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Optical Properties of SnS_2 Thin films Prepared By Chemical Spray Pyrolysis

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Abstract

Thin films of tin disulphide SnS_2 with different thicknesses (2500,4000,5000)A^0 have been prepared by chemical spray pyrolises technique on substrate of glass with temperature (603)K . The effect of thickness on the optical properties of SnS_2 has been studied.the optical study that includes the absorptance and transmittance spectra in the wavelength range (300-900)nm demonstrated that the value of absorption coefficient (α)) was greater than (10^4 cm^{-1}) the electronic transitions at the fundamental absorption edge were of the indirect kind whether allowed and forbidden . Absorption edge shift slightly towards higher wave length.The value of energy gaps (E_g) for all the films prepared are decreased with increasing the thickness. Absorption and transmission spectra were used to find the optical constant including refractive index(n), extinction coefficient (k), imagenary and real part of dielectric constant ($£_i$, $£_r$), and it was found that all the optical constant was affected .

Key word: tin disulphide, SnS_2 Optical properties , thin films

Introduction

Tin forms a variety of sulfides, SnS_2, Sn_2S_3, Sn_3S_4, Sn_4S_5, SnS and numerous polysulfide anions . Due to their electrical and optical properties these binary compounds have a high potential use in opto-electronic devices and photocondu- ctive cells . Tin disulfide was first synthesized some 200 years ago and has more than 70 polytype structures . Tin disulfide adopts the PbI2 layered structure with hexagonal unit cell, in which tin atoms are located in the octahedral sites betwen two hexagonally close packed sulfur slabs to form sandwich structure.The SnS_2 SnS2 layer is stacked on top of one other along the crystallographic *c*-axis and is held together by weak Van der Waals forces . Present day technologists are busy using these materials in designing opto-electronic devices, a part of solar collectors, etc. Thin films of tin sulfides have been grown by spray pyrolysis , chemical bath , and chemical vapour deposition either from organometallic precursors [1,2,3,4].

High absorption region observed for most semiconductors at $\alpha \geq 10^4$ cm^{-1} , the absorption is due to the transitions between extended states in both bands.The imperial formula that governs this transition have been found by Tauc[5] And Kaliannan Optical properties of SnS_2 thin films were studied by Thangaraju found that the SnS_2 thin films which prepared by chemical spray pyrolysis had a high absorption cofficoent and allowed dirct transition were observed in films[11].
Optical properties of SnS2 thin films were studied by C. Cifuentes ,et.al.[12] they ound SnS2 thin films had a high absorption coefficient (greater than 10^4 cm^{-1}) and an energy band gap E_g of about 1.3 eV, indicating that this compound has good properties to perform as absorbent layer in thin film solar cells.

The aim of this research is a preparation of SnS_2 thin films and studying the optical properties The main task was the effect of the thickness on optical properties of SnS_2 thin films which were prepared by using the chemical spray pyrolysis technique. Experimental :-

SnS_2 thin films were prepared by spray pyrolysis of aqueous solution of($SnCl_4.H_2O$) and thiourea NH_2SCNH_2 . The molar concentration of the solution equals to 0.3 mole/liter.In order to prepare the solution 0.1 molar few grams[(2.62935 gm)$SnCI_4$ .H_2O , and (0.57093 gm) NH_2SCNH_2 concentrations from these two materials are weighted by electronic balance (Mettler AE-160) with sensitivity(10^{-4} gm) needed from each of them , melated in 25 cm^3 of distilled water , according to the following equation:

$$M = (W_t / M_{wt}) . (1000/ V) \ldots\ldots\ldots(1)$$

W_t: weight of the material (gm)

V: Volum of water (ml)

M:molarity(mol/l)

Mwt: Molecular weight (gm/mol)

