكل مؤكد مع نموذج المتذبذب الاحادي.

Introduction

Recently much attention has been paid for ZnS thin film, since it is a promising material for low cost photovoltaic conversion of solar cell, its conductivity is controllable by using various dopants such as Al, Ag , and Cl, tin sulfide exists in a variety of phases such as SnS, Sn_2S_3,SnS_4 and SnS_2, due to bonding characteristics of tin and sulfur, it can have p or n type conduction (an excess of tin changes the type of conductivity from p to n type). SnS is reported to have a direct band gap and indirect band gap depends on the conditions of preparation, according to Prince-Loferski diagrams, a high conversion efficiency of about 25% can be obtained using SnS in photovoltaic devices, in addition it is also useful as heated mirrors in solar control coatings [1-6].

Sns thin films could be prepared using different techniques such as chemical deposition, thermal evaporation, chemical bath deposition, co-evaporation plasma-enhanced, chemical vapor deposition and spray pyrolysis [7-12].

In the present work we show the results of the effect of chlorine doping on the inter-band transition of SnS and the results of the dispersion parameters deduced from wimple and Didomenico theory.

Experimental details

The optical energy band gap (E_g^{opt}) and the type of optical transition was analyzed using the equation foe the near-edge absorption proposed by Bardeen et al [13]:

$$(\alpha h\upsilon)^r = A(h\upsilon - E_g^{opt}) \qquad (1)$$

Where α is the absorption coefficient, $h\upsilon$ is the photon energy, E_g^{opt} is the optical energy gap, A constant and r is characterizes the transition process we can see that r = 2 for direct allowed and r=1/2 for indiect forbidden transition .

Fig. (1) Shows the curves of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ for SnS and SnS:Cl. The curve has a good straight line fit with higher energy rang above the absorption edge. The direct energy gap E_g have been calculated as 1.35 eV for pure and (1.32, 1.30, 1.27) eV for doped SnS with 1%, 2%, 3% chlorine respectively the value of pure SnS is in good agreement with the reported data on single crystal and polycrystalline films grown by other techniques [14-17].

