The Effect of Cobalt Dopant on Structural and Optical Properties of Tin Sulfide Thin Films

Hanaa Kadem Essa[1], Saja Faez Hassan [2], Oday Ali Chichan[3]
[1]Department of Physics, College of Education, Mustansiriyah University, Iraq.
[2]Department of Physics, College of Education for Pure Sciences, University of Babylon.

Abstract

SnS and SnS: Co thin films wad deposit by chemical spray pyrolysis (CSP) method on 450□C heated glass substrates. XRD study revealed that the films all films are polycrystalline diffraction, and the predominant peak was (111) plane. The grain size of SnS and doped SnS: 3 % Co is 19.07 nm and 21.58 nm, respectively, whereas the strain (%) parameter decreases 18.17 to 16.06. The produced film has a transparency of about 85%, which declines as the doping concentration increases. The optical band gap reduced from 1.57 eV for SnS thin film to 1.45 eV for 3 % Co doped Tin sulfide film. The absorption coefficient (α) increases with Cobalt content, whilst the extinction coefficient and refractive Index have decreased with Cobalt content in Tin sulfide thin films.

Keywords: Tin sulfide, Cobalt doping, X-ray diffraction, optical properties, band gap.

Introduction

Given Giving its favorable physical characteristics, tin sulfide (SnS) is a highly beneficial chemical compound for a wide range of technical applications including but not limited to optoelectronics, photo voltaics, and solar cells. Modifying the molecular arrangement of the molecules can control these features. [1]. SnS is a p-type semiconductor [2]. SnS has an optical band gap of 1.3 eV and is an IV-VI compound [3]. Theoretically, SnS has a conversion efficiency of 24% [4]. A significant number of techniques for depositing SnS thin layers were realized. as CSP [5], CVD [6], CBD and electro deposition [7,8], and PVD [9]. For solar cells, the thermal vaporization technique produces stoichiometric layers with an approved thickness of several micro metres that are devoid of pinholes, well adhesive to the base, and have high electro-physical properties for use in solar cells. [10]. This study used a low-cost technique (CSP) to prepare SnS thin films with various doping concentrations. The structural and morphology properties of the produced Tin sulfide thin films have been examined. The transmittance and some optical constants of the produced films are also measured in the range between 300-900 nm. Moreover, the influence of Co doping on optical energy gap is also shown.

Experimental

SnS and SnS: Co films were grown via CSP. 0.1M of Sn [$C_4H_6SnO_4$] and 0.1M of [$CH4N_2S$] as sources of Sn and S ions respectively. Doping was made by adding ($CoCl_3$) molecules which resolve by redistilled water. HCl have added the solution to make it clear. This solution was applied to a warmed glass substrate that was fixed at 400 ^oC. Following a large number of experiments, the best parameters were determined to be as follows. The spraying rate was set at 5 milliliters per minute, the sprayer time was followed by an interval of one minute to completely limit cooling, and the carrier gas that was chosen was nitrogen. The distance that separated the base and the injector was 30 centimeters. The gravimetric method was used to perform the measurements, and the findings were revealed to be in the range of 310±35 nm. With the help of a double beam spectrophotometer (UV Spectrophotometer Shimadzu Model UV-1800), the optical characteristics such as transmittance and absorbance were measured and recorded. The XRD (X-ray diffractometer (Shimadzu, model: XRD-6000, Japan) was used to examine the structure of the film in which the film structure probably came from., while the AFM (AA 3000 Scanning Probe Microscope) was employed to establish the film morphology.

Results and Discussion

Figure 1 displays XRD patterns of the intended films. It can be observed that the films have peaks at 28.62°, 33.13°, 56.31° and 69.42° attributed to the (111), (200), (220) and (400) planes respectively. The Figure offers a diffraction peak at (2θ = 28.62°) with Miller indices (111) indicating a crystal structure, which agreed with ICDD card No-05-0566.

