

Research Article

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Nickel doping effect on the structural and optical properties of indium sulfide thin films by SILAR

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Abstract: Undoped and nickel doped indium sulfide ($\text{In}_2\text{S}_3\text{:Ni}$) thin films have been deposited on indium tin oxide (ITO) coated glass substrates by successive ionic layer adsorption and reaction (SILAR) method. The doping concentration of Ni has been adjusted as 4%, 5% and 6% (in molar ratio of nickel ions to indium ions). The effects of Ni doping on the structural, morphological, compositional and optical properties of the In_2S_3 thin films are investigated. The x-ray diffraction patterns show that deposited film has cubic structure with amorphous nature of In_2S_3 and its crystallinity deteriorates with increasing doping concentration. The SEM measurements show that the surface morphology of the films is affected from the Ni incorporation. The direct band gap of the films decreases from 2.33 eV to 1.61 eV with increasing Ni dopant. Energy dispersive x-ray spectroscopy (EDS) has been used to evaluate the chemical composition and shown that S/(Ni+In) ratio in films decreases from 1.18 to 0.40 with Ni content. Optical properties of the films have been performed by a UV-Vis spectrophotometer. The direct band gap of the films decreases from 2.33 eV to 1.61 eV with increasing Ni dopant. Moreover, optical parameters of the films such as refractive index (n), extinction coefficient (k), real (ϵ_1) and imaginary (ϵ_2) parts of dielectric constant have been determined by using absorbance and transmittance spectra. The investigations showed that the Ni doping has a significant effect on the physical properties of SILAR produced In_2S_3 thin films.

Keywords: doping; thin films; optical constant; growth from solutions.

1 Introduction

Indium sulfide (In_2S_3) as a III-VI group semiconductor compound with α (cubic), β (tetragonal) and γ (trigonal) crystalline phases is an interesting material because of its remarkable properties such as stability, transparency, photoconductive nature, large band gap changing between 2.10 eV [1] and 3.91 eV [2], n-type conductivity [3] and low hazard material compared with cadmium sulfide, cadmium selenide [4], and cadmium telluride. Among these three crystalline phases, β - In_2S_3 is the most stable one at room temperature. It is an ideal material used as a layer in CuInS_2 (CIS), Cu(In,Ga)Se_2 (CIGSe), and CdTe-based thin film solar cells [5]. Many researchers have been trying to tune the optical and electrical properties of In_2S_3 by doping thin films for thin film solar cells applications. It is well known that metal dopant acts as electron donors in semiconductor thin films [6] and leads to more electrons available in the valence band.

In the previous work, we deposited In_2S_3 thin films with different complex agent volume, triethanolamine (TEA), on microscope glass substrates at room temperature using the chemical bath deposition technique (CBD) [7]. There are many works on In_2S_3 thin films doped with elements such as Sn [8], Co [9], Al [10], As, Sb or Bi [11], Na [12], Cu [13] and Ag [14]. However, there is no attempt on nickel doping of the In_2S_3 thin films. In this work, undoped and Ni doped indium sulphide ($\text{In}_2\text{S}_3\text{:Ni}$) thin films have been synthesized on indium tin oxide (ITO) coated glass substrates for the first time. The present work is focused on the changes in the structural, morphological, compositional and optical properties of the In_2S_3 thin film when doped with Ni dopants. Undoped and Ni doped films have been synthesized using a simple and inexpensive SILAR technique which provides easy coating of the samples at room temperature [15,16]. In this technique, thin films are obtained by dipping substrate into separately placed cationic and anionic precursors, and then rinsing with deionized water after each immersion. The deposition rate and the thickness of the

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Table 1: Preparation conditions of $\text{In}_2\text{S}_3:\text{Ni}$ thin films.

Material	Film Thickness (nm)	[Ni]/[In] (%)	pH		SILAR cycle	Dipping time (s)	Rinsing time (s)
			In	S			
$\text{In}_2\text{S}_3:\text{Ni}$	444	0	3.92	10.63	70	40	40
$\text{In}_2\text{S}_3:\text{Ni}$	395	4	4.03	10.62	75	40	40
$\text{In}_2\text{S}_3:\text{Ni}$	360	5	4.02	10.62	75	40	40
$\text{In}_2\text{S}_3:\text{Ni}$	317	6	4.03	10.62	75	40	40

film may be easily controlled by changing the deposition cycles of SILAR.

