Structural and Optical Properties of SnS₂:Cu Thin films prepared by chemical Spbay Pyrolysis

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Abstract:

Thin films have been prepared from the tin disulphide (SnS₂), the pure and the doped with copper (SnS₂-Cu) with a percentages (1,2,3,4)% by using a chemical spray pyrolysis technique on substrate of glass heated up to(603K) and with thicknesses (0.7±0.02)μm, after that the films were treated thermally with a low pressure (10⁻⁷ mbar) 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 absorbance and transmittance spectra in the wavelength range (300-500) 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.

The absorption and transmission spectra were used to find the optical constant involving refractive index(n), extinction coefficient(k), imaginary and real part of dielectric constant \(\varepsilon_r=\varepsilon_0\) , 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 thermally.

Key word: Optical, Structural Properties, SnS₂, SnS₂: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.

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because of the technological importance of their practical applications\cite{4}.

High absorption region observed for most semiconductors at $\omega \geq 10^4 cm^{-1}$; the absorption is due to the transitions between extended states in both bands. The empirical formula that governs this transition has been found by Tauc \cite{5}.

Optical properties of SnS$_2$ thin films were studied by Thangaraju et al.\cite{6}, Ji et al.\cite{7}, Yang et al.\cite{8}, and Sanchez et al.\cite{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$_2$O 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 of SnCl$_4$.H$_2$O and (0.572g) of SnS$_2$ were used. Concentrations of these two materials are weight needed from each of them, melted in 25 liters of distilled water, according to the following equation:

\[
M = \left( \frac{W_i}{M_{mol}} \right) \cdot (1000/V)
\]

\text{(1)}

\text{Wt: Weight of the material (gm), V: Volume (L), M: Mole concentration (M/L), M wt: Molecular weight (gm/mol)}

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 2 Kg 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:

\[
\text{NH}_2\text{SCNH}_3 + 4\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{H}_2\text{S} + 4\text{NH}_3 + 2\text{SO}_2
\]

\[
\text{SnCl}_6 + 2\text{H}_2\text{S} + 4\text{H}_2\text{O} \leftrightarrow \text{SnS}_2 + \text{H}_3\text{O}^- + 6\text{Cl}^-
\]

\text{(2)}

To prepare SnS$_2$:doped with copper Cu, we added CuCl(1,2,3,4wt%) to SnCl$_4$.H$_2$O and CS(NH$_2$)$_2$ solution. According to the following equation:

\[
\text{CuCl}_2 \rightarrow \text{Cu} + \text{Cl}_2\uparrow
\]

\text{.............(3)}

SnS$_2$ and SnS$_2$:Cu films were prepared on glass substrates. The thickness of prepared samples were in the range of \((0.7 \pm 0.2)\mu m\) which determine using Weight Method and optical 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 CuK$\alpha$ radiation from a Philips pM

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1050/70 diffractometer. The values of interplaner spacing and intensity ration is exactly the same as that of the ASTM data of SnS₂ the golden-yellow colour of the films becomes grey-black when the samples are heated to 403°C, mostly probably due to the formation of SnS or Sn₃S₄ 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 model UV-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 SnS₂ 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 crystalized with a strong peak at (001) directions, while in fig. (1c,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], Khelai et.al. [1] and Sanchez et.al [9] but it disagreement with Kawanro et.al [11]

2. The Transmission And Absorption Spectrum

The experimental transmission spectrum for as-deposited and heat treated pure SnS₂ films and doped with Cu (1.2,3,4wt%) films, respectively, in the wavelength 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 (α = 2.303 (α/d)) [12] where d is the thickness of the film, (α) the absorbance represents the logarithm of the reciprocal (1/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 SnS₂ 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 10⁶cm⁻¹, and found that the α decreases with heat treatment for all samples as shown in (6a), and this is due to the increasing the value of optical energy gap after annealing process. This result agrees with the result of Thangaraj et.al [10].