Grain size (D) was calculated from the highest intensity peaks utilizing Scherrer's equation [11, 12].

$$D = \frac{0.9\lambda}{\beta cos\theta} D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

Wavelength (λ) of X-ray used is equal to (1.5406 Å), β represents FWHM and θ is diffraction angle. *D* changes its value from 19.07 to 21.58 nm with Cobalt content as evidenced in Table. 1

Dislocation density (δ), which represents a number of defects of the film and strain (ε) are also evaluated [13, 14].

$$\delta = \frac{1}{D^2} \delta = \frac{1}{D^2} \qquad (2)$$

$$\varepsilon = \frac{\beta cos\theta}{4} \varepsilon = \frac{\beta cos\theta}{4} \qquad (3)$$

whilst dislocation density decreased from 27.49 to 21.47, whilst strain decreased from 18.17 to 16.06.

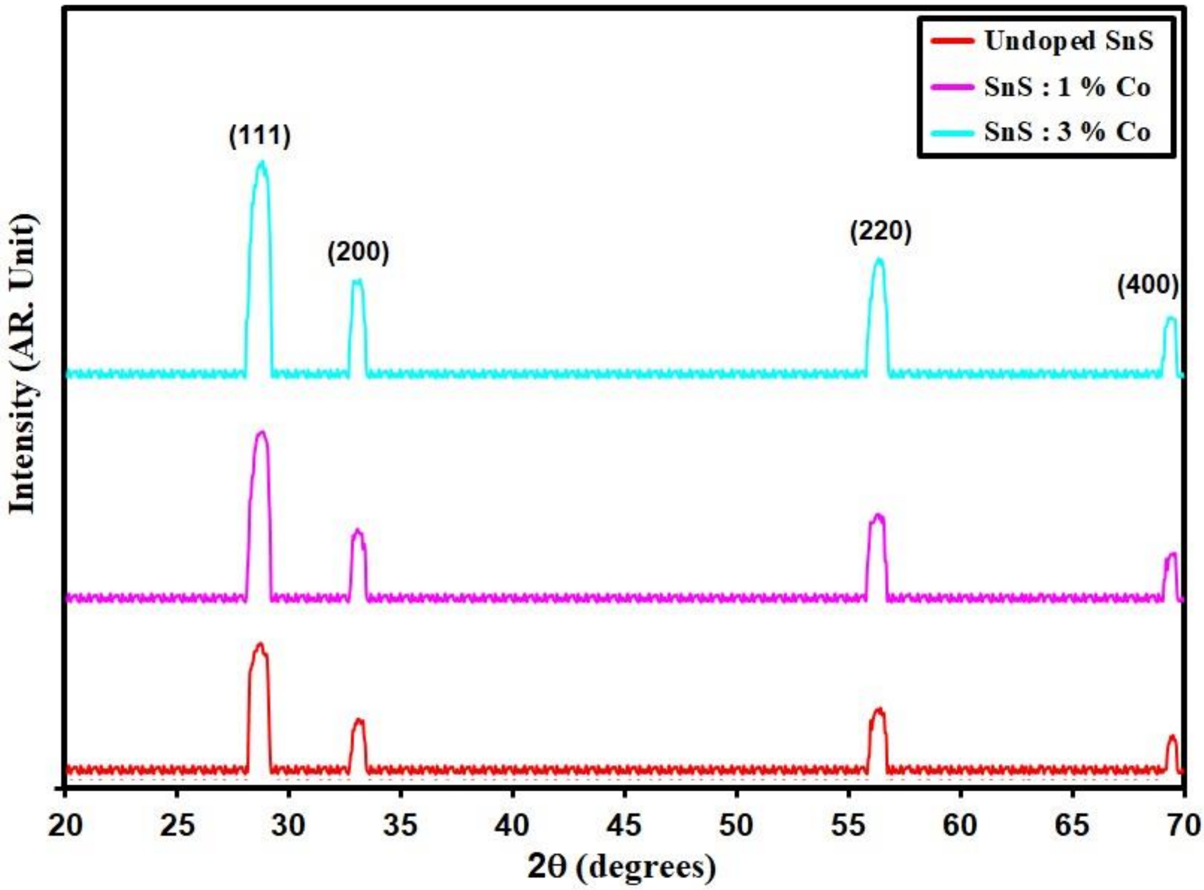

Figure1. XRD-patterns a crystalline size.