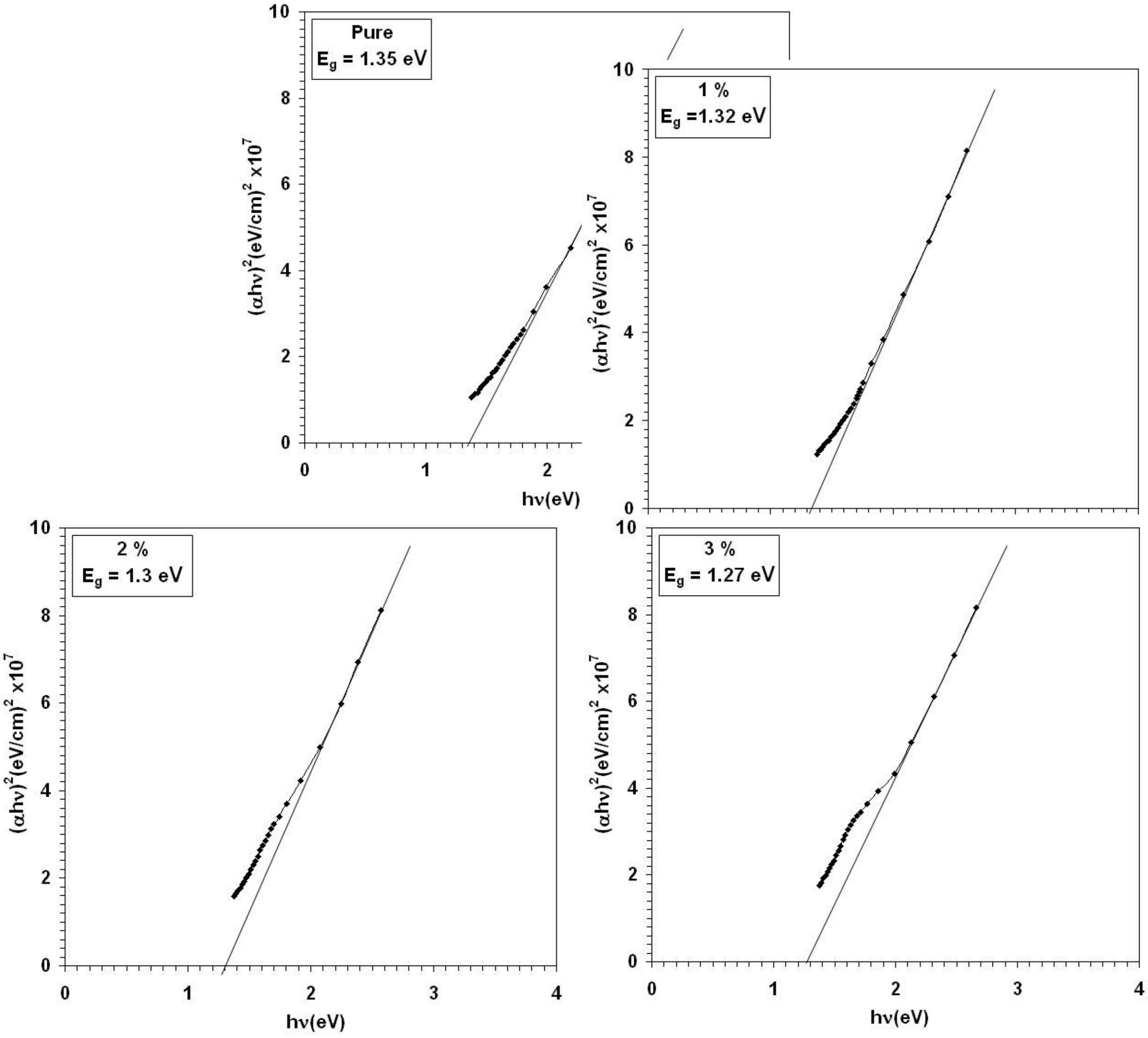

Fig. (1): $(\alpha h\nu)^2$ versus hυ for the as deposited films.

Fig. (2) Illustrate the dependence of $(\alpha h\upsilon)^2$ versus of photon energy(hυ).

It can be shown from the fig, that the value of undoped SnS is 1.2 eV, which is in good agreement with the literature [4.18].

