Structural and Optical Properties of SnS_2:Cu Thin films prepared by chemical Spbay Pyrolysis

Nada K. Abass* ***Anwar A.Baker**** ***Asmaa J. Cadhum****
Nedhal A. Mahmood**
Date of acceptance 28/ 2 / 2010

Abqtract:

Thin filis have been prepared from the tin disulphide (SnS_2), the pure and the doped with copper (SnS_2:Cu) with a percentages (1,2,3,4)% by using ahemical spray pyrolysis techniqee on substrate of glass heated up to(603K)and sith thicknesses (0.7±0.02)µm ,after that the films were treated thermally with a low pressure (10^{-3}mb) and at a temperature of (473K) for one hour.

The influence of both doping with copper and the thermal treatment on some of the physical characteristics of the prepared films(structural and optical) was studied.

The X-ray analysis showed that the prepared films were polycrystalline Hexagonal type.

The optical study that included the absorptance and transmitance spectra in the weavelength range (300-900)nm demonstrated that the value of absorption coefficient (α) was greater than (10^4 cm^{-1}) for the pure and doped films and that the electronic transitions at the fundamental absorption edge were of the indirect kind whether allowed or forbidden and the value of the optical energy gap in the case of the indirect transition, the allowed decreased from (2 eV) to (1.8,1.7,1.5,1.2)eV at the doping percentages (1,2,3,4)% respectively, also it was found that the value of energy gap for the pure and doped films increased after annealing.

Tthe absorption and transmission spectra were used to find the optical constant including refractive index(n), extinction coefficient (k), imaginary and real part of dielectric constant (ε_1 & ε_2) , and it was found that all the optical constant was affected by changing the doping percentages; in addition to being affected after treating the films thermall*y*

Key word: Optical, Structural Properties, SnS_2, SnS_2:Cu

Introduction :

The electronic and optical properties of semiconductor materials are tunable varying their shapes and sizes[1,2,3].

The optical properties of semiconductors are often subdivided into those that are electronic and those that are lattice in nature. The electronic properties concern processes involving the electronic states of the semiconductor, while the lattice properties involve vibrations of the lattice (absorption and creation of phonons). Lattice properties are of considerable interest, but it is the electronic properties which receive the most attention in semiconductors

*physics Department, College of Science for Women, University of Baghdad
**. physics Department, College of education, University of Deala

because of the technological importance of their practicalapplications[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].

Optical properties of SnS_2 thin films were studied by Thangaraju et.al.[6],Ji et.al. [7],Yanng et.al.[8], and Sanchez et.al.[9].

The aim of this research is a preparation of (SnS_2:Cu) with a percentages (1,2,3,4)% and studying its optical properties .Indeed, the main task was studying the effect of the heat treatment and composition on optical properties of pure SnS_2 and ***SnS_2:Cu*** thin films which were prepared by using the chemical spray pyrolysis technique

Material and methods:-

SnS_2 layers were prepared by spray pyrolysis of aqueous solution of $SnCl_4.H_2O$ and thiourea. The molar concentration of the solution should be equal to 0.3 mole/liter. In order to prepare the solution of 0.1 molar few grams ,[(2.62935 gm) $SnCl_4.H_2O$,and(0.57093gm)CS(NH2)2]concentrations from these two material are weight needed from each of them, melted in 25 liter of distilled water, according to the following equation:

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

Wt:Weight ofthe material (gm),V:Volum (L),M:Moleculaconcentration (M/L),Mwt:Molecular weight (gm/M)

This composition was optimum to give higher optical transparency. The obtained solution is immediately sprayed with the help of double nozzle sprayer onto 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 capillary was surrounded by a bubble tube through which the compressed air was blown at 2Kg cm^{-2}. The sprayer set up has been described elsewhere. The substrate were heated to a temperature of about 603°C for 20 min before spraying in small amounts to avoid excessive cooling of hot substrate during spraying. To obtain films of uniform thickness the distance between sprayer and substrate was kept 30 cm and spray rate was 10 cm^3 min^{-1}. Reproducible films were obtained from successive runs. The chemical reaction can be described as:

$$NH_2SCNH_2 + 4H_2O \xrightarrow{\Delta} 2H_2S + 4NH_3 + 2SO_2$$

$$SnCl6 + 2H_2S + 4H_2O \rightleftharpoons SnS_2 + H_3O^- + 6Cl^- \quad \ldots(2)$$

To prepared SnS_2:doped with copper Cu,we added CuCl(1,2,3,4wt%) to $SnCl_4.H_2O$ and $CS(NH_2)_2$ solution. according to the following equation:

$$CuCl_2 \rightarrow Cu + Cl_2\uparrow \quad \ldots\ldots\ldots\ldots\ldots(3)$$

SnS_2 and SnS_2:Cu films were prepared on glass substra

The thickness of prepared samples were in the range of (0.7±0.2μm) which determine using Weight Method **and o**ptical Interference method.

the films were clear, transparent and golden-yellow in colour. The coating was found to be stable and has a very good adhesive properties. Optical microscopic studies shows that samples prepared by spray pyrolysis method exhibit very smooth surfaces free from pinholes. To confirm the films purity and structure X-ray diffraction pattern has been taken using CuKα radiation from a Philips pM

1050/70 diffractometer. The values of interplaner spacing and intensity ration is exactly the same as that of the ASTM data of SnS_2. the golden-yellow colour of the films becomes grey-black when the samples are heated to 403C, mostly probably due to the formation of SnS or Sn_2S_3 phase.

We have carried out detailed analysis of optical data in order to investigate the possible optically allowed transitions at room temperature.

The transmission and absorption spectra were obtained over the range (200-1200)nm by UV-VISIBLE recording spectrometer (Shimadzu modelUV-160) .

The optical measurements were repeated on fifteen samples of different thickness and the repetition of results was observed. The reproducibility of data in the films prepared sequentially from the same composition ratio indicates the constancy of composition of the films.