Table 1 Grain size, optical band gap and structural parameters of the grown films.

Specimen	2 θ (°)	(hkl) Plane	FWHM (°)	E_g (eV)	*D* (nm)	δ (× 10^{14}) (lines/m^2)	ε (× 10^{-4})
Undoped SnS	28.62	100	0.428	1.57	19.07	27.49	18.17
SnS: 1% Co	28.60	100	0.408	1.51	20.50	23.79	16.90
SnS: 3% Co	28.57	100	0.383	1.45	21.58	21.47	16.06

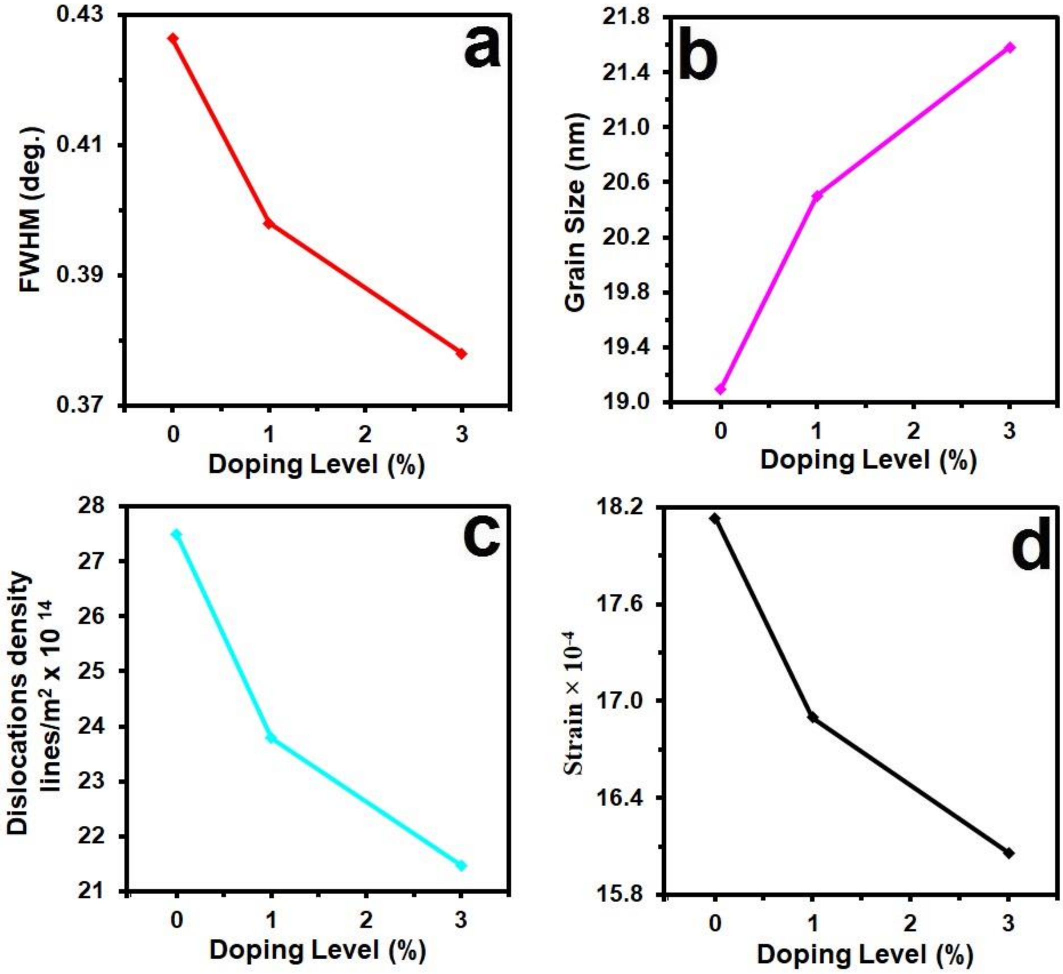

Figure 2. FWHM (a) *D* (b) δ (c) ε (d) of the grown films.