2 Experimental Details

The $\text{In}_2\text{S}_3:\text{Ni}$ thin films have been deposited on indium tin oxide (ITO) coated glasses with sheet resistances of 9.5 Ω/square (76 mm \times 26 mm \times 1 mm) at room temperature by SILAR method. For the deposition of these films, the concentration of nickel ions is adjusted by controlling the quantity of nickel chloride in the mixture, varying as 0%, 4%, 5% and 6% (in molar ratio of nickel ions to indium ions). Before the deposition, the substrates have been initially washed by detergent, boiled in deionized water, and cleaned in methanol, acetone and deionized water for 10 min sequentially. Following air drying, the deposition of $\text{In}_2\text{S}_3:\text{Ni}$ thin films were carried out at room temperature. The ITO substrate was immersed in cation precursor solution, containing 0.1 M indium (III) acetate [$\text{In}(\text{CH}_3\text{COO})_3$; Merck; 99.99% purity; pH \sim 4.02] and 0.1 M nickel (II) chloride ($\text{NiCl}_2 + 6\text{H}_2\text{O}$; Merck; ACS. Reag.) for 40 s, and then rinsed with deionized water for 40 s before it was immersed in solutions containing 0.05 M sodium thiosulfate [$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; 99.5% - 100.5% purity; pH \sim 10.62] for additional 40 s. The substrate was rinsed again with deionized water for 40 s to remove the unreacted ions. By repeating above SILAR steps for 70 times and 75 times for undoped and doped films respectively, thin film of $\text{In}_2\text{S}_3:\text{Ni}$ was deposited on ITO substrate.

XRD patterns were carried out using x-ray diffractometer with CuK α radiation (XRD, Bruker/AXS-D8, $\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 20° to 70° , while surface morphology was studied by scanning electron microscope (SEM, EVO40-LEO). The elemental composition of the films was examined using energy dispersive x-ray spectroscopy (EDS) attached to the SEM. For the optical transmittance measurements, a Perkin Elmer Lambda 4S UV-Vis spectrophotometer in the wavelength range of 400–1100 nm at room temperature has been used. Film

thicknesses (t) were determined gravimetrically with a precision microbalance by assuming the density of bulk In_2S_3 as 4.845 g cm^{-3} . Film thickness shows a reduction with increasing Ni concentration as seen in Table 1.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and Discussions

Figure 1 shows the diffraction patterns of ITO substrate and the $\text{In}_2\text{S}_3:\text{Ni}$ thin films. Deposited films are amorphous in nature. When compared with the standard 2θ and d values, it can be concluded that the obtained film is cubic In_2S_3 structure (JCPDS card no. 65-0459). As can be seen in Figure 1, the substrate effect is more dominant in the films deposited at Ni concentration of 0% and 4%. However, the crystallinity of the film deteriorates more with increasing Ni incorporation and results with disappearing of diffraction peaks coming from substrate in the film deposited at 6% Ni dopant. Our XRD results are in agreement with the literature [13] and [17] in which Mane et al. reported cubic structure with amorphous nature of In_2S_3 films on glass substrates using SILAR method.

The surface morphology of ITO substrate and $\text{In}_2\text{S}_3:\text{Ni}$ thin films are shown in Figure 2. As can be seen, the surface of the films shows granular structure with cracks.

The compositional analysis of $\text{In}_2\text{S}_3:\text{Ni}$ thin films was performed by EDS and the results are listed in Table 2. The EDS results confirm the presence of O, In, S and Ni elements in the synthesized films. It can be seen that the deposited films show excess of oxygen increasing with increasing Ni content. This is an expected result because of the aqueous solution method used. Kamoun et al. [10] reported that the presence of Al leads to an increment in adsorption of oxygen in the sample. The average ratio for atomic percentage of S/(In+Ni) is 1.18 for deposited films and it decreases to a value of 0.40 with increasing Ni dopant.

