


Cite this: *RSC Adv.*, 2020, 10, 21180

# Investigation of the effect of S/In molar ratio on physical properties of sprayed $\text{In}_2\text{S}_3$ thin films

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Indium sulfide ( $\text{In}_2\text{S}_3$ ) thin films have been synthesized on glass substrates using the spray technique (CSP). The S : In molar ratio was varied from 1 to 4 in the starting solution. The Raman analysis confirms the formation of the  $\beta\text{-In}_2\text{S}_3$  material and the absence of a secondary phase. The EDS analysis reveals that our layers are pure. The thin film surface is free of cracks, as observed in AFM images. Optical transmission achieved 80% in the visible and near infrared region. The refractive index ( $n$ ) is affected by the changes in the S/In molar ratio. The optical parameters, single oscillator energy ( $E_0$ ), dispersion energy ( $E_d$ ) and high frequency dielectric constant ( $\epsilon_\infty$ ), are calculated via the Wemple–DiDomenico model. In addition, the photoconductivity kinetics in  $\text{In}_2\text{S}_3$  films for S/In = 2 were investigated and analyzed. The  $I$ – $V$  characteristics and the photoresponse were also studied.

Received 31st March 2020  
Accepted 27th May 2020

DOI: 10.1039/d0ra02945a

rsc.li/rsc-advances

## 1. Introduction

Most promising sulfide based semiconductor materials have been used as light absorbers in solar cells such as chalcopyrite  $\text{CuInS}_2$ , paramagnetic insulator  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$ , antimony sulfide  $\text{Sb}_2\text{S}_3$  and sulfide indium  $\text{In}_2\text{S}_3$ . The thermodynamic efficiency of various devices is of wide interest because of the relevance of this parameter for energy conversion.

The efficiency of MEH-PPV/H-CuInS<sub>2</sub> hybrid solar cells was studied by Yue *et al.*<sup>1</sup> Hierarchical  $\text{CuInS}_2$  was deposited with the induction of histidine by solvothermal method. The authors found that devices based on H-CuInS<sub>2</sub> synthesized with smaller size (0.5 HD) displayed higher energy conversion efficiency of 0.59%. The chalcopyrite  $\text{CuInS}_2$  quantum dots ( $\text{CuInS}_2$ -QDs) with different sizes synthesized by the solvothermal method was used in MEH-PPV- $\text{CuInS}_2/\text{TiO}_2$ -NA solar cells.<sup>2</sup> The authors obtained a peak efficiency of 1.60% for the 5.4 nm  $\text{CuInS}_2$ -QDs. In addition, this efficiency is comparable to the QDSSCs based on CdS sensitized  $\text{TiO}_2$ -NA.<sup>3</sup>

Recently, a series of  $\text{Fe}_{1-x}\text{Co}_x\text{S}_2$  ( $x = 0\text{--}0.5$ ) solid solutions have been synthesized and served as counter electrodes in dye sensitized solar cells (DSSCs).<sup>4</sup> The results reveal high power conversion efficiency of 8.36% than those solid solutions

materials over Pt of 7.66%. Wu *et al.*<sup>5</sup> studied hybrid  $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$  n-i-p solar cells with  $\text{Sb}_2\text{S}_3$  layers of different thickness by CBD method. They reported an optimum efficiency of 1.65% with  $\text{Sb}_2\text{S}_3$  thickness of 175 nm.

However, the use of cadmium (Cd) in PV devices is undesirable from the viewpoint of environmental safety,<sup>6</sup> serious efforts have been made to substitute the CdS by other non-toxic (Cd-free). Indium sulfide ( $\text{In}_2\text{S}_3$ ) is one of the possible candidates to replace CdS a buffer layer. This compound is an n-type semiconductors which belongs to III–VI group. Hetro-junction such as CIGS/ $\beta\text{-In}_2\text{S}_3$  (ref. 7) achieved a conversion efficiencies of 15.7%. This demonstrates that comparable conversion efficiencies can be obtained respect to commonly used CdS buffer (16%).<sup>8</sup> Osman *et al.*<sup>9</sup> observed that there is no difference between both structures of CdS and  $\text{In}_2\text{S}_3$ , they found also that the efficiency of CIGS solar cells with both layers is comparable. It's 24.14% and 24.28% with  $\text{In}_2\text{S}_3$  and CdS respectively.