Results analysis and discussion:

1.X-Ray Diffraction: Fig (1) show the XRD patterns obtained for as deposited and heat treated pure SnS_2 films and doped with Cu (4wt%).According to (ASTM) cards, the structure of the films showed a polycrystalline hexagonal structure. The analysis is demonstrated the reflection surfaces [(001).(002),(003)] and the films have crystallized with a strong peak at (001) directions, while in fig.(1-c,d) the strong peak at(001) directions, this means that this plane is suitable for crystal growth. This results are similar to those obtained by Amalraj et.al.[10], Khelia et.al. [1] and Sanchez et.al.[9] but it disagreement with Kawano et.al.[11]

2- **The Transmission And Absorption Spectrum**

The experimental transmission spectrum for as-deposited and heat treated pure SnS_2 films and doped with Cu (1,2,3,4wt%) films, respectively, in the wavelenght range (300 – 900)nm at room temperature are shown in Figs.(2).

All spectra show good transparency (T > 85%) and reveal very pronounced interference effects for photon energies below the fundamental absorption edge . They also display a clear explicit absorption edge interrelated to the optical band gap. It is clear from these figures that spectral characterization are affected by heat treatment. This fact is due to the increase in the grain size observed for heat-treated samples[11].

3-Absorption Coefficients:The absorption coefficient α were determined from the region of high absorption i.e. at the fundamental absorption edge of the films using the equation ($\alpha = 2.303\ (x/d)$ [12]where d: is the thickness of the film,(x) the absorbance represents the logarithm of the reciprocal (T)).Fig.(3a and b) shows the dependence of the absorption coefficient on the Cu concentration as a function of photon energy for as-deposited and annealed pure SnS_2 films and doped with Cu (1,2,3,4wt%) films .From this figure we can observe that the optical absorption coefficient for all films were fairly high values reached above $10^4 cm^{-1}$, and found that the α decreases with heat treatment for all samples as shown in (6b), and this is due to the increasing the value of optical energy gap after annealing process. This result agrees with the result of Thangargju et.al.[10].

4- The Optical Energy Gap Measurements: The optical energy gap values (E_g^{opt}) for SnS_2 and SnS_2:Cu films have been determined by using Tauc [5]equation ($(\alpha(\nu)h\nu = B(h\nu - E_g^{opt})$) where ν is the frequency of the incident radiation, B is constant, which depends on density of state (DOS) of conduction and valence bands, E_g^{opt} is the optical energy gap [13], r is a constant depend on the nature of the transition.

) which is used to find the type of the optical transition by plotting the relations $(\alpha h\nu)^2$, $(\alpha h\nu)^{2/3}$, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ versus photon energy (hν) and select the optimum linear part. It is found that the first relation yields linear dependence, which describes the allowed indirect transition. E_g^{opt} is then determined by the extrapolation of the portion at (αhν =0) as shown in Figs.(4a and b).

The optical energy gap SnS_2 was 2eV and these results agree with the results of the energy gap versus concentration studied by Amalraj et.al.[10] and with George et.al.[14].

The optical energy gap was found to increases after heat treatment, this increasing is attributed to existence of a tails below the fundamental absorption edge (near the bands) which observed in the absorption coefficient Fig.(5a), which is a characteristic of most of the optical data on polycrystalline semiconductors which is considered to be determined mainly to the structural disorder existing at the grain boundaries[16], these tails decreased after heat treatment due to the increasing in crystallite size and the grain boundaries became more ordered than in as-deposited films.

5- Optical Constants

5-1 Refractive Index: Fig.(6) shows the variation of refractive index with photon energy as-deposited and annealed SnS_2 and SnS_2:Cu films have been determined by using the equation:

$$\boldsymbol{n}=\left(\frac{4R}{(R-1)^2}-k^2\right)^{1/2}-\frac{(R+1)}{(R-1)}$$

where R is the reflectance[8], k is the extinction coefficient . It is found from this figure that the refractive index decreases with the increasing of wavelength of the incident photon.

We can observed the appearance of a peak occur in dispersion of the refractive index of the films, this was attributed to the rapid change in the optical absorption coefficient in the vicinity of the absorption edge[14].

The refractive index increases after the heat treatment probably due to the increase of the compactness of the films after the heat treatment simultaneously with the increase of the crystallite size.

5-2 Extinction Coefficient

The extinction coefficient[15], which calculated from the relation: $k=\frac{\alpha\lambda}{4\pi}$

The relation between the extinction coefficient and wavelength for SnS_2 and SnS_2:Cu films deposited at 603K and heat treated at 473K with different values of x is shown in Fig.(6). From this figure it is found that the extinction coefficient (k) takes the similar behavior of the corresponding absorption coefficient.

One can deduce from this figure that the extinction coefficient increased with decreasing the photon energy up to ≈ 3.647eV due to the high values of the absorption coefficient at this range of wavelength, after that the extinction coefficient increased very slightly which is associated with the increasing of the transmittance in this region and the large decreasing of the absorption coefficient at this wavelength.