In order to examine the effect of doping on the optical properties of the films, the absorbance and transmittance

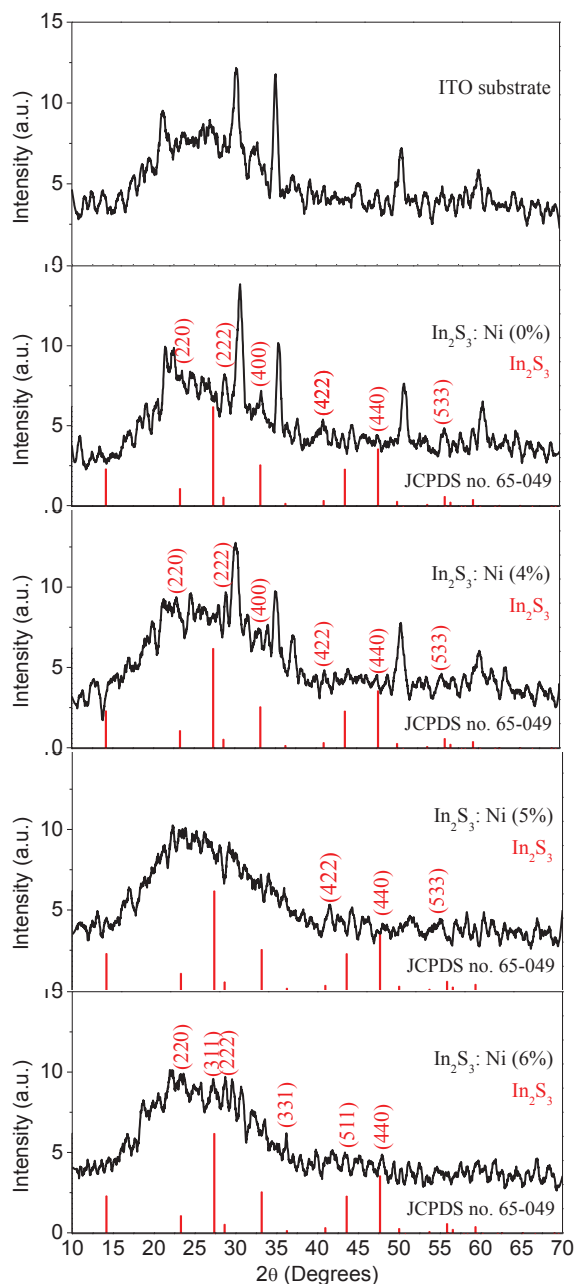


Figure 1: X-ray diffraction patterns of $\text{In}_2\text{S}_3:\text{Ni}$ thin films.

measurements were performed at room temperature in the wavelength range 400–1100 nm as shown in Figure 3. The films exhibit average transmittance between 47% and 74% and in the visible region.

In order to calculate the band gap of the films, optical absorption of the films was studied at room temperature. The absorption coefficient (α) of the films was calculated from the normalized transmittance (T) data using the formula:

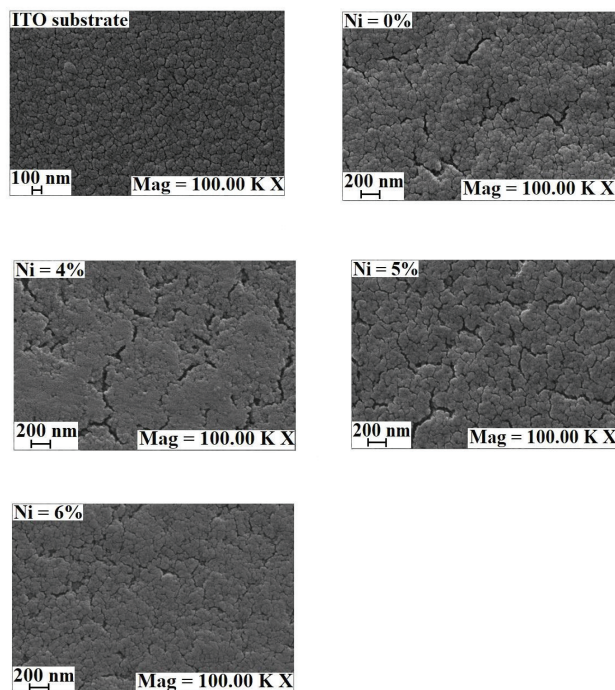


Figure 2: SEM micrographs of $\text{In}_2\text{S}_3:\text{Ni}$ thin films obtained at 100 kx magnification.