This composition was optimum to give higher optical transparency . The obtained solution is immediately sprayed by used double nozzle sprayer on to heated.Substrate of glass plates, the upper container of the nozzle has 4 cm diameter and was connected to capillary of 0.127 mm through the stopcock .The capiliary was surrounded by a tube through which the compressed air was blown at 2Kg cm^{-2} . The sprayer set up has been described. The substrate were heated to a temperature of about 603 K for 20 min before spraying in small amounts to avoid excessive cooling of hot substrate during spraying .The distance between sprayer and substrate was kept 30 cm and spray rate was 10 cm^3 min^{-1} . The period of sprying sec thin stopping period for 55 sec reproducible films were obtained from successive runs.the chemical reaction can be described in equation as:

$$NH_2SCNH_2 + 4H_2O \rightarrow 2H_2S + 4NH_3 +\uparrow 2CO2 \ldots(2)$$

$$SnCI_6 + 2H_2S + 4H_2O \rightarrow SnS_2 +4\ H_3O^- + 6CI^- \ldots\ldots\ldots(3)$$

The transmission and absorption spectra were obtained over the range (300-900)nm by using UV-VISIBALE recording spectrometer (Shimadzu model UV-160).

The absorption coefficient (α), refractive index(n) and extinction coefficient (k)has been calculated from the equations respectively [5]:

$$\alpha = 2.303A/t \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$[(R+1)/(R-1)]-K^2)^{1/2}-n=\frac{4R}{(R-1)2} \ldots(5)$$

$$k= \alpha\lambda/4\pi \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Where R is the reflectance , t is the thickness of the sample which measured by Gravimetric method ,the real and imaginary part of dielectric constant (ε_r)and (ε_i)can be calculated by using equation: [9,10]

$\varepsilon_r = n^2 - k^2$……………(7)

$\varepsilon_i = 2nk$…………………….(8)

Results and Discussion

Fig(1,2) shows the absorptance and reflectance spectrum for SnS_2 thin films as a function of thickness t =(2500,4000,5000)A^0 from these spectrum the energy gap and optical constants have been determined in general, the absorption edge shifting to higher wavelength.Also the absorptance increase with the increase of thickness and the reflectivity is increased in range(1.3-2.35) eV then the reflectivity is decrease till to highest value. The dominate feature of energy (hυ) dependence of the absorption (α) is the onset of absorption near the region of interband transitions from valance band to conduction band at $\alpha > 10^4\ cm^{-1}$ the optical energy gap of materials E_{+g} obtained from the equation(9) near the band edge[11,12]:

$\alpha h\nu = B(h\nu - E_g)^r$ ..(9)

Where B is constant , r is a number = 2 for allowed direct transition , and r= 3 for forbidden direct transition.Fig (3) shows the variation of the absorption coefficient with photon energy which calculated from equation (3) as a function of thickness, it is found in 700 nm that α increased with the increase of thickness from $(0.357\text{-}0.365\text{-}0.432)\times10^4$)cm^{-1} for (t=2500,4000 and5000)A^0respectively and this attributed to the increase of concentration by the increase of thickness led to increase in the number of collisions with material and an increase in the values of absorption coefficient (α).[10]

The variation of $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^{1/3}$ as a function of hυ are shown in Figs (4,5) for indirect transitions for three value of thickness. The band gap energy is obtained by intercepting the linear portion of the absorption curves to the energy axis [11]. The values of optical energy gap as shown in table (1) from this result the value of E_g decreased for all transitions with the increase of thickness .[6]

Fig(6) shows the variation of K with wavelength, we can see from this figure that the value of K increases with the increase of thickness due to the increase of the number of photon collisions with the material this increase resulted to increasing value of absorption coefficient and this agrees with equation(6).the refractive index (n)which calculated from equation(5) is shown in Fig (7) and its increase with thickness this agree with the result in reference[12]. Also Figs (8,9) show the variation of the imaginary and real part of dielectric constant ($\varepsilon_i$and ε_r) as a function of thickness and photon energy which were calculated from the equation (7 ,8) . The behavior of ε_r is similar to(n) due to the smaller value of K^2 comparison of n^2 in equation(7)so high value of the curves with the increase of thickness, while ε_i is mainly depends on the K values, which are related to the variation of α, its found that ε_i increases with the increase of thickness.

Conclusions

1The absorptance increases with the increase of thickness and the absorption edge shifting to higher wave length,the reflectivity is increased in the range (300-550)nm then decreased.
2- Its found that α,the value of extinction coefficient and refractive index (n) increases with the increase of thickness.
3- It is found that ε_i, ε_r increases with the increase of thicknesses.

4- The value of E_g decreased for all transitions with the increase of thicknesses.

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Table(1): shows the variation of optical energy gap of SnS_2 thin films with thickness.

