The Effect of Chlorine Concentration on the Optical Constants of SnS Thin Films

Nadir Fadhil Habubi*

Sami Salman Chiad* Reem Saadi Khaleel*

Received 3, January, 2011 Accepted 20, May, 2011

Abstract:

Chlorine doped SnS have been prepared utilizing chemical spray pyrolysis.

The effects of chlorine concentration on the optical constants were studied. It was seen that the transmittance decreased with doping, while reflectance, refractive index, extinction coefficient, real and imaginary parts of dielectric constant were increased as the doping percentage increased. The results show also that the skin depth decrease as the chlorine percentage increased which could be assure that it is transmittance related.

Key words: SnS, thin films, optical constants, spray pyrolysis, doping.

Introduction:

Recently much attention has been payed 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 variety of phases such as SnS, Sn_2S_3 , SnS_4 and SnS₂. Due to bonding characteristics of tin an 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 direct band gap and indirect band gap dependent 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 heat mirrors in solar control coatings [1-6].

SnS thin films could be prepared using different technique 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.

Materials and Methods:

Tin sulphide and chlorine doped tin sulphide were prepared by spray pyrolysis on corning glass substrate kept at a temperature of 400 °C, already were ultrasonically cleand with acetone and methyl alcohol followed by rinsing in distilled water. The deposition parameters such as flow rate, carrier gas pressure and nozzle to substrate distance were kept constant during deposition as 5 ml/min. 1 bar and 29 cm, respectively.

The starting solution was prepared using $SnCl_2.2H_2O$, n, ndimethylethiourea and $NH_4Cl.SnCl_2$ was dissolved in a mixture of isorpyl alchol and deionized water, while

^{*} Al_Mustansiriyah University, College of Education, Physics Dept

thiourea and NH₄Cl were dissolved in deionzed water all of these were milled so that the final concentration would be 0.1 M. The chlorine doping was in the range of 1-3%. Concentration film thickness was estimated by weighing method and were in the range of (300-350) nm. Optical absorbance and transmittance measurements for the film were carried out using UV/VIS double beam spectrophotometer (schimadzu 160Å Japan Company) in the wavelength range (300-900) nm

Results and Discussions:

The optical transmission (T) spectrum at room temperature was taken by using spectrophotometer in the wavelength range of (300-900) nm in order to determine the optical characterization of SnS and SnS:Cl thin films. This spectra is shown in Fig. (1), it is obviously seen that undoped SnS high transmission about 80% exhibit, while this value decreases as the chlorine concentration increased the as deposited films, all the transmission curve indicates a smooth increase and nearly saturated at 600 nm, this smooth increase may be due to high crystalline nature of the prepared films [13.14].

The reflectance for all the samples as a function of photon energy is shown in Fig. (2). The curve shows that the reflectance increases as the doping increased up to a certain maxima where all the sample in this maxima nearly have the same value after that these is a fall in the values of reflectivity, this could be attributed to surface roughness.

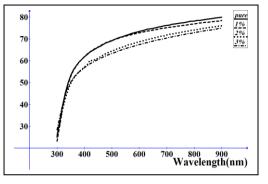


Fig. (1) Transmittance versus wavelength for the as deposited films.

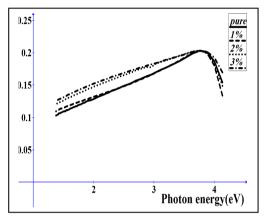


Fig. (2) Reflectance versus photo energy for the as deposited films.

Fig. (3) Shows the refractive index of the SnS and SnS:Cl films as a function of photo energy. the refractive index increase as the doping percentage increased, the behavior of the graphs seems to be the same as the reflectance, the refractive index increase from (1.6-1.93) and it varies with photon energy and percentage and seems to have its maximum value at to the peak maxima which was nearly constant for all the samples. These values of refractive index are within the range found (1.5-4.6) in the literature^[15,16].

Fig. (4) Also shows the variation of the imaginary part of the complex refractive index, which is the extinction coefficient k of the SnS and chlorine doped SnS as a function of photon energy.