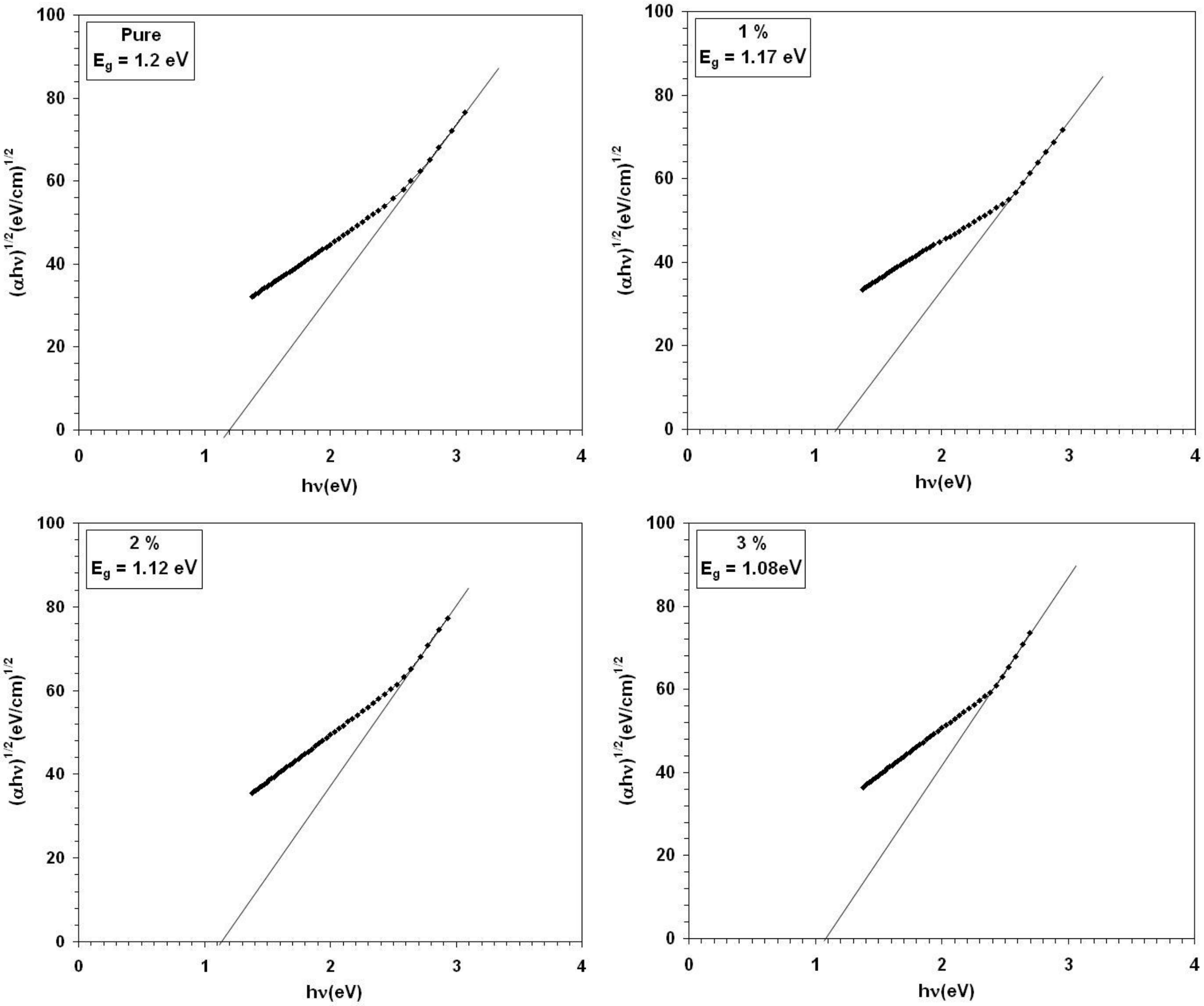

Fig. (2): $(\alpha h\nu)^{1/2}$ versus hυ for the as deposited films.

It is known that the absorption coefficient near the band edge shows an exponential dependence on photon energy described by the following relation [19]:

$$\alpha = \alpha_o \exp\left(\frac{h\upsilon}{E_U}\right) \text{ --------(2)}$$

Where (α_o) is constant, ($h\upsilon$) is the photon energy, and E_U is the Urbach energy which corresponds to the width of the band tail and can be evaluated as the width of the localized state. Thus the plot of lnα versus hυ should be linear and Urbach can be obtained from the slope. Fig (3) illustrates ln α versus hυ, Urbach energy was calculated from the reciprocal gradient of the linear portion of these curves, the width of band tail i.e Urbach energy increases as the chlorine percentage increase (370-500) meV.