Figure 3 displays the optical absorption spectrum of all SnS films. The transparency of the films lowered when the Cobalt dopant concentration was raised. The absorption coefficient (α) of the film could be counted using the relation [15]:

$$\alpha = \frac{2.303\,A}{t} \quad (4)$$

Where (A) represents the absorption of the film, (t) is the film thickness. Fig. (4) Shows the relation of absorption coefficient (α) and doping concentration. The absorption coefficient slightly rise with increasing Cobalt content.

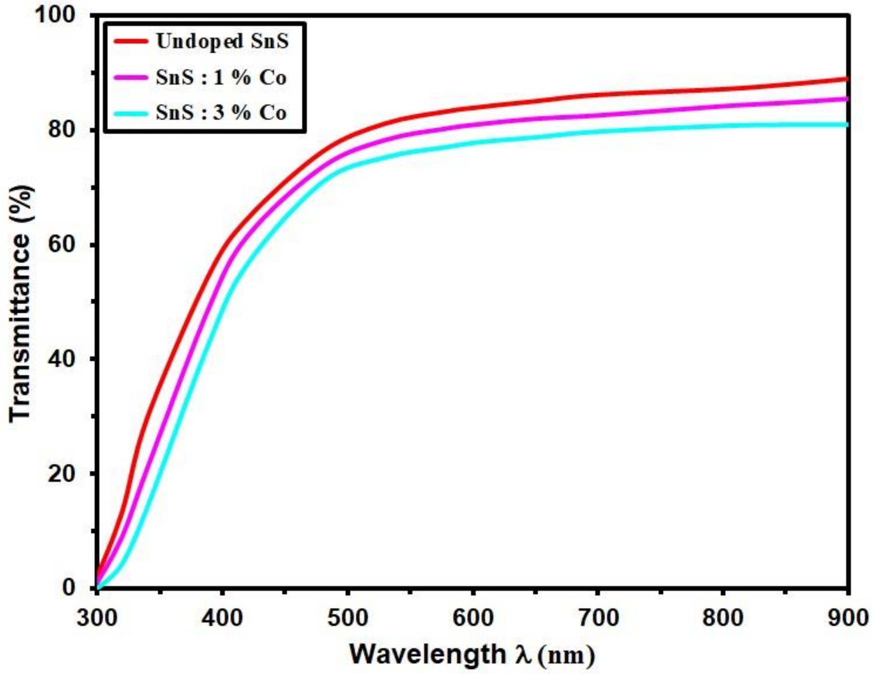

Fig. 3: Transparency of the grown films.

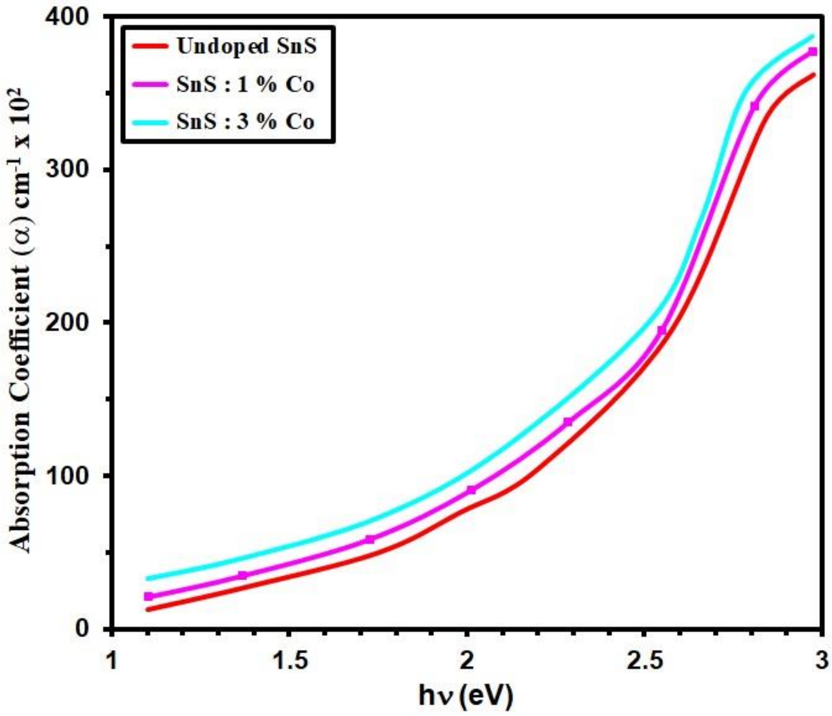

Fig. 4: the absorption coefficient for deposited films.