Table 2: The EDS analysis of $\text{In}_2\text{S}_3:\text{Ni}$ thin films.

Material	Atomic (at. %)					
	O	S	In	Sn	Ni	S/(In+Ni)
$\text{In}_2\text{S}_3:\text{Ni}$ (0%)	77.06	10.74	9.07	3.13	0	1.18
$\text{In}_2\text{S}_3:\text{Ni}$ (4%)	91.74	2.98	2.15	1.53	1.60	0.79
$\text{In}_2\text{S}_3:\text{Ni}$ (5%)	91.95	2.77	2.32	1.51	1.45	0.74
$\text{In}_2\text{S}_3:\text{Ni}$ (6%)	92.81	1.74	3.32	1.05	1.08	0.40

$$\alpha = -\frac{1}{t} \ln(T) \quad (1)$$

where t is the film thickness. The band gap energy (E_g) is determined using the Tauc's relation:

$$ah\nu = K(h\nu - E_g)^n \quad (2)$$

where K is a constant depending on transition probability, $h\nu$ is a photon energy, E_g is the optical band gap, n is an index that characterizes the optical absorption process and theoretically equal to 1/2 for allowed direct transition and 2 for indirect transition [18]. Figure 4 shows the plot of $(ah\nu)^2$ versus photon energy for the films. The optical band

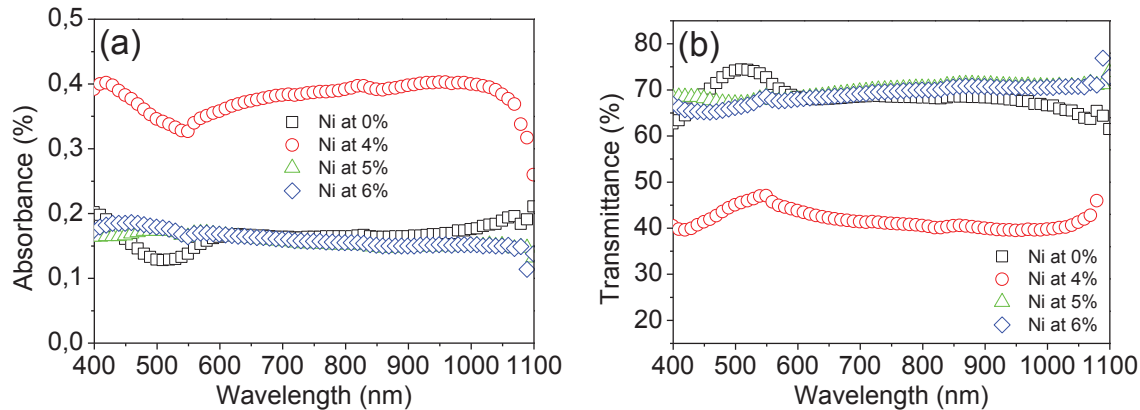


Figure 3: (a) The absorbance and (b) transmittance spectra of $\text{In}_2\text{S}_3:\text{Ni}$ thin films.

Table 3: Optical parameters for $\text{In}_2\text{S}_3:\text{Ni}$ thin films ($\lambda = 600$ nm).

Materials	E_g (eV)	n	k	ε_1	ε_2
In_2S_3 Ni = 0%	2.33	1.84	0.18	3.35	0.64
In_2S_3 Ni = 4%	1.99	2.33	0.43	5.26	2.00
In_2S_3 Ni = 5%	1.75	1.84	0.22	3.32	0.80
In_2S_3 Ni = 6%	1.61	1.82	0.25	3.26	0.91

gaps of the films were determined from the intercept of $(ah\nu)^2$ versus $h\nu$ curves and obtained E_g values are given in Table 3. The optical band gaps of the films decrease from 2.33 eV to 1.61 eV and shift towards the red region as the Ni concentration in the films increases, whereas Barreau et al. [3,12] found that the optical band gaps of In_2S_3 thin films, grown by physical vapor deposition, increased from 2.10 eV to 2.95 eV with increasing Na concentration. The shifting in E_g of the films may be attributed to the band shrinkage effect. The narrowing band gap energy is due to the existence of Ni impurities in the In_2S_3 structure, which induce the introduction of shallow donor levels due to doping. This red shift of E_g could be an increase in carrier concentration with Ni doping. Moreover, a red shift is attributed to a reduction in S concentration (an increase in sulfur vacancies), detected from compositional analysis in Table 2, leads to a reduction in the optical energy gap for In_2S_3 : Ni thin films. The measured band gaps are consistent with reported values 2.3 eV [16]. Timoumi et al. [19] reported a band gap changing between 1.61 eV and 2.19 eV for In_2S_3 thin films deposited on glass substrates by vacuum thermal evaporation method.