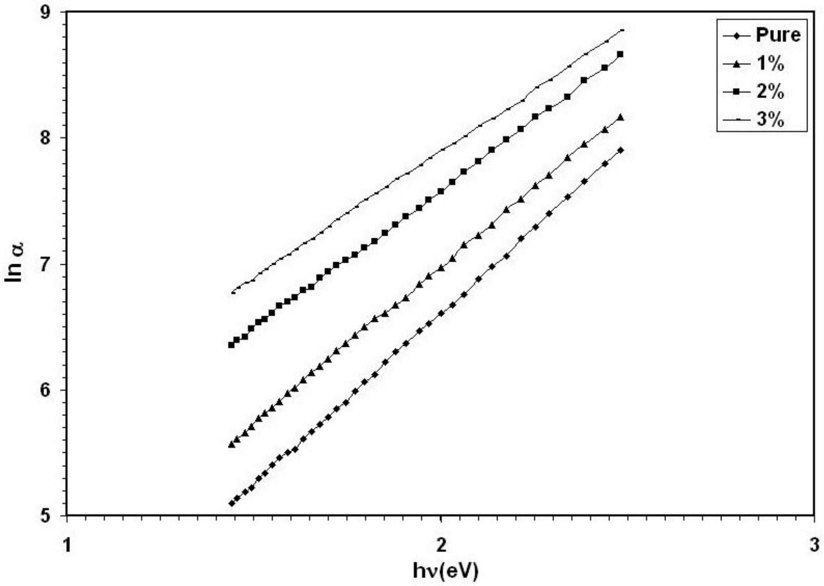

Fig. (3): Illustrate ln α versus hυ.

Table (1) the optical parameters of PMMA and copper sulfate doped PMMA.

Sample	E_d (eV)	E_o (eV)	n_{lwl}	ε_∞	M_{-1}	M_{-3} $(eV)^{-2}$	S_o x10^{13} m^{-2}	λ_o nm	E_U meV
Pure	9.87	3.6	1.93	3.725	2.74	0.211	3.12	290	370
1%	10.87	3.48	2.03	4.121	3.12	0.257	3.38	304	400
2%	11.18	3.22	2.11	4.452	3.47	0.334	3.42	307	454
3%	12.3	3.198	2.20	4.840	3.84	0.375	3.75	320	500

Urbach energy values change inversely with the optical band gap of films, the decrease in E_g is attributed to the increase of disorder of the material occurred by doping.

This increase leads to a redistribution of states from band to tail, thus allows for a greater number of possible bands to tail and tail to tail transitions [20].

The refractive index is a significant factor in optical communication and in designing devices for spectral dispersion and the refractive index dispersion data below the inter- band absorption edge are important for technological applications of the optical materials.

The dispersion data of the refractive index can be described by a single-oscillator model [21]:

$$n^2 = 1 + \frac{E_o E_d}{E_o^2 - (h\upsilon)^2} \quad (3) \text{ ------------}$$

Where n is the refractive index, E_o is oscillator excitation energy for electronic transitions and E_d is the dispersion energy

Which is the measure of the strength inter-band optical transition, this model describes the dielectric response of transitions below the optical gap.

The values of E_o and E_d is for inter-band optical transitions are calculated from Fig. (4) for all the samples under investigation and their values were tabulated in table (1) from these values, the long wavelength limit of refractive index n_{lwl} can be determined using the expression:

$$n_{lwl} = \sqrt{1 + \frac{E_d}{E}} \quad (4) \text{ ------------}$$

Their values were also tabulated in table (1) these values of the refractive index are within the rang found (1.5-4.6) in the literure [22-24], the value of the static dielectric constant $\varepsilon_\infty = n^2_{lwl}$ was calculated and their value was listed in Table (1), as can be seen that ε_∞ increases as the doping percentage increases.