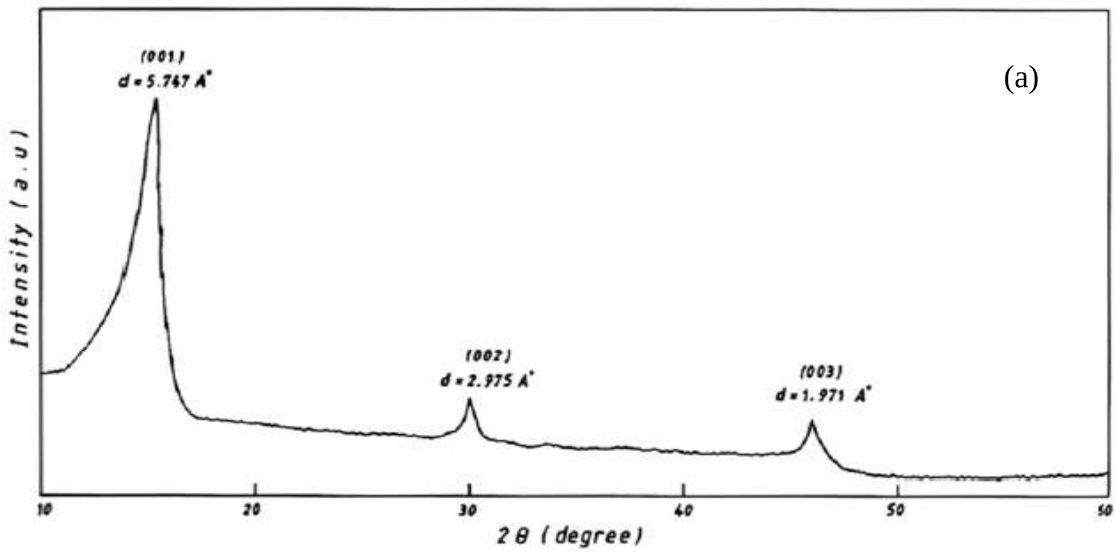
The extinction coefficient is affected by heat treatment, which is decreased after annealing process. This behavior of the extinction coefficients values similar to that of the absorption coefficients for the same reasons as mentioned before.

5-3 Dielectric Constant

Figs.(7) and (8) show the variation of the real (ε_1, which calculated from the relation $\varepsilon_1 = n^2 - k^2$ [16,17]) and imaginary (ε_2, which calculated from the relation $\varepsilon_2 = 2nk$ [17]) parts of the dielectric constant with photon energy as-deposited and annealed SnS_2 and SnS_2:Cu films. The behavior of ε_1 and ε_2 is the same as that of n and k, respectively with the variation of x values and heat treatment. This due to that the variations of ε_1 mainly depends on the value of (n^2), because of the smaller values of (k^2) comparison with (n^2), while the imaginary part of the dielectric constant mainly depends on (k) values which were related to the variations of absorption coefficient.

4-Conclusions

1. The X-ray diffraction observed that the prepared films were of poly crystalline kind of the hexagonal.
2. It is observed from the transmission spectrum that the thin films surfaces and thickness was uniform .
3. The refractive index in SnS_2 and SnS_2:Cu films varies with varying the composition by non-linear relation. The refractive index increases after heat treatment due to the increasing in the films compactness.
   The variation of real and imaginary parts of dielectric constant have similar trends as for refractive index and extinction coefficient respectively according to Maxwell's equations
4.