The transmittance and absorbance data were used to calculate the optical constants such as refractive index (n), extinction coefficient (k), real (ε_1) and imaginary (ε_2) parts of dielectric constant. The n is described by the Fresnel formulae [20]:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$

where R is the reflectance and k is given by $\alpha\lambda/4\pi$. The dependence of n and k on wavelength for the films are shown in Figures 5(a) and (b), respectively and results are listed in Table 3. At $\lambda = 600$ nm, the n value of deposited films first increases from 1.84 to 2.33 and then decreases to the value of 1.82 with Ni concentration. The present n values are also in good agreement with the literature for In_2S_3 thin films (1.6–1.84) [21] and (2.5) [22]. Esmaili et al. [13] found the n value between 1.0 and 2.5 for $\text{In}_2\text{S}_3:\text{Cu}$ thin films deposited by CBD. The k values are consistent with our previous data (0.33–0.72) [7] but they are lower than Ref. [13] in which $\text{In}_2\text{S}_3:\text{Cu}$ thin films were deposited by CBD. At $\lambda = 600$ nm, the k value varies between 0.18 and 0.43 with the increase in Ni concentration. The k values are consistent with the reported data obtained by Kaleel et al. [23] in which $\text{In}_2\text{S}_3:\text{Cu}$ thin films were obtained by spray pyrolysis method.

The ε_1 and ε_2 were calculated by using Eqs. (4) and (5):

$$\varepsilon_1 = n^2 - k^2 \quad (4)$$

$$\varepsilon_2 = 2nk \quad (5)$$

Figures 5(c) and (d) show the plots of ε_1 and ε_2 , respectively. At $\lambda = 600$ nm, the ε_1 value first increases from 3.35 to 5.26 and then decreases to the value of 3.26 with Ni concentration. The ε_2 value varies between 0.64 and 2.00 as seen in Table 3. Both ε_1 and ε_2 values are consistent with the previous data [7,23].