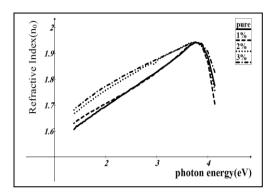


Fig. (3) Refractive index versus photo energy for the as deposited films.

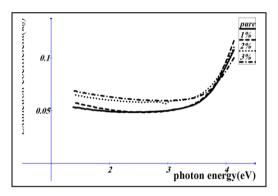


Fig. (4) Extinction coefficient versus photo energy for the as deposited films.

The extinction coefficient (k)of the films was calculated using the relation [13]:

$$k = \frac{\alpha \ \lambda}{4 \ \pi} ---(1)$$

Where $\Box \Box \Box$ is the absorption coefficient, all the values of k are quite small, which allows the light wave to traverse the sample several times.

As seen in the figure the rapid change in the extinction coefficient at high is due to the band-to-band excitation.

The skin depth could be calculated using the following relation [17]:

$$\chi = \frac{\lambda}{2 \pi k} \quad ---(2)$$

Where \Box is the wavelength of the incident photon, k is the extinction coefficient.

Fig. (5) Shows the variation of skin depth as a function of wavelength for as deposited thin films. It was mentioned that the depth increase as the wavelength increase, this behavior could be seen for the samples, but the skin depth increases as the doping percentage increases so the skin depth is transmittance related.

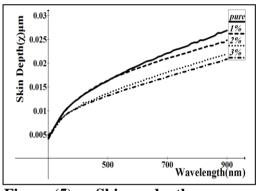


Fig. (5) Skin depth versus wavelength for the as deposited films.

The values of real (ε_r) and imaginary

 (ε_i) parts of dielectric constant for different incident photon energies can be obtained from the value of n and k using the relation ^[16]:

$$\varepsilon_{\rm r} = n^2 - k^2 \quad \text{---(3)}$$

$$\varepsilon_i = 2nk - \text{---(4)}$$

In the present study the value of (\mathcal{E}_r) increase as the photon energy increase as illustrated by Fig. (6) Showing a maxima above 3.5 and the decrease again for all the samples under investigation, while the values of (\mathcal{E}_i) remain almost constant for the photon energy below 3.4, with a sharp decrease after 3.4.

The behaviors seems to be applied for all the samples under investigation, the value of (\mathcal{E}_r) is greater than the value of (\mathcal{E}_i) .

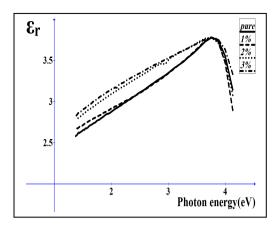
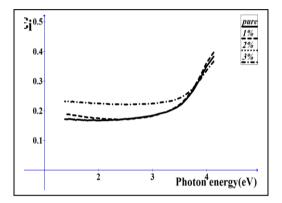
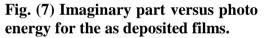


Fig. (6) Real part versus photo energy for the as deposited films.





Conclusions :

SnS and chlorine doped SnS have been successfully prepared by chemical spray pyrolysis the transmittance of undoped SnS is greater than the doped one, the skin depth show the same behavior which indicate that the skin depth is related to the transmittance. the value of refractive index was in the range of values obtained by other researchers.

The reflectance, refractive index, extinction coefficient, real and imaginary parts of dielectric constant, all of these constant are decrease upon doping.

References :

1. Devika, M., Reddy, N. K., Ramesh,K., Gumnaselhar, K. R., Gopal, E. S. R. and Reddy, K. T. R. 2006. Influence of Annealing on Physical Properties of Evaporated SnS Films, Semicond. Sci. Technol., 21:1125-1131.