$\text{In}_2\text{S}_3$  is currently researched as a result of its important properties in relation with the optoelectronic devices.<sup>10</sup>  $\beta\text{-In}_2\text{S}_3$  is recognized as a direct band gap semiconductor ranging from 2.0 to 2.75 eV, with a high stability, high optical transmittance (>80%) and controllable electrical properties, modified chemical composition and deposition parameters.<sup>11,12</sup> These characteristics of  $\text{In}_2\text{S}_3$  films make it a useful material for several applications.  $\text{In}_2\text{S}_3$  can be used in light-emitting diode (LED) and lithium-ion batteries.<sup>13,14</sup> Due to its absorption in the UV and visible region,  $\text{In}_2\text{S}_3$  is considered as photodetector.<sup>15</sup> Also, this material can be used for gas sensing and photocatalytic applications owing to its thermal stability, good response and reversibility, low defect density and simple synthesis process.<sup>16,17</sup>

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$\text{In}_2\text{S}_3$  exists in three different crystalline phases  $\alpha$ ,  $\beta$  and  $\gamma$  which depend on the growth temperature.<sup>12,18</sup>  $\beta\text{-In}_2\text{S}_3$  is the most stable phase at room temperature.<sup>19,20</sup> It crystallizes in a defect spinel structure with a high degree of tetrahedral and octahedral vacancy sites.<sup>21,22</sup>

Various techniques were commonly used for preparing  $\text{In}_2\text{S}_3$  such as spray pyrolysis,<sup>23,24</sup> ultrasonic dispersion,<sup>25</sup> physical vapor deposition,<sup>26</sup> chemical bath deposition,<sup>27</sup> vacuum thermal evaporation,<sup>28</sup> etc. Among these methods, the spray pyrolysis technique is of particular interest because it is economical and allows growing large area  $\text{In}_2\text{S}_3$  thin films. Furthermore, this technique has been applied to fabricate various type of materials such as ZnO and carbon nanofibres (ECN/ $\text{TiO}_2$ ).<sup>29,30</sup> Indeed, Ngo *et al.*<sup>30</sup> presented a comparative study between ZnO films deposited by spray coating and ZnO prepared by spin coated. They found that the spray coated sample have higher efficiency (3.76%) than spin coated ZnO (3.11%) due to the increase in FF from 42.38% to 63.14%. So that, to choice of technique is one of important factor in solar cells application.

The physical properties of  $\text{In}_2\text{S}_3$  thin films are strongly affected by the deposition parameters.<sup>25</sup> Several authors have reported that 340 °C is a good substrate temperature for obtaining best crystallinity.<sup>31,32</sup> Thus, various works showed that the S/In ratio has an effect on the structure, the crystallite

size<sup>33–35</sup> and the optical band gap of the  $\text{In}_2\text{S}_3$  films.<sup>11,36</sup> Zhang *et al.*<sup>37</sup> have reported that the grain size increases from 32 nm to 34.1 nm with the increase of S/In molar ratio from 1 to 4. Furthermore, the high transmittance is found in the visible and near-infrared range. The energy band gap increases significantly when S/In ratio varies from 1 to 2, then decreases from 2.46 eV to 2.4 eV when S/In increases from 2 to 4. John *et al.*<sup>11</sup> have reported that the use of sulfur-rich solution (S/In = 8/2 instead of S/In = 2/1) decreases the energy band gap from 2.81 to 2.64 eV. The photoluminescence (PL) properties of  $\text{In}_2\text{S}_3$  at different S/In ratios have been reported by Elfarrass *et al.*<sup>33</sup> They showed that all the films have two emission bands (green and red band). In addition, Bhira *et al.*<sup>38</sup> have demonstrated that  $\text{In}_2\text{S}_3$  thin film has high photoconductivity. Therefore, investigations on the effect of S/In ratio on the  $\text{In}_2\text{S}_3$  optical properties are very important, to obtain films that are capable to ensure stable and high efficient devices.

In this work, we report the study of the effect of S/In ratio on the physical properties of  $\text{In}_2\text{S}_3$  thin films.