4. The Optical Energy Gap Measurements: The optical energy gap values (E₉) for SnS₂ and SnS₂-Cu films have been determined by using Tuac (αhv)νhν =B(hν-E₉) where ν is the frequency of the incident radiation, B is constant, which depends on density of state (DOS) of
conduction and valence bands, $E_g^{\text{opt}}$ 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 $(\alpha h\nu)^2$, $(\alpha h\nu)^{5/3}$, $(\alpha h\nu)^{2}$ and $(\alpha h\nu)^{3}$ versus photon energy ($h\nu$) and select the optimum linear part. It is found that the first relation yields linear dependence, which describes the allowed indirect transition. $E_g^{\text{opt}}$ is then determined by the extrapolation of the portion at $(\alpha h\nu =0)$ as shown in Figs. (4a and b).

The optical energy gap SnS$_2$ was 2 eV 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:

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

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[13], which calculated from the relation:

$$\kappa = \frac{\alpha \lambda}{4\pi}$$

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 ($\kappa$) 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 \( \varepsilon_1 \) which calculated from the relation \( \varepsilon_1 = n^2 - k^2 \) \(^{[16],[17]} \) and imaginary \( \varepsilon_2 \) 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 \( \varepsilon_1 \) and \( \varepsilon_2 \) 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 \( \varepsilon_1 \) 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-SnS2 films as-deposited and, b-SnS2 films annealed to 473K, c-SnS2:2.4%Cu films as-deposited, d-SnS2:2.4%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$_{0.8}$Te$_{0.2}$ thin film at different composition (a) as-deposited (b) annealed.
Fig. (4-a) The variation of \((\alpha h\nu)^{1/2}\) with photon energy for SnS₂-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 $(ohv)^{1/2}$ with photon energy for SnS$_2$-Cu film after annealing (A) pure - (B) 1%Cu - (C) 2%Cu - (D) 3% Cu - (E) 4%Cu.
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:


الخواص المحضرة بطريقة التحلل الكيميائي الحراري

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الخلاصة:

ال>m حضرت أغشية رقيقة من ثنائي كربونيد التصدير (SnS2) (النقيّة والشمعية بالنسب) بنسب التشويب (1,2,3,4,5)% بنقية الرقائق الكيميائي الحراري (SnS2:Cu) على قطع من الزجاج سماكة بدرجة حرارة (Chemical spray pyrolysis technique) (603K) وسمك (0.02 · 0.7μm) وبعد ذلك تم عمل معايير الأغشية تحت ضغط وصاف و زوايا (10°) بدرجة حرارة (673K) لمدة ساعة واحدة. رس تأثير كل من التشويب بالنصل والمسح والمسح الحراري (التيدين بدرجة حرارة 647K) على بعض الخصائص البصرية لأغشية المصدرة (التركيبية والبصرية أظهرت عمليات قواعدية POLYCRYSTALLINE) (الأشعة السينية) بأن الصورة المحضرة ذات تركيب من الأغشية تحت ضغط وصاف و زوايا (10°) السطحية التي تمت التlcية الإلتصاصية والذاتية في المدى الطيفي (300-900 nm) على أن معامل الإلتصاص للأغشية الشمعية أكبر من ×104 لمن 100 nm انقلاب الإلتصاص. السطحية كانت من نوع الإلتصاص: نسب التشويب (+1)−1 من 2 في S2 في E (1.94 eV) في حالة (1.8,7,1.5,1.4,1,2,3,4,5,6,7) وحدة الهيدروكربون قوة البصرية للفئات المنفردة: $

\text{R} = \frac{k}{\text{معامل الإلكسارية}}$

(1) وحدة الهيدروكربون قوة البصرية للفئات المنفردة. ووجد أن جميع النواتج البصرية تتأثر بنسب التشويب، كما أنها تتأثر بعد معامل الأغشية حرارة.