Thickness(A^0)	E_g(eV)at r=2	E_g(eV)at r=3
2500	1.3	0.2
4000	1.24	0.15
5000	1.2	0.1

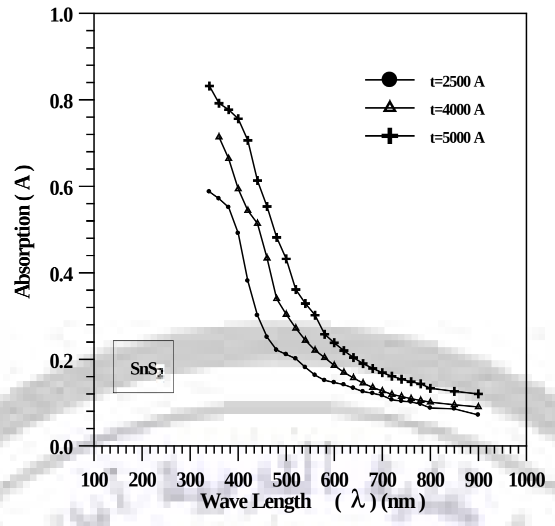


Fig.(1): The absorption spectrum of SnS_2 thin films With different thickness

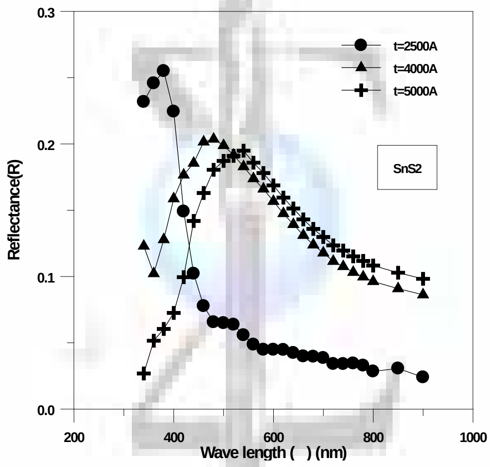


Fig .(2):The reflectance spectrum of SnS_2 thin films with different thicknesses

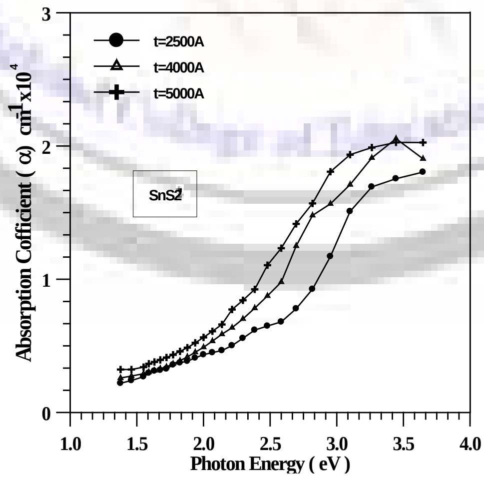
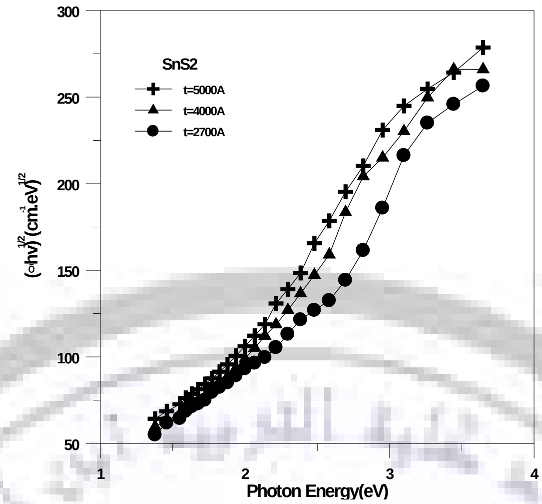
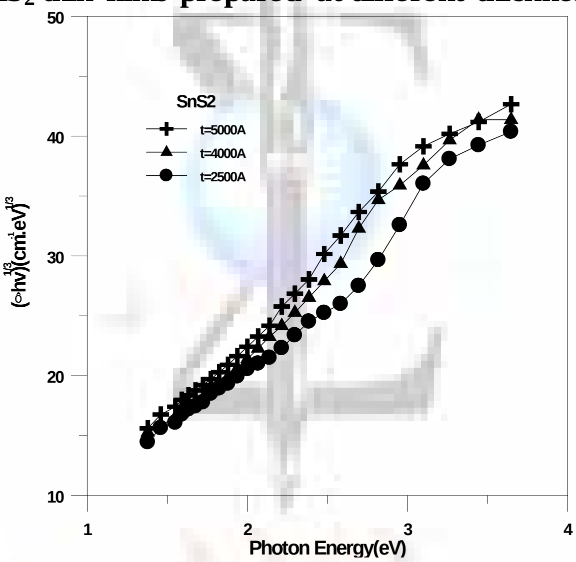