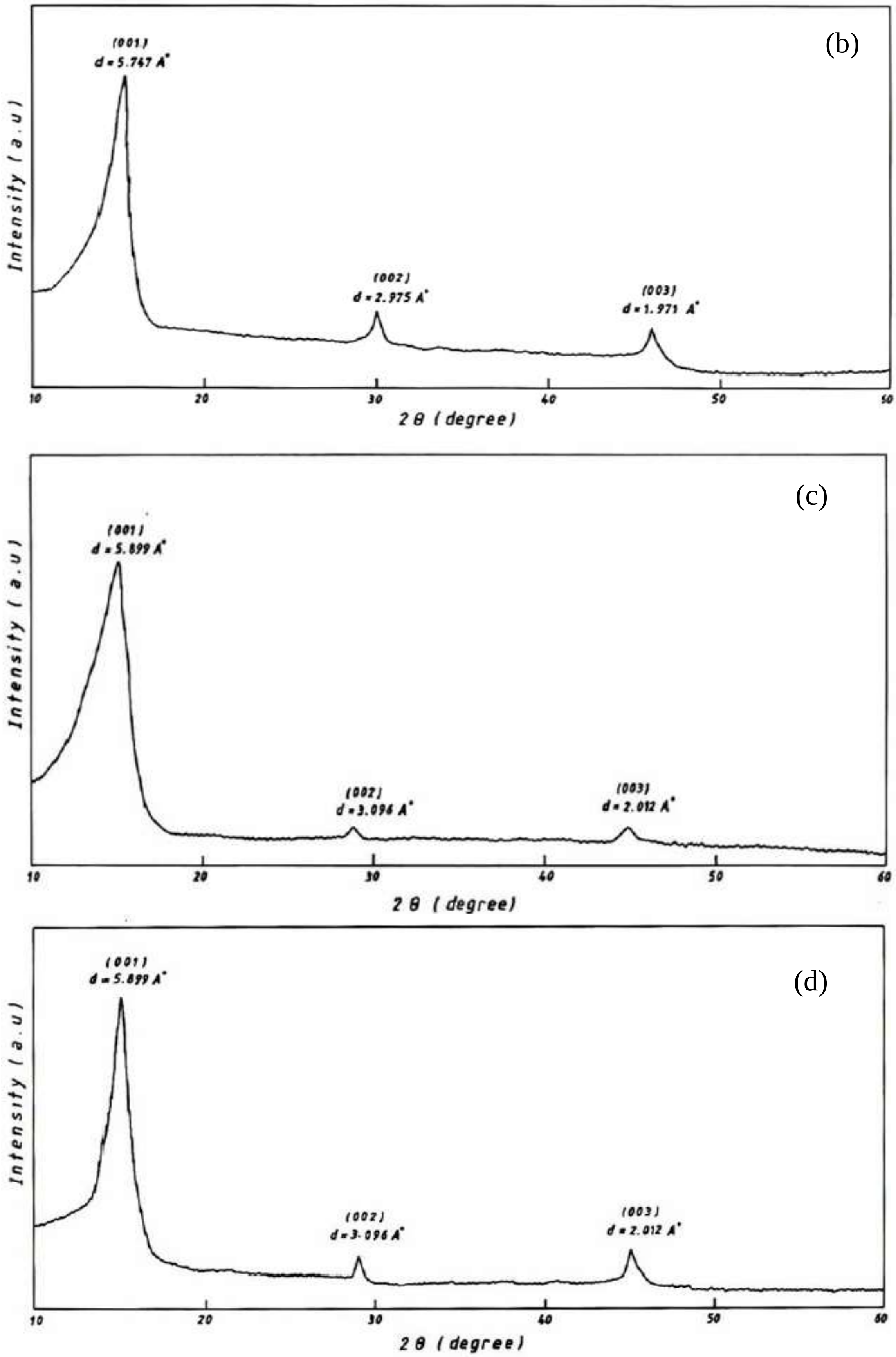


Fig. (1) XRD pattern for a-SnS2films as-deposited and, b-SnS2 films annealed to 473K ,c- SnS2:4%Cu films as-deposited ,d- SnS2:4%Cu films annealed to 473K.

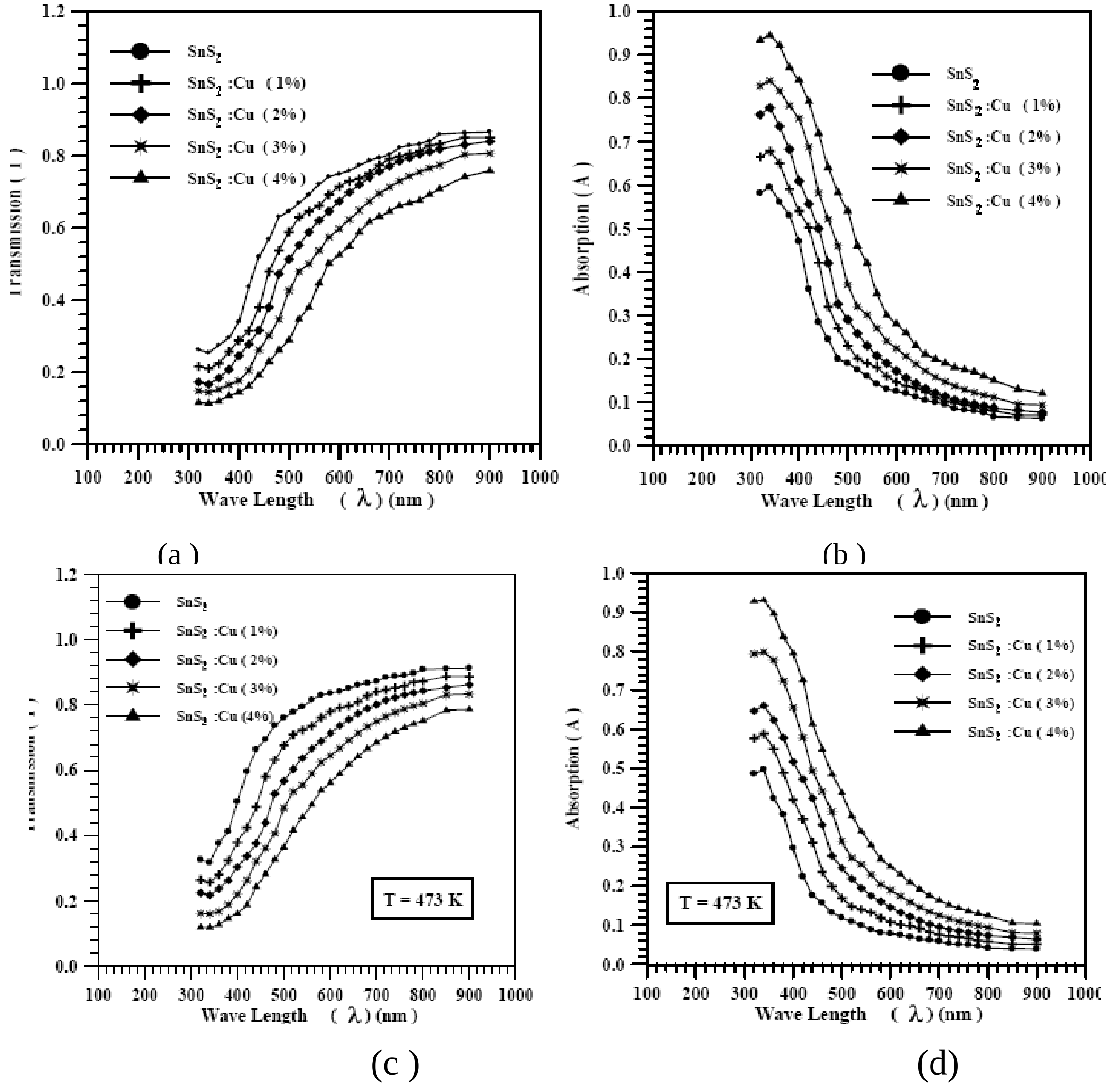


Fig.(2) Transmission spectrum of a-SnS_2:0,1,2,3,4%Cu films as-deposited and,c-SnS2 films annealed to 473K ,absorption spectrum of b- SnS_2:0,1,2,3,4%Cu films as-deposited , and d- annealed to 473K.