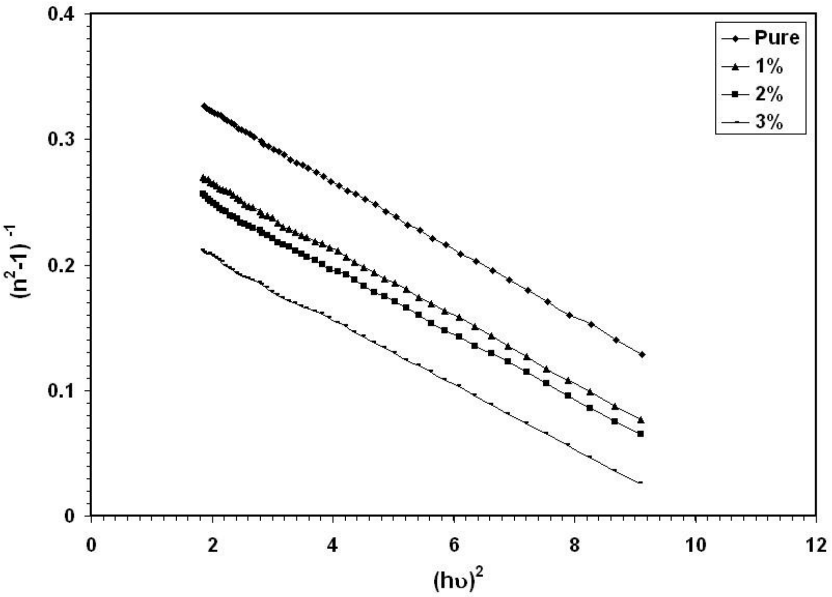

Fig. (4) $(n^2-1)^{-1}$ as a function of $(h\upsilon)^2$.

The single-oscillator parameters E_o and E_d is related to the imaginary of ε_i of the complex dielectric constant. The ε_i parameter includes the_desired response information about electronic and optical properties of the optical material thus, the fact that the moments of ε_i spectrum are determined is very important for the optical application of the optical material studied. The M_{-1} and M_{-3} moments of the optical spectrum can be obtained from the following relations [25]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (5) \text{ ------------}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (6) \text{ ------------}$$

Their values were listed in table (1) according to the single oscillator model proposed by DiDomenico and wimple [26]:

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1-(\lambda_o/\lambda)^2} \quad (7) \text{ ------------}$$

Where λ_o is an average oscillator wavelength, S_o is the average oscillator strength and λ is the wavelength of the incident light, the values S_o and λ_o were tabulated in table (1).

The linear relation between $(n^2-1)^{-1}$ and $(1/\lambda^2)$ is expected from equation (7).

$(n^2-1)^{-1}$ of the as deposited thin films as a function of $(1/\lambda^2)$ is shown in the inset of Fig. (5) Proves the validity of the above model, the values were listed in Table (1).

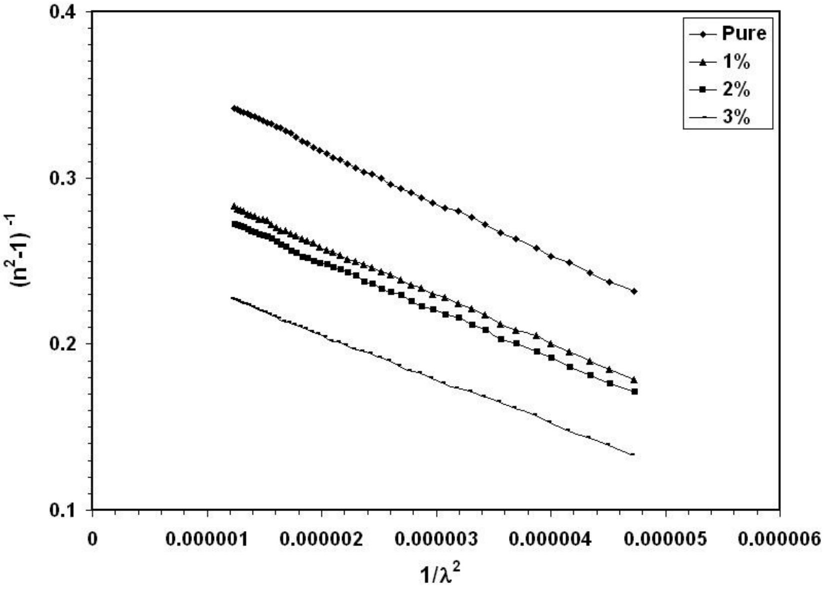

Fig. (5) $(n^2-1)^{-1}$ as a function $(1/\lambda^2)$.

Conclusions

SnS and SnS:Cl which were prepared by chemical spray pyrolysis shows direct and indirect transitions.

The energy gap for both transitions were decreasing as the doping percentage increase, while the Urbach tail vales were increased by doping.

We conclude also that the refractive index dispersion curve obey the single oscillator model.

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