

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

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Abstract

SnS and SnS: Co thin films were deposited by chemical spray pyrolysis (CSP) method on 450°C heated glass substrates. XRD study revealed that the 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 from 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 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

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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 [C₄H₆SnO₄] and 0.1M of [CH₄N₂S] as sources of Sn and S ions respectively. Doping was made by adding (CoCl₃) 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 °C. 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].

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

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].

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

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

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

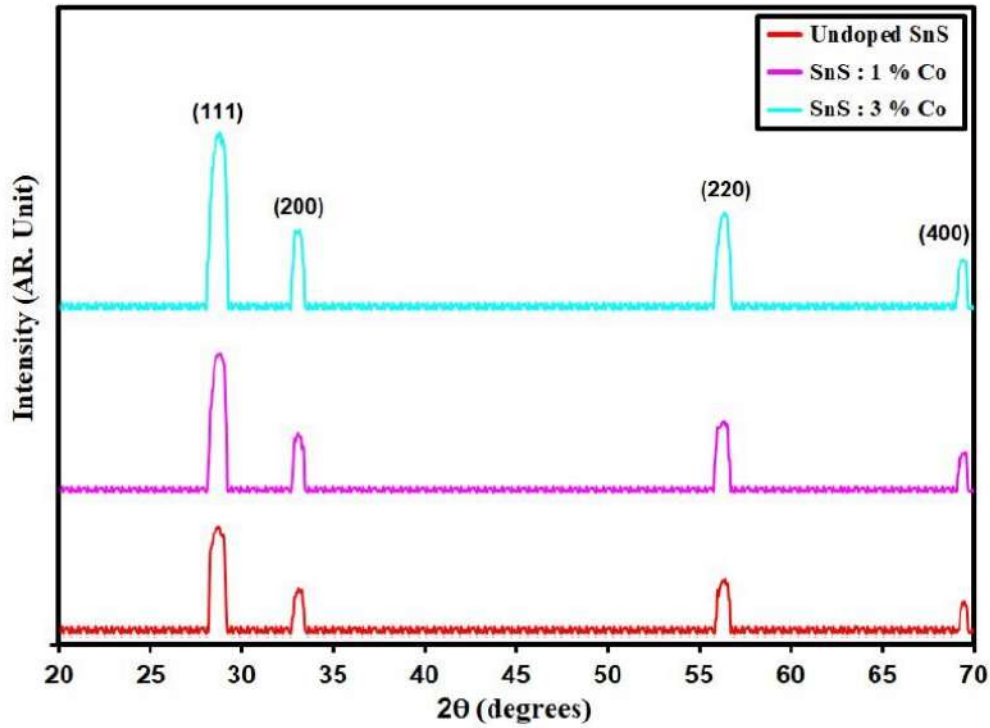


Figure1. XRD-patterns a crystalline size.

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

Specimen	2θ ($^{\circ}$)	(hkl) Plane	FWHM M ($^{\circ}$)	E_g (eV)	D (nm)	δ ($\times 10^{14}$) (lines/m ²)	ϵ ($\times 10^{-4}$)
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