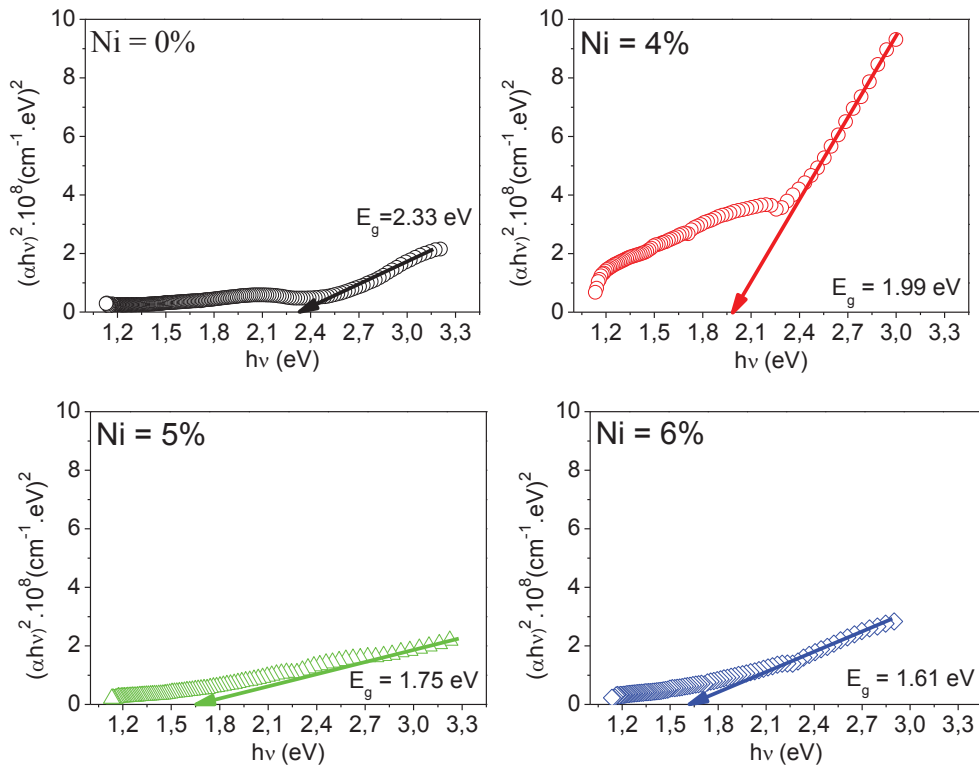


Figure 4: Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ $\text{In}_2\text{S}_3:\text{Ni}$ thin films.

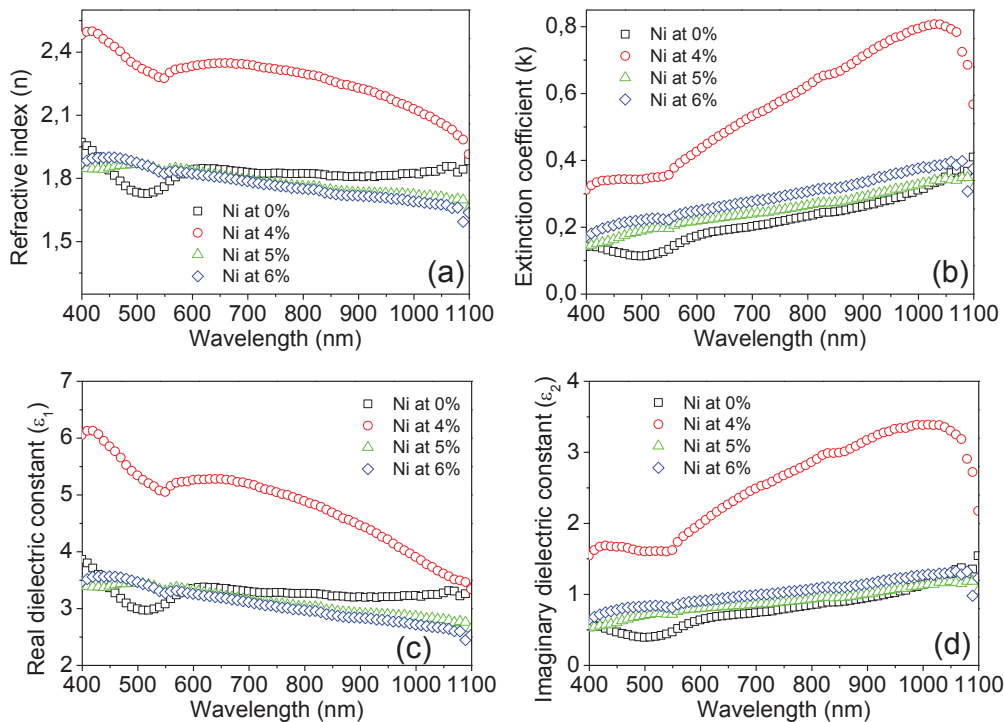


Figure 5: The variation of (a) refractive index, (b) extinction coefficient, (c) real and (d) imaginary dielectric constant for $\text{In}_2\text{S}_3:\text{Ni}$ thin films.

4 Conclusions

In_2S_3 :Ni thin films are deposited on ITO substrate by SILAR technique. The SILAR is a simple and economic technique and useful for large area thin film depositions with low cost. The effect of Ni dopant on the structural, morphological, optical and electrical properties is studied. The S/(In+Ni) ratio in the films decreases from 1.18 to 0.40 with Ni content. The XRD result shows that deposited films have cubic structure with amorphous nature of In_2S_3 and their crystallinity deteriorates with increasing doping concentration. The E_g values of the films are affected from the incorporation of Ni and resulted a reduction with Ni doping. The optical parameters such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant were determined. These results show that the Ni doping modifies the structural, morphological and optical properties of the In_2S_3 thin films.

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Conflict of interest: Authors state no conflict of interest.

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