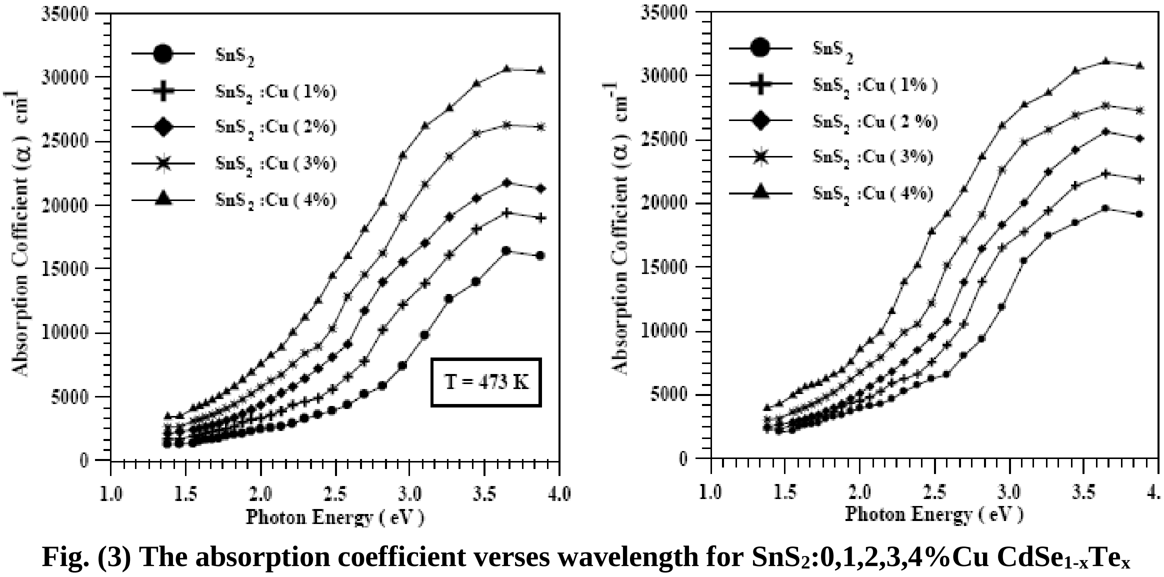


Fig. (3) The absorption coefficient verses wavelength for SnS_2:0,1,2,3,4%Cu $CdSe_{1-x}Te_x$ thin film at different composition (a) as-deposited (b) annealed.

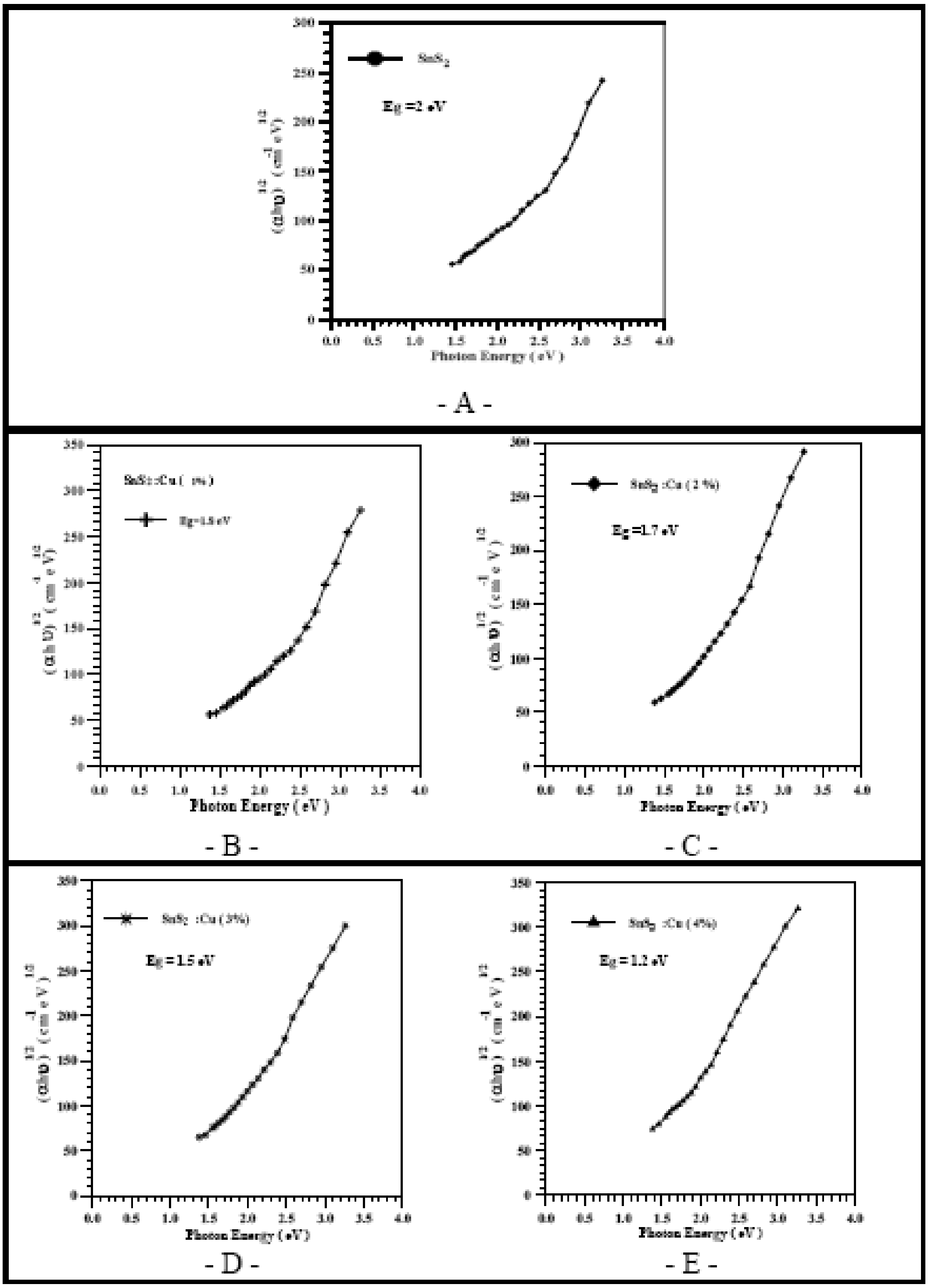


Fig. (4-a) The variation of $(\alpha h\nu)^{1\backslash 2}$ with photon energy for SnS_2:Cu **film at different composition (A) pure - (B) 1%Cu ,(C)- 2%Cu ,(D)-3% Cu(E)-4%Cu.**