## 2. Experimental details

$\text{In}_2\text{S}_3$  thin films were produced by spray pyrolysis method using an aqueous solution of indium chloride(III) and thiourea, on glass substrate. The concentration of the precursor  $\text{InCl}_3$  is

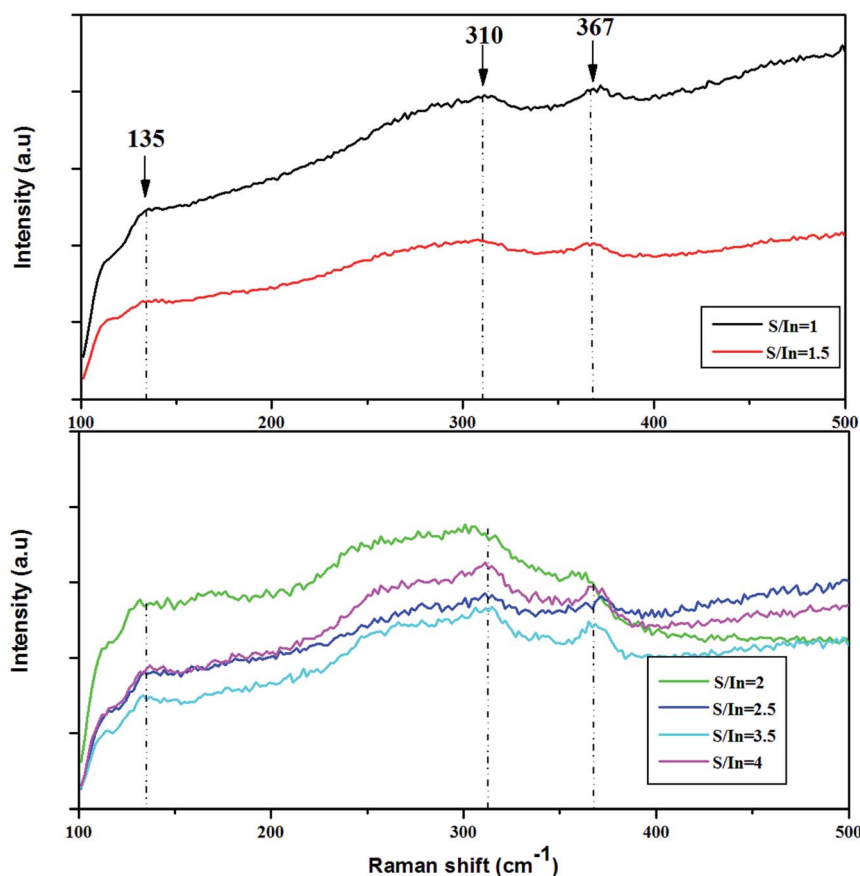
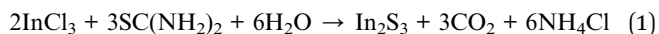


Fig. 1 Raman spectra of  $\text{In}_2\text{S}_3$  thin films for different S/In molar ratios.



$10^{-2}$  mol L $^{-1}$ . The S/In ratio in the solution varied in the range 1–4. The substrate temperature was fixed at 340 °C within an accuracy of  $\pm 5$  °C, in agreement with<sup>31,32</sup>. Compressed nitrogen was used as a carrier gas at a flow rate of 6 L min $^{-1}$ .

The formation of In<sub>2</sub>S<sub>3</sub> results from the following endothermic reaction:



The Raman analysis were conducted using a Jobin-Yvon microRaman spectrometer (T64000) with an argon laser line of 514 nm. The composition of films was done by energy dispersive spectroscopy (EDS). The surface morphology was performed by atomic force microscopy using an XE-100 instrument (Park Systems Corporation). Photoluminescence (PL) measurements were performed at room temperature using laser excitation wavelength of 655 nm. Transmittance spectra measurements have been done using a Shimadzu UV 3101 PC spectrophotometer in the wavelength range from 350 to 1900 nm. The *I*-*V* characteristics measured in dark and under illumination were performed using a (HP4140B) source/picoammeter. Moreover, the photoresponse of In<sub>2</sub>S<sub>3</sub> thin films was investigated by illuminating the film with a neon light

source. The resistance of the sample is measured by using a (HP4140B) Keithley Digital multimeter, interfaced to a computer for data acquisition.

### 3. Results and discussion

#### 3.1. Structural characterization

The quality of sprayed films was characterized by Raman spectroscopy. It's a powerful technique which allows to determine the phase and the structure of films. Besides, this technique provides the information about the vibration mode in the crystalline phase. The Raman spectra for our films are presented in Fig. 1, which were recorded in the energy region between 100 and 500 cm $^{-1}$ . All the spectra reveal broad bands at 135, 310 and 367 cm $^{-1}$  with low intensity, showing nano-crystalline nature of the layers. These present bands seem to be typical relative to cubic structural ( $\beta$ -In<sub>2</sub>S<sub>3</sub>).<sup>39,40</sup> The peak at 135 cm $^{-1}$  can be assigned to the E<sub>g</sub> mode, and the peaks at 310, 367 cm $^{-1}$  to the A<sub>1g</sub> mode.<sup>40–42</sup> The band appeared at 310 cm $^{-1}$  is related to the symmetric stretching vibrating mode of InS<sub>4</sub> tetrahedral.<sup>43</sup> Furthermore, the shift in the position of the bands with molar ratio S/In could be due to the presence of strain developed in the films. The shift is in order of 2 cm $^{-1}$ .