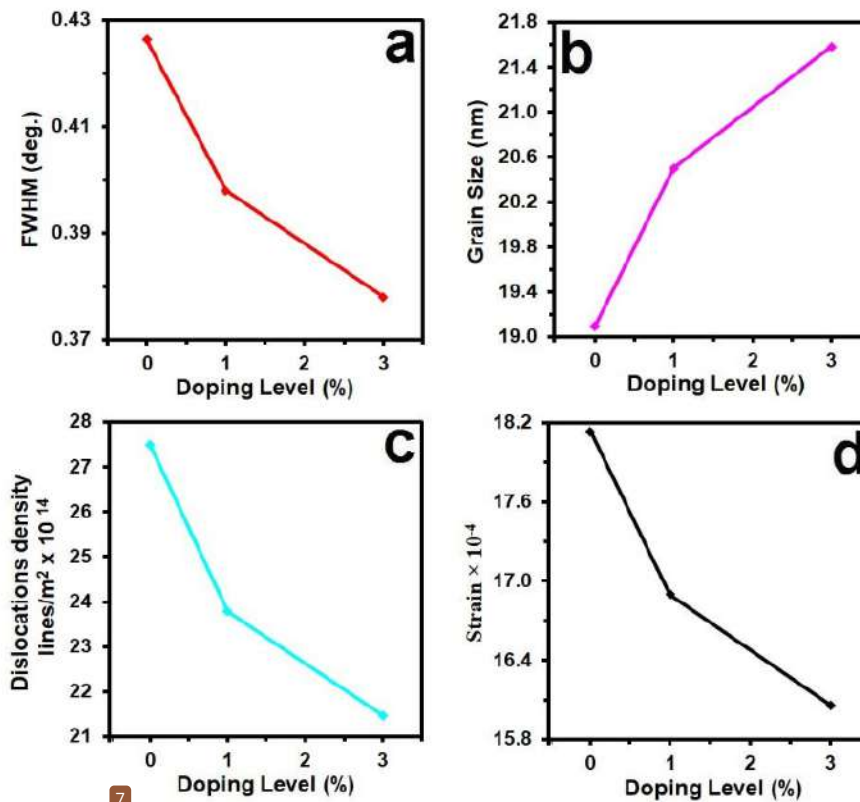


Figure 2. FWHM (a) D (b) δ (c) ϵ (d) of the grown films.

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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]:

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

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.

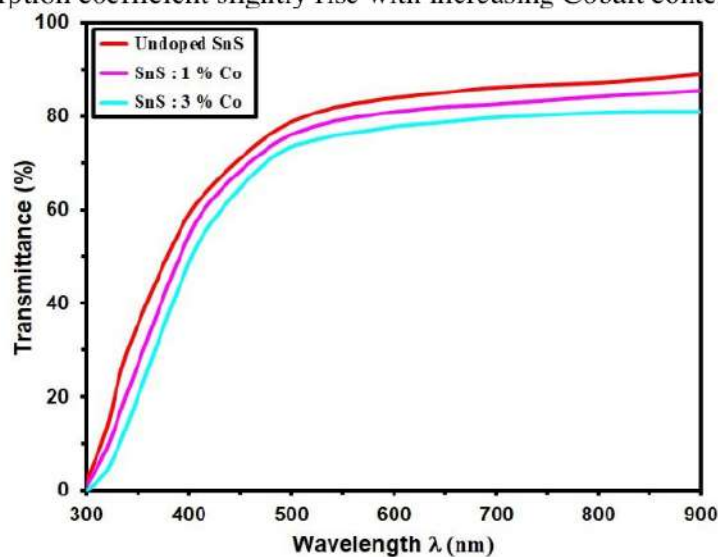


Fig. 3: Transparency of the grown films.

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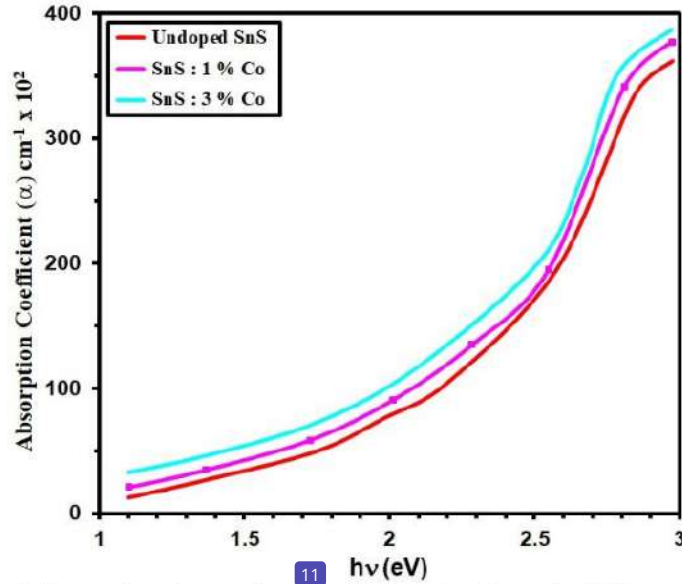


Fig. 4: the absorption coefficient for deposited films.

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

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

Where A is the constant, $(\alpha h\nu)^2$ against $(h\nu)$, 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].

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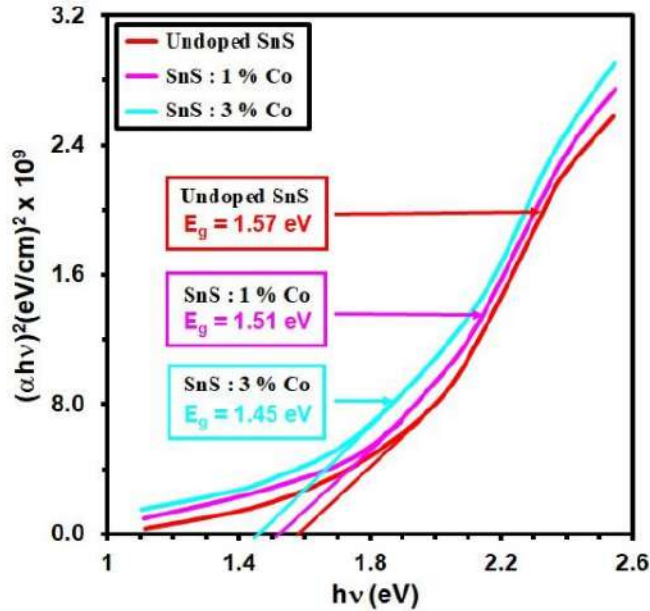


Fig. 5: $(\alpha hv)^2$ versus $h\nu$ for the SnS with different Cobalt doping.