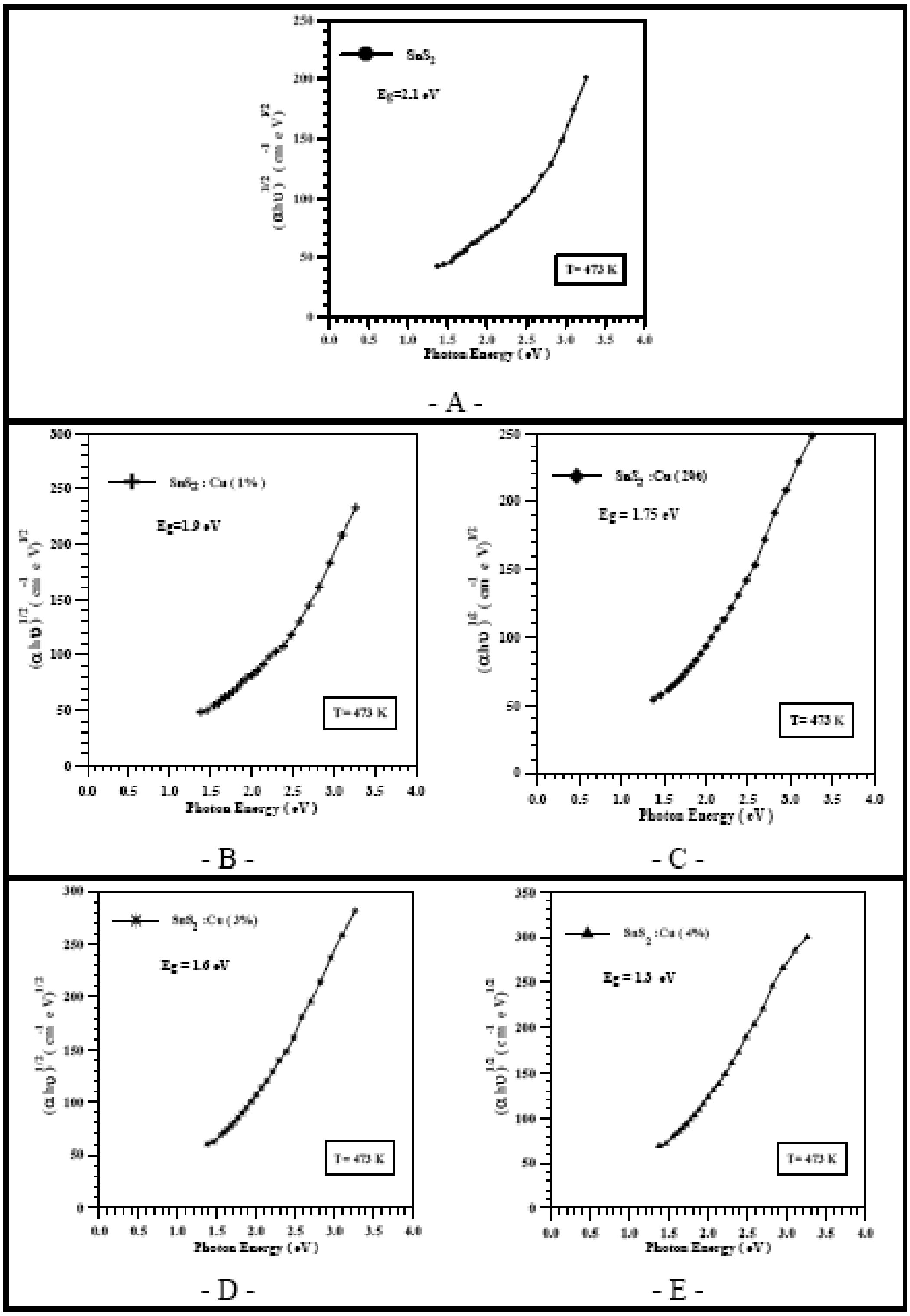
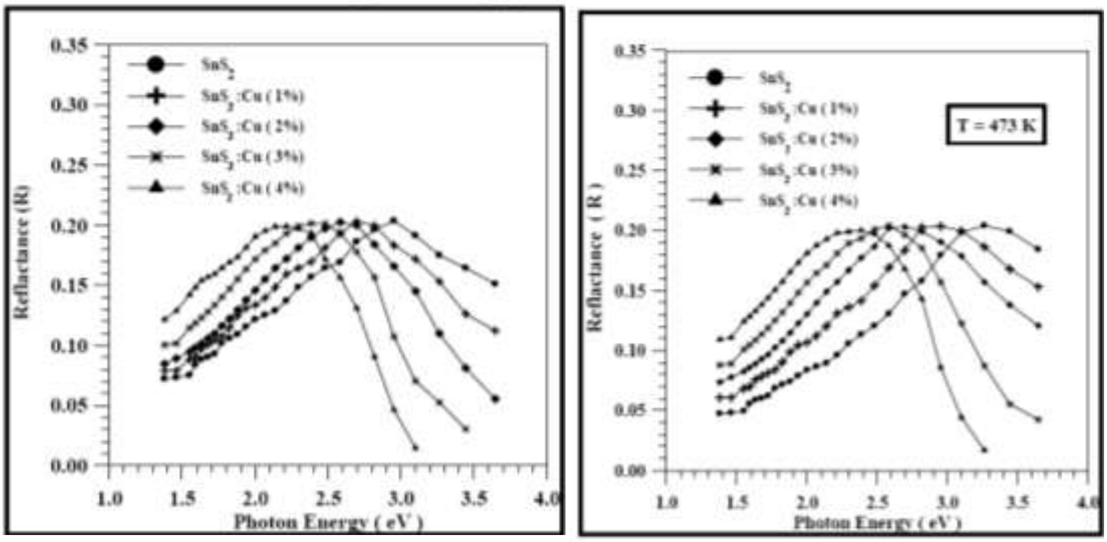


Fig. (4-b) The variation of $(\alpha h\nu)^{1\backslash 2}$ with photon energy for $SnS_{2:}Cu$ **film after annealing (A) pure - (B) 1%Cu ,(C)- 2%Cu ,(D)-3% Cu(E)-4%Cu.**



(a) (b)

Fig.(5) The refractive index as a function of wavelength for as a-deposited and b-annealed SnS_2:Cu thin films.