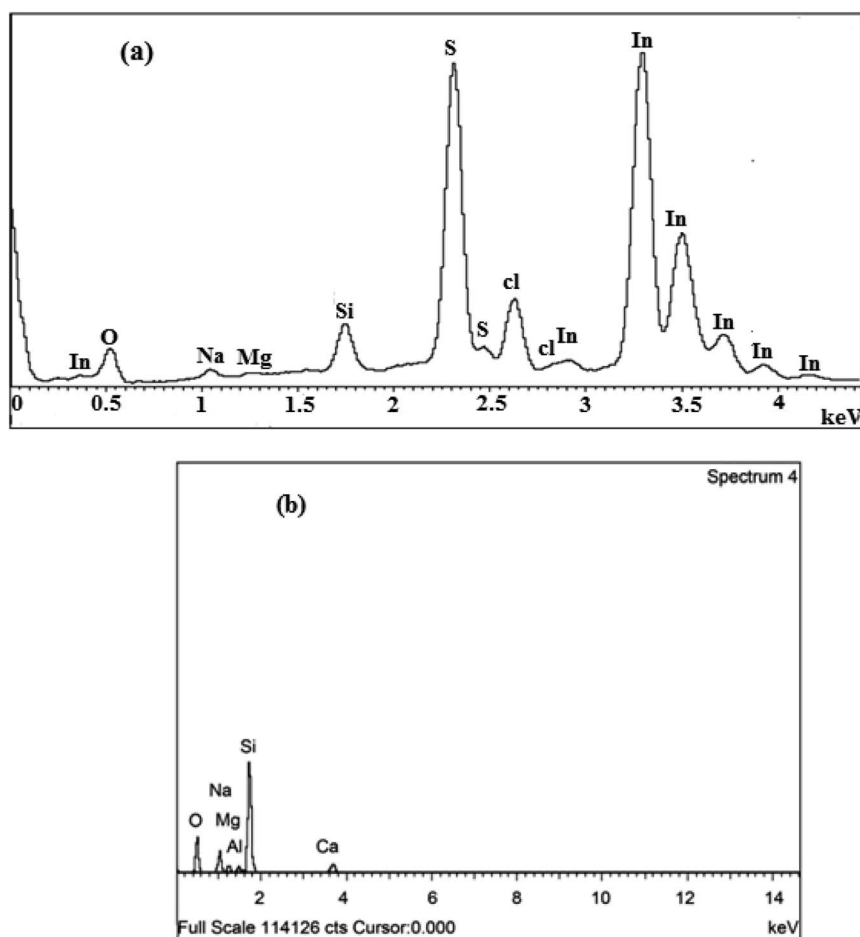


Fig. 2 (a) EDS spectra of thin films at different S/In molar ratios. (b) EDX spectrum of glass substrate.<sup>45</sup>



**Table 1** Chemical composition of  $\text{In}_2\text{S}_3$  films

S/In	S (at%)	In (at%)	S/In
1	24.60	25.01	0.98
1.5	52.18	42.34	1.23
2	41.93	33.51	1.24
2.5	46.92	36.76	1.27
3.5	41.02	32.08	1.28
4	41.02	32.08	1.28

This induces the deviation in the interplanar spacing in crystal lattice. The change of S/In ratio does not affect the structure of the layers. In addition, we noticed the absence of secondary phases in the all layers. This finding proved the results obtained by XRD analysis.<sup>44</sup>

### 3.2. EDS analysis

The compositional analysis of  $\text{In}_2\text{S}_3$  thin films at different S/In molar ratios was carried out employing EDS as shown in Fig. 2a and Table 3. The EDS spectrum confirms the presence of