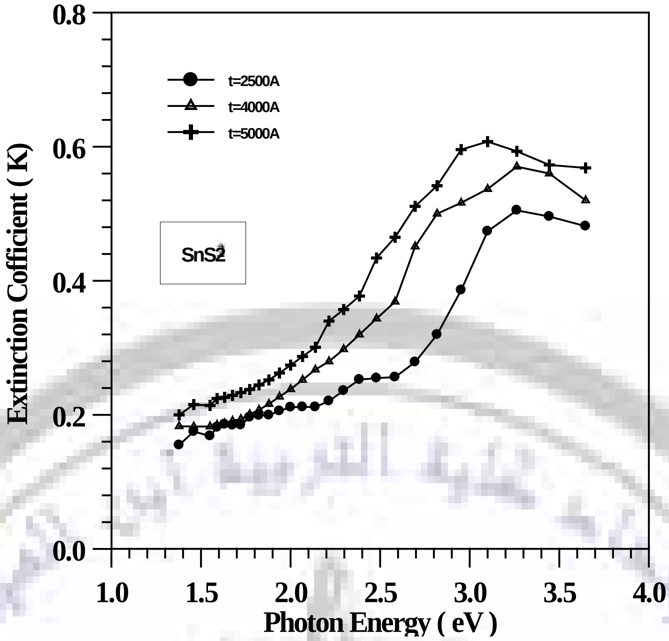
Fig.(3): The variation absorption coefficient of SnS_2 thin films with photon energy as a function of thickness



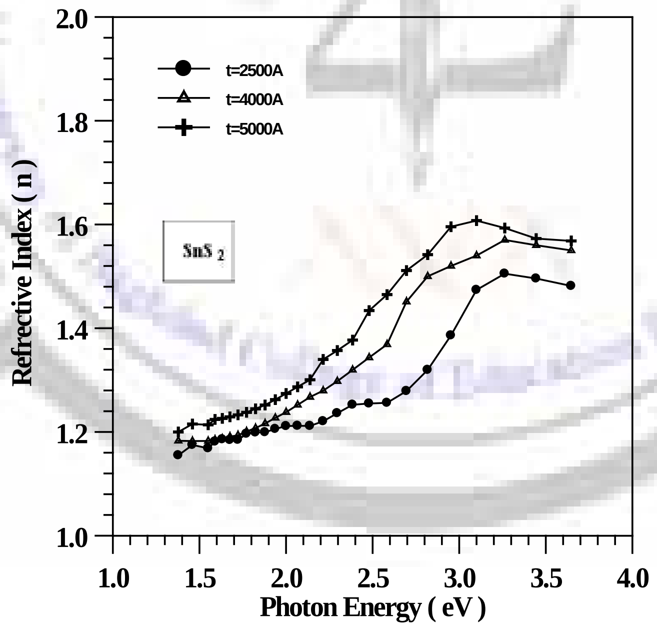
Fig(4):shows plots $(\alpha h\nu)^{1/2}$ against photon energy of SnS_2 thin films prepared at different thicknesses