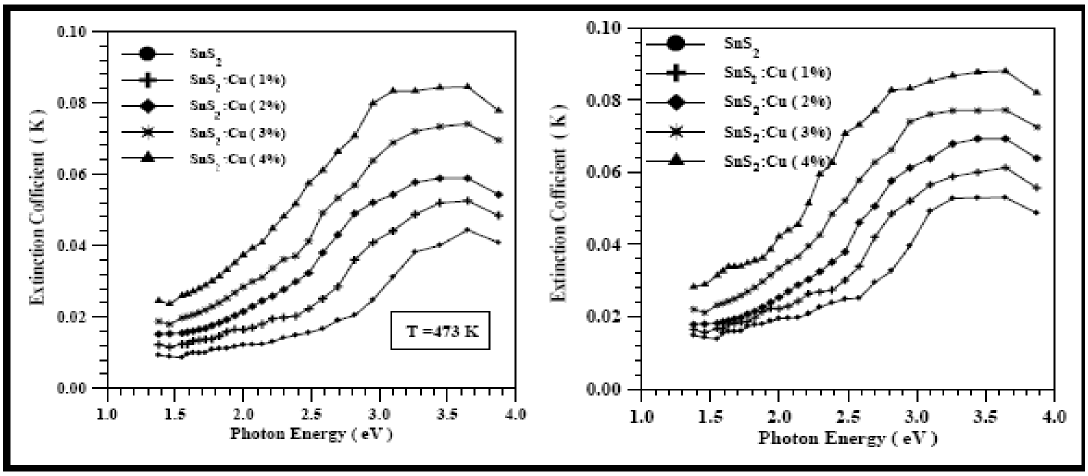


Fig.(6) The extinction coefficient versus wavelength for as-deposited and annealed SnS_2:Cu thin films.

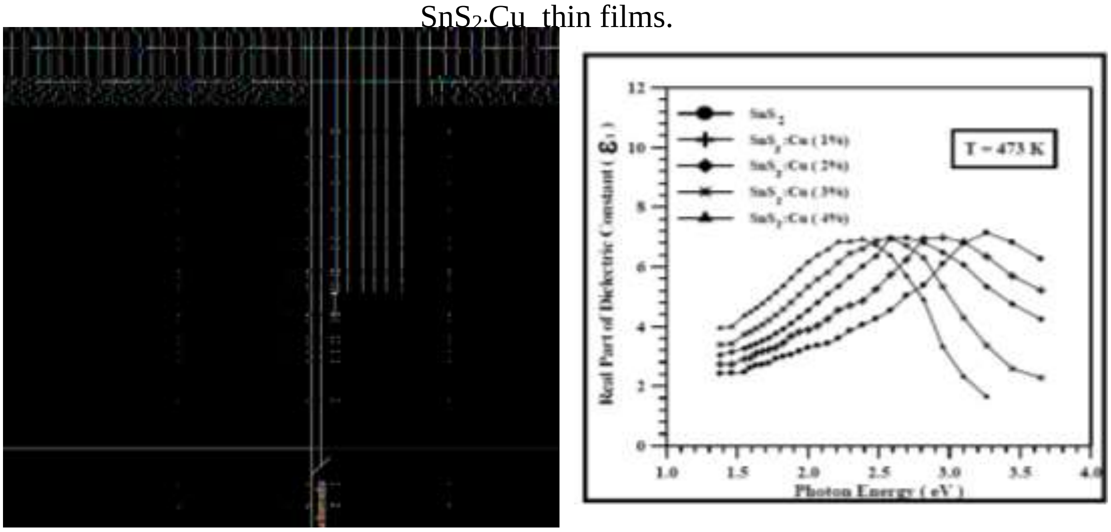
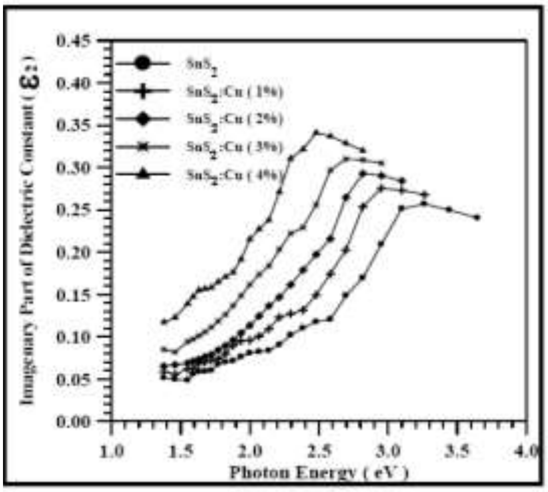


Fig.(7) The real part of dielectric constant as a function of wavelength for as-deposited and annealed SnS_2:Cu thin films



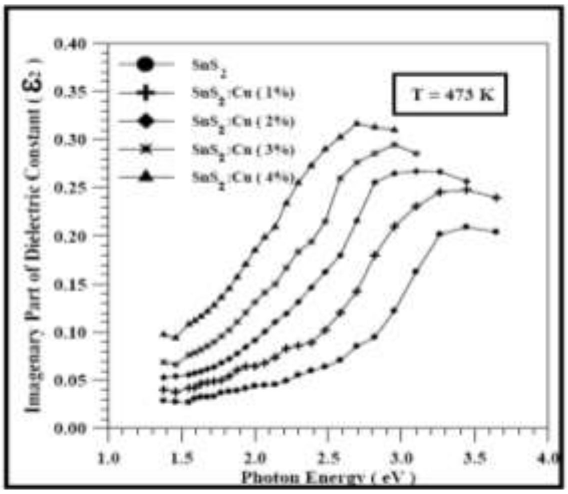


Fig.(8) The imaginary part of dielectric constant versus wavelength for as-deposited and annealed $SnS_{2:}$C thin films

References:

[1]. C. Khelia C., Maiz F.,Mnari M., Ben Nasrallah T., Amlouk A. and Belgacem, (2000) Eur. Phys. J. Ap. **9** ,187 – 193.