- 2. Yue, G. H., Wang, L. S., Wang, X., Chen, Y. Z. and Peng, D. L. 2009. Characterization and Optical Properties of the Single Cryatalline SnS Nonowire Arrays, Nonoscale Res. Lett., 4: 359-363.
- **3.** Ghosh, B., Das, M., Banerjee, P. and Das. S. 2008. Fabrication of Vacuum Evaporated SnS/CdS Heterojunction for PV Applications, Solar Energy Material and Solar Cells, 39:1009-1104.
- **4.** Reddy, N. K. and Reddy, K. T. R. 2005. SnS Films for Photo Voltaic Applications: Physical Investigations on Sprayed Sn_xS_y Films, Physica B, 368:25-31.
- Cifuentes, C., Botero, M., Calderon, C. and Gordillo. 2006. Optical and Structural Studies on SnS Films Grown By Co-Evaporation, Braz. J. of Phys., 36(3B):1046-1049.
- Reddy, K. T. R., Reddy, N. K. and Miles, R. W. 2006. Photovoltaic Properties of SnS Based Solar Cells, Solar Energy Material and Solar Cells, 90: 3041-34046.
- Avellaneda, D., Delgado, G., Nair, M. T. S. and Nair, P. K. 2007. Structural and Chemical Transformations In SnS Thin Films Used in Chemically Deposited Photo Voltaic Cells, Thin Solid Films, 515: 5771-5776.
- Ray, S. C., Karanjai, M. K. and Gupta, D. D. 1999. Structure and Photo Conductive Properties of Dip Deposited SnS and SnS₂ Thin Films and Their Conversion to Tin Dioxide by Annealing in Air, Thin Solid Films, 350: 72-78.
- 9. Li, Y., Tu, J. P., Huang, X. H., Wu, H. M. and Yuan, Y. F. 2007. Net Like SnS/ Carbon Nano Composite

Films Anode Material for Lithium Ion Batteries, Electro Chemistry Communications, 9: 49-53

- 10. Ichimura, M., Takeuch, K., Ono, Y. and Aria, E. 2000. Electrochemical Deposition of SnS Thin Films, Thin Solid Films, 361-362: 98-101.
- **11.** El-Nahass, M. M., Zeyada, H. M., Aziz, M. S. and El-Ghamaz, N. A. 2002. Optical Properties of Thermally Evaporated SnS Thin films, Optical Materials, 20: 159-170.
- 12. Cheng, S., He, Y. and Chen, G. 2008. Structure and Properties of SnS Films Prepared by Electro-Deposition In Presence of EDTA, Materials Chemistry and Physics, 110: 449453.
- **13.** Turan, E., Kul, M., Aybek, A. S. and Zor, M. 2009. Structure and Properties of SnS Semiconductor

Films Produced by Chemical Bath Deposition, J. Phys. D: Phys., 42:245408 (6pp)

- Rodriguez, M. C., Martinez, H., Juarez. A. S., Alvarez, J. C., Silver, A. T. and Calixto, N, E. 2009. Structural, Optical and Electrical Properties of Tin Sulfide Thin Films Grown by Spray Pyrolysis, Thin Solid Films, 517: 2497-2499.
- **15.** Nozaki, H., Onoda, M., Sekita. M. and Wada, T. 2005. Variation of Lattice Dimensions in Epitaxial SnS Films on MgO (001), J. of Sol. Stat. Chem., 178 (1): 245-252.
- **16.** Pankove, J. I. 1971. Optical Processes in Semiconductor Pretice-Hall, New Jersey, 92.
- **17.** Eloy, J. F. 1984. Power Lasers, National School of Physics, Grenoble, France, John Wiley and Sons, 59.

تاثير تركيز الكلور على الثوابت البصرية لاغشية كبريتيد القصدير الرقيقة

سامي سلمان جياد * نادر فاضل حبوبي * ريم سعدي خليل *

* الجامعة المستنصرية – كلية التربية – قسم الفيزياء

الخلاصة:

حضر كبريتيد القصدير المشوب بالكلور باستخدام التحلل الكيميائي الحراري. درس تاثير تركيز الكلور على الثوابت البصرية. لقد وجد بان النفاذية تقل بالتشويب، بينما الانعكاسية، معامل الانكسار، معامل الخمود، ثابت العزل بجزئيه الحقيقي والخيالي، كل هذه العوامل تزداد بازدياد نسبة التشويب. اثبتت النتائج ايضا بان عمق القشرة يقل بزيادة نسبة التشويب مما يؤكد بان لعمق القشرة علاقة بالنفاذية.