The band gap was calculated using the relation [16]:

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^{\frac{1}{2}} \qquad (6)$$

Where A is the constant, $(\alpha h\upsilon)^2$ against (hυ), plots are offered in Figure 5. As SnS is a direct transition semiconductor. E_g decreased from 1.57 to 1.45 eV as the 3 % Co doping. In fact, increasing Cobalt content may prompt a deformation of crystalline state, which leads to modifications in the electronic structure [17]. As a result, the reduction in optical band gap with growing Cobalt content can be related to the existence of unstructured defects, which increase the density of localized states in the bandgap and, as a result, lower the energy gap [18].

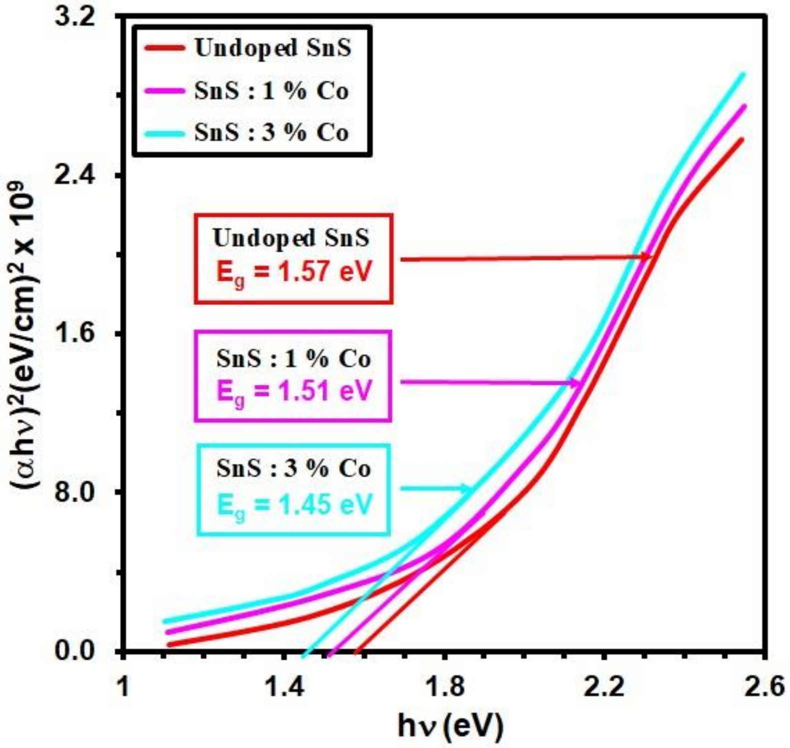

Fig. 5: $(\alpha h\nu)^2$ versus hν for the SnS with different Cobalt doping.

Index of refraction (n) of the films is a valuable parameter for optoelectronic devices design. Such designs like optical filters, solar cells, and high stability resistors. For calculations of n and extinction coefficient (k) of the films at various wavelengths, the following relations are used [19, 20]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad \text{----- (7)}$$

$$k = \frac{\alpha\lambda}{4\pi} k = \frac{\alpha\lambda}{4\pi} \quad \text{----- (8)}$$

Where R is the reflectivity, and λ is the wavelength. Index of refraction of the films was counted as in Eq. (7) and the variation of n according to wavelength is shown in Figure 6. Samples used showed the same behavior in n spectra. A little lower in refractive index values with increasing Cobalt content in Tin sulfide thin films is noticed. The samples' (n) values vary between (3.25–3.11). Lowering the refractive index can refer to the density and surface roughness [21]. All samples have the same variation in their k value, and they all have the same tendency according to the curves of n. The k value of a material is directly related to the absorption quality of the material. As may be seen in Figure 7, k values become quite insignificant only at long wavelengths, because of films transparency. The films' n and k are lowered with increasing Co content.