[2]. Mandalidis S., Kalomiros J., Kambas K. and Anagnostopoulos A. (1996), J.Mater Sci. **31 ,**5975-5978

[3]. Sankapal B.,ManeR. and Lokhande C. (2000) , Mater. Res. Bull.**35 ,** 2027 – 2035.

[4]HodesG.,ManassanJ.,NeaguS.,CahenD.andMirovskyY.(1982),ThinSolidFilms,90 , 433.

[5] Ravichandran D., Francis Xavier P.,Sasikala S. and S. Moorthy Babu, (1996) , Bull. Master. Sci, Vol. 19, N.3, 437.

[6] Thangaraju B. and Kaliannan P. (2000), J. Phys. D: Appl. Phys. **33 ,**1054 – 1059.

[7] Ji Y., Zhang H., Ma X. , XuJ. and Yang D. (2003), J. Phys. Condens. Mater. **15 ,** 661 – 665.

[8]Yang Q., Tang K., WangC. , Zuo J., Zhang D. and Qian Y. (2003), Thin Solid Films **436 ,** 203 –207.

[9]Sanchez A. Tiburcio A. and Ortiz A. (2005), Thin Solid Films **480 – 481**, 452 – 456.

[10] - Amalraj L., Sanjeeviraja C.and Jayachandran M. (2002), J. Cryst.Growth. **234**, 683 – 689.

[11] Kawano K., Nakata R. and Sumita M. (1989), J. Phys. D: Appl. Phys. **2,** 136 – 141

[12] HodesG., CahenD., Manassan J. and Pavid M.(1970), J. Electrochem.Soc., 127 , 2252.

[13] Mirovsky Y., Tenne R., Hodes G.and Cahen D. (1982), Thin Solid Films, 91 , 349.

[14] George J. and Joseph K. (1982) , J . Phys. D: Appl. Phys. **15** ,1109 – 1116.

[15] Budyonnaya L., Pavelets A., Khanat L. (1983) , Thin Solid Films, 138 , 163.

[16] Ermolovich I., Shinkman M., Sanitarov V. and Kalinkin I. (1983), Sov. Phys. Semicond., 17, 923.

[17] Ermolovich I. and (1986)Milenin V. (1986) , Phy. Stat Sol. (b) 133 , 611.

الخواص SnS2:Cuالرقيقة المحضرة بطريقة التحلل الكيميائي الحراري التركيبية والبصرية لأغشية

*ندى خضير عباس * أنوار علي باقر* أسماء كاظم* نضال علي***

*قسم الفيزياء ،كلية العلوم للبنات ، جامعة بغداد
** قسم الفيزياء ، كلية التربية ، جامعة ديالى

الخلاصة:

حضرت أغشية رقيقة من ثنائي كبريتيد القصدير (SnS_2) النقية والمشوبة بالنحاس بنسب التشويب (1,2,3,4)% بتقنية الرش الكيمياىٔ (SnS2:Cu) بنسب التشويب (1,2,3,4)% بتقنية الرش الكيميائي الحراري (Chemical spray pyrolysis technique) على قواعد من الزجاج مسخنة بدرجة حرارة (603K) وبسمك μm (0.02 ± 0.7) وبعد ذلك تمت معاملة الأغشية حرارياً تحت ضغط واطئ mb(3- 10) بدرجة حرارة K 473 لمدة ساعة واحدة درس تأثير كل من التشويب بالنحاس والمعاملة الحرارية (التلدين بدرجة حرارة K 473 على بعض الخصائص الفيزيائية للأغشية المحضرة (التركيبية والبصرية أظهرت فحوصات الأشعة السينية بأن الأغشية المحضرة ذات تركيب متعد التبلورPolycrystalline)ومن النوع السداسي (Hexagonal) تبين من الدراسة البصرية التي شملت أطياف الإمتصاصية والنفاذية في المدى الطيفي-300 (900) أن قيم معامل الإمتصاصα للأغشية النقية والمشوبة اكبر من nm(1-104 cm) كما وجد أن الإنتقالات الألكترونية عند حافة الإمتصاص الأساسية كانت من نوع الإنتقال غير المباشر بنوعية المسموح والممنوع، وإن قيمة فجوة الطاقة البصرية في حالة الإنتقال غير المباشر المسموح تقل من eV 2الى eV عند نسب التشويب (1,2,3,4)% (1.94eV الىeV في حالة (1.2,1.5,1.7,1.8) على التوالي بينما تقل من (1.1,1.3,1.5,1.7) الانتقال غير المباشر الممنوع ولنسب التشويب نفسها، وكذلك وجد أن قيمة فجوة الطاقة للأغشيةالنقية والمشوبة تزداد بعد التلدين كما استعملت أطياف الإمتصاصية والنفاذية أيضًا في إيجاد الثوابت البصرية المتضمنة الجزء الحقيقي لثابت العزل(1) ε ومعامل الخمود k ومعامل الانكسار n والانعكاسية R والجزء الخيالي لثابت العزلε2 ووجد أن جميع الثوابت البصرية تتأثر بتغير نسب ، التشويب، كما إنها تبدي تأثرًا بعد معاملة الأغشية حرارياً.