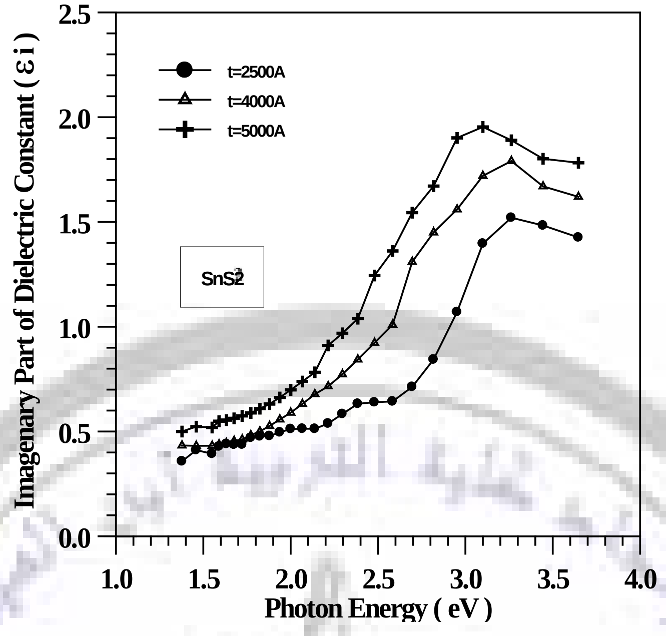
Fig(5):shows plots $(\alpha h\nu)^{1/3}$ against photon energy of SnS_2 thin films prepared at different thicknesses



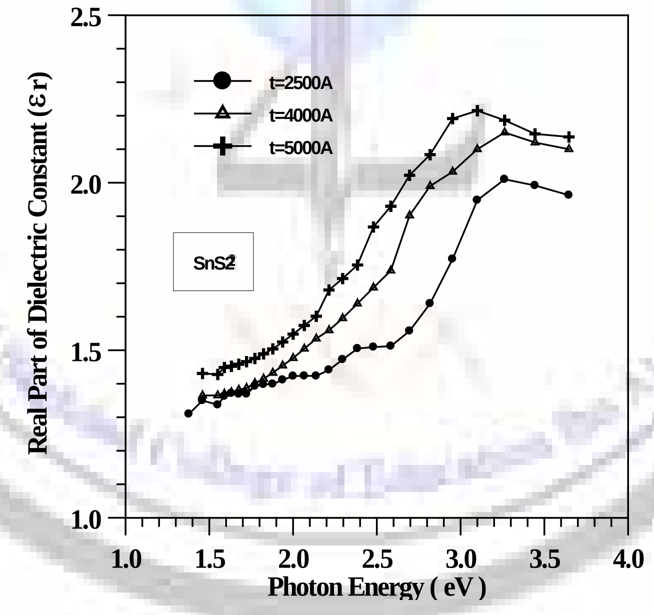
Fig(6):The variation of extinction coefficient with photon energy for SnS_2 thin filmsas a function of thickness



Fig(7):The variation of the refractive index with photon energy for SnS_2 thin films as a function of thickness



Fig(8):The variation of the imaginary part of the dielectric constant with photon energy for SnS_2 thin films as a function of thickness



Fig(9):The variation of the real part of the dielectricconstant with photon energy for SnS_2 thin films as a function of thickness

الخواص البصرية لأغشية SnS_2 المحضرة بطريقة الرش الكيميائي الحراري

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قسم الفيزياء ¡كلية العلوم ¡ الجامعة المستنصرية

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الخلاصة

حضرت اغشية رقيقة من ثنائي كبريتيد القصدير (SnS_2)بطريقة الرش الكيميائي الحراري (Chemical spray pyrolysis technique) على قواعد من الزجاج مسخنة بدرجة حرارة (603)K وبسمك (2500,4000,5000)A.ÓÑÏ تاثير السمك في الخواص البصرية التي تضمنت اطياف الامتصاصية والنفاذية في المدى الطيفي (300-900)nmäÇ قيم معامل الامتصاص (α) للاغشية المختلفة اكبر من (10^4cm^{-1}) كما وجد ان الانتقالات الالكترونية عند حافة الامتصاص الاساسية كانت من نوع الانتقال غير المباشر بنوعيه المسموح والممنوع وان قيمة فجوة الطاقة البصرية في حالة الانتقال غير المباشر المسموح تقل بازدياد السمك كما استعملت اطياف الامتصاصية والنفاذية في ايجاد الثوابت البصرية المتضمنة الجزء الحقيقي والخيالي لثابت العزل ومعامل الخمود ومعامل الانكسار .

الكلمات المفتاحية: ثنائي كبريتيد القصدير, الاغشية الرقيقة, الخواص البصرية