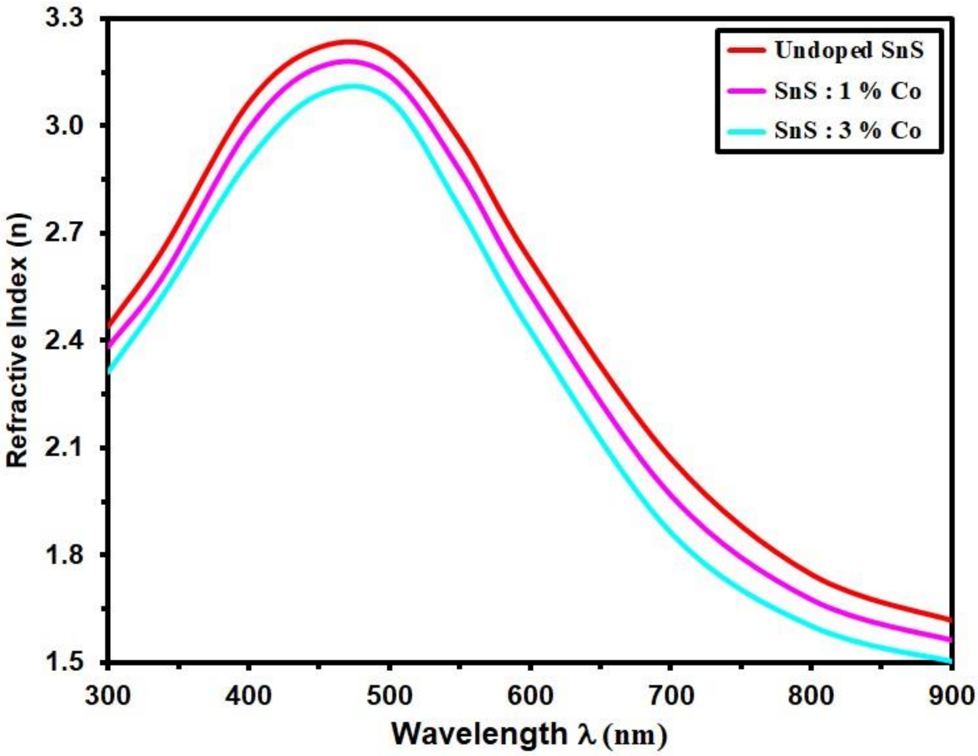

Fig. 6. Index of refraction for grown films.