Index of refraction (n) of the films is a valuable parameter for optoelectronic devices design. Such designs include 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]:

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

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

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

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only at long wavelengths, because of films transparency. The films' n and k are lowered with increasing Co content.

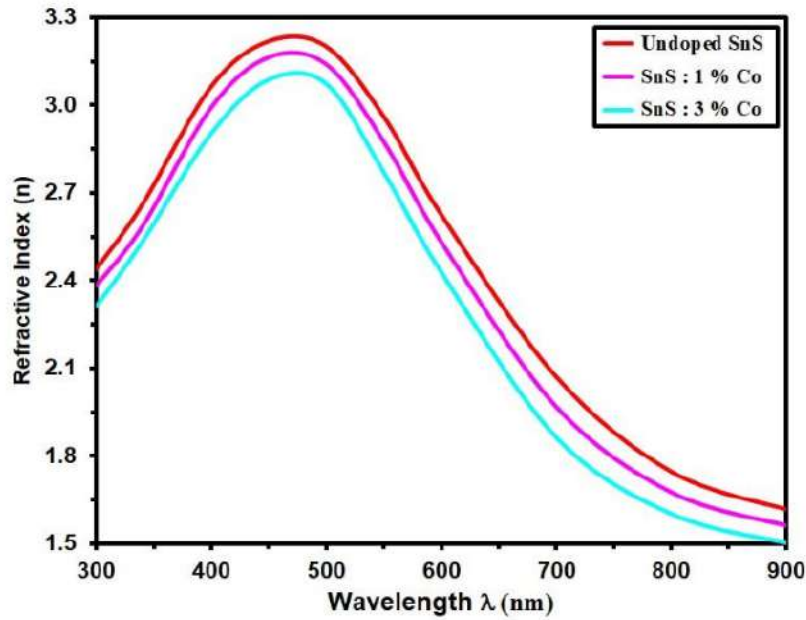


Fig. 6. Index of refraction for grown films.

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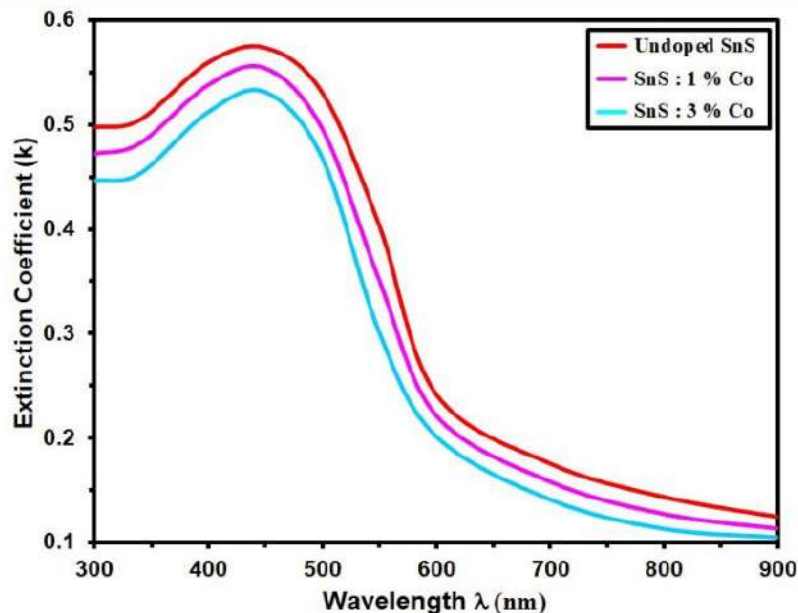


Fig. 7: Extinction coefficient of the grown films.

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.

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تأثير التشويب بالكوبلت على الخواص التركيبية والبصرية لأغشية كبريتيد القصدير الرقيقة

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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 منوي. اثبت تحليل حيود الاشعة السينية بان الأغشية المحضرة كانت متعددة التبلور وبتجاه ساند (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.

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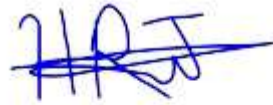
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