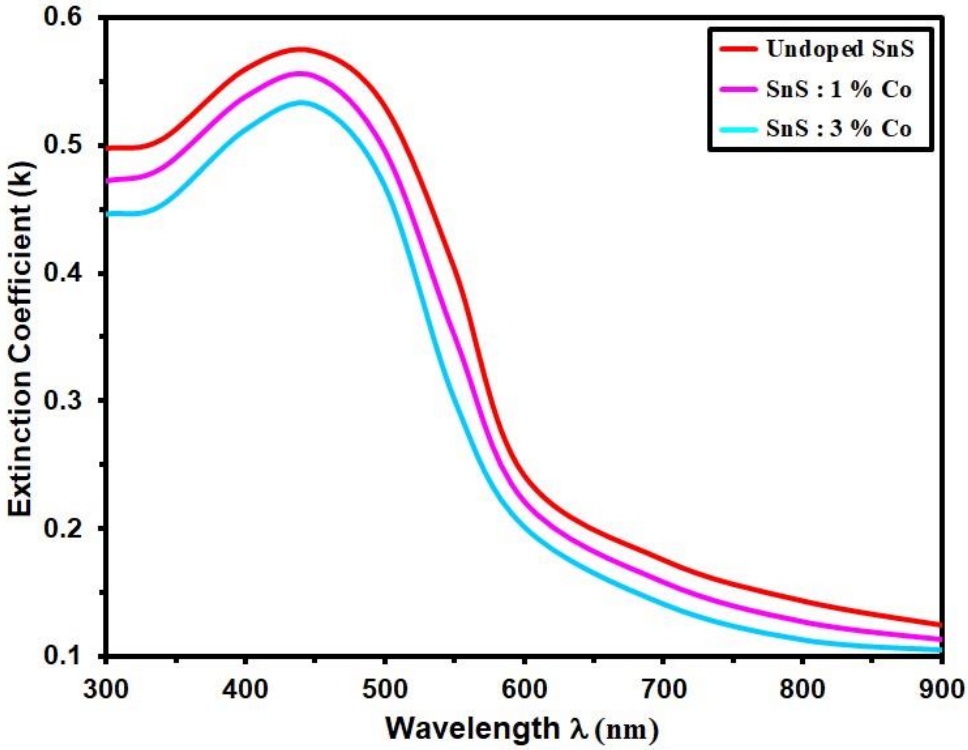

Fig. 7: Extinction coefficient of the grown films.

Conclusion

Undoped SnS and Cobalt doped Tin sulfide films have grown successfully via CSP technique. The influences of two Cobalt concentrations (1% and 3%) on the film growth, its optical, structural and morphological properties have been studied. XRD result showed the predominant peak of maximum intensity corresponds to the preferred orientation (100) for SnS films at 3% Cobalt. The crystallite sizes were raised from 19.07 nm to 21.58 nm, whilst strain decreased from 18.17 to 16.06, whilst dislocation density decreased from 27.49 to 21.47. optical bandgap tuning were estimated from UV-Vis spectra. The maximum transmittance and the minimum bandgap value of 1.45 eV were observed. The absorption coefficient (α) increases with Cobalt content in Tin sulfide thin films.

References

[1] A. Starvinadis, J. M. Smith, C. A. Cattley, A. G. Cook, P. S. Grant, and A. A. R. Watt, "SnS/PbS nano crystal heterojunction photovoltaics", Nanotechnology, Vol.21, pp.185202–185208, (2010).

[2] A. Tanuševski and D. Poelman, "Optical and photoconductive properties of SnS thin films prepared by electron beam evaporation", Sol. Energy Mater. Sol. Cells, Vol. 80, pp. 297-303, (2003).

[3] M. Parenteau and C. Carlone, "Influence of temperature and pressure on the electronic transitions in SnS and Snse semiconductors", Phys. Rev., Vol. 41, No. 8, pp. 5227–5234, (1990).

[4] B.K. Pandey and Ram Gopal, "Synthesis and Mn doped Band gap Engineering in SnS Nanoparticles," Materials Letters, 272, 127840-127852(2020).

[5] Sudha M, Duraisamy P. Optical and structural studies on SnS thin films grown by spray pyrolysis technique. J Optoelectron Adv Mater 2012; 11:999-03.

[6] Engelken R D, McCloud H E, Lee C, Slayton M and Goreishi H 1987 Journal of the Electrochemical Society 134 p 2696

[7] Safonova M, Nair P K, Mellikov E, Garcia A R, Kerm K, Revathi N, Romman T, Mikli V and Volobueva O 2014 J Mater Sci: Mater Electron 25 3160

[8] Mishra K, Rajeshwar K, Weiss A, Murley M, Engelken R D, Slayton M and McCloud H E 1989 Journal of the Electrochemical society 136 p1915

[9] Goswami A and Mitra A 1975 Indian Journal of Pure and Applied Physics 13 p 508

[10] Ogah O E, Zoppi G, Forbes I and Miles R W 2008 Proc. 23 EUPVSEC, 1-5 Sept., Valencia, Spain

[11] W. Guang-Pu, Z. Zhi-Lin, Z. Wei-Ming, G. Xiang-Hong, C. Wei-Qun, H. Tanamura, M. Yamaguchi, H. Noguchi, T. Nagatomo, O. Omoto, Proceedings of the 1st IEEE World Conference on Photovoltaic Energy Conversion, Honolulu, U.S.A., Dec 5–9, 1994, p. 365.

[12] A. Javed, Q. Ain and M. Bashir, "Controlled growth, structure and optical properties of Fe-doped cubic π- SnS thin films," J. Alloy. Compd. 759, 14-21(2018).

[13]Calixto-Rodriguez M, Martinez H, Sanchez-Juarez A, Campos-Alvarez J, Tiburcio-Silver A, Calixto ME. Structural, optical, and electrical properties of tin sulfide thin films grown by spray pyrolysis. Thin Solid Films 2009; 517:2497-99.

[14] Reddy KN, Reddy KTR. Preparation and characterization of sprayed tin sulphide films grown at different precursor concentrations. Mater Chem Phys 2007; 102:13-18.

[15] Messaoudi M, Aida MS, Attaf N, Bezzi T, Bougdira J, Medjahdi G. Deposition of tin(II) sulfide thin films by ultrasonic spray pyrolysis: Evidence of sulfur exo-diffusion. Mater Sci Semicond Process 2014; 17:38-42.

[16] Lopez S, Ortiz A. Spray pyrolysis deposition of SnxSy thin films. Semicond Sci Technol 1994; 9:2130-3.
[17] Reddy KN, Reddy KTR, Fisher G, Best R, Dutta PK. The structural behaviour of layers of SnS grown by spray pyrolysis. J Phys D Appl Phys 1999; 32:988-90.
[18] Sajeesh TH, Warrier AR, Sudha Kartha C, Vijayakumar KP. Optimization of parameters of chemical spray pyrolysis technique to get n and p-type layers of SnS. Thin Solid Films 2010; 518:4370-4.
[19] Thangaraju B, Kaliannan P. Spray pyrolytic deposition and characterization of SnS and SnS2 thin films. J Phys D Appl Phys 2000; 33:1054-9.
[20] Ray SC, Malay KK, DasGupta D. Structure and photoconductive properties of dip-deposited SnS and SnS2 thin films and their conversion to tin dioxide by annealing in air. Thin Solid Films 1999; 350:72-8.
[21] H. Zhang, Y. Balaji, N. Mehta, M. Heyns, M. Caymax, I. Radu, A. Delabie, "Formation mechanism of 2D SnS2 and SnS by chemical vapor deposition using SnCl4 and H2S," 6172-6178(2018).

تأثير التشويب بالكوبلت على الخواص التركيبية والبصرية لأغشية كبريتيد القصدير الرقيقة

هناء كاظم عيسى[1] ، سجى فائز حسن[2] ، عدي علي جيجان[3]
[1،2] قسم الفيزياء، كلية التربية، الجامعة المستنصرية.
[3] قسم الفيزياء، كلية التربية للعلوم الصرفة، جامعة بابل.

مستخلص البحث:
تم تحضير أغشية رقيقة من كبريتيد القصدير غير المطعم والمطعم بالكوبلت باستخدام تقنية التحلل الكيميائي الحراري على قواعد زجاجية مسخنة بدرجة حرارة 450 مئوي. اثبت تحليل حيود الاشعة السينية بان ألاغشية المحضرة كانت متعددة التبلور وباتجاه سائد (111). قيمة الحجم الحبيبي لكبريتيد القصدير وكبريتيد القصدير المشوب بالكوبلت بنسبة 3% تبلغ 19.07 نانومتر و21.58 نانومتر على التوالي، بينما قلت المطاوعة المايكروية من من 18.17 إلى 16.06 . تبلغ نفاذية الأفلام المحضرة بحدود 85٪ ، والتي تنخفض مع زيادة تركيز التشويب. تنخفض قيمة فجوة النطاق البصرية من 1.57 فولت للأغشية كبريتيد القصدير الرقيقة إلى 1.45 فولت لكبريتيد القصدير المشوب بالكوبلت بنسبة 3% . يزداد معامل الامتصاص (α) مع زيادة تركيز الكوبلت، بينما ينخفض معامل الانقراض ومعامل الانكسار مع تركيز الكوبلت في اغشية كبريتيد القصدير الرقيقة.