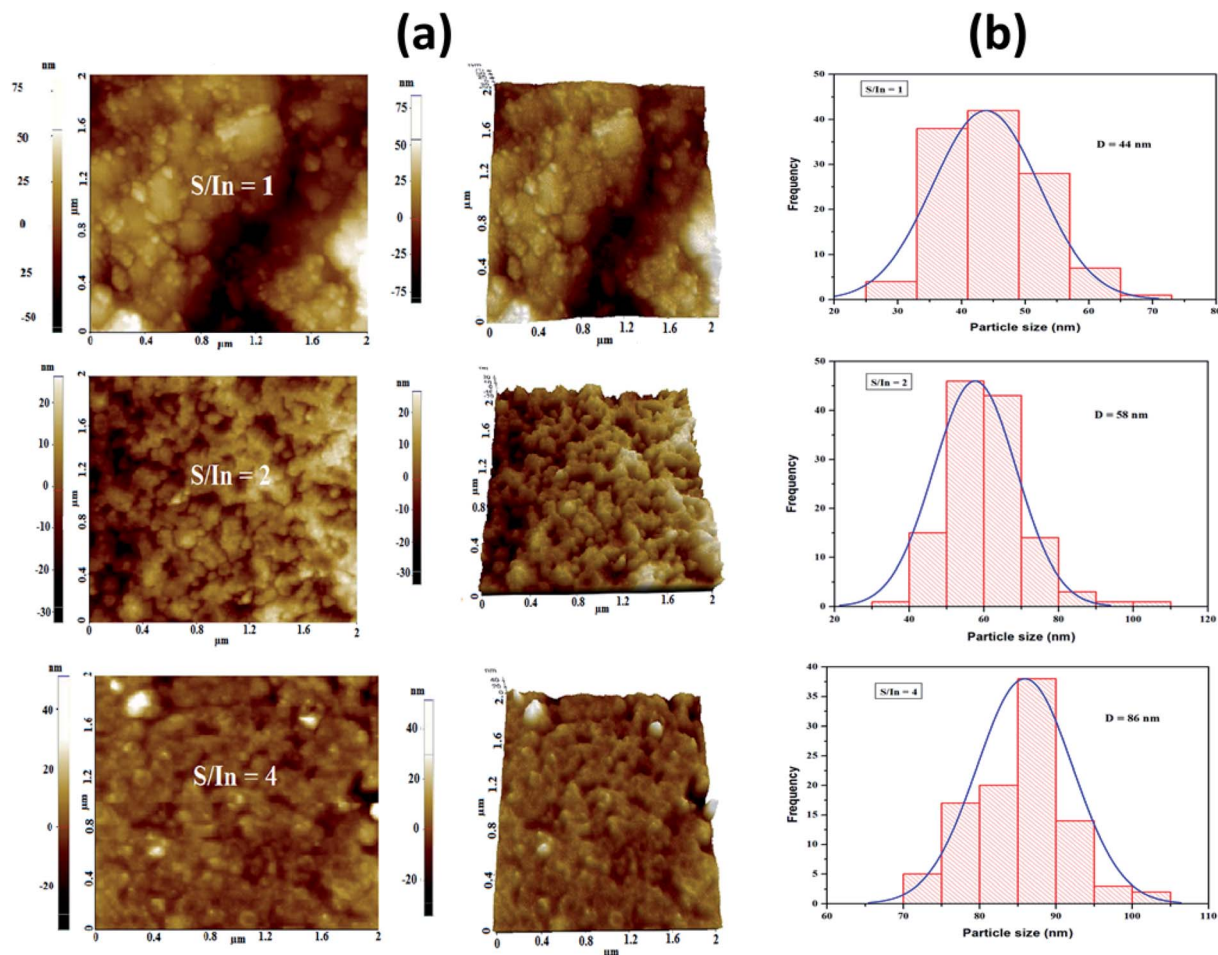
**Table 2** Evolution of RMS roughness of  $\text{In}_2\text{S}_3$  films with different S/In molar ratios

S/In	1	1.5	2	2.5	3.5	4
RMS (nm)	20	15	11	9	8	6

In and S elements in the films, their atomic percentages are given in Table 1. It can be seen that when the S/In increases in the solution, the S/In in the films increases and varies from 0.98 to 1.29. The Cl peak arises from the  $\text{InCl}_3$  precursor. Also, we notice the presence of various elements such as Si, O, Na and Mg which are provided from glass substrates (see Fig. 2b).<sup>45</sup> Therefore, the EDS analysis confirms the purity of deposited  $\text{In}_2\text{S}_3$  thin films.

### 3.3. Morphological characterization

Fig. 3a shows 2D and 3D NC-AFM images ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of  $\text{In}_2\text{S}_3$  films for S/In ratios equal to 1, 2 and 4. As observed from the AFM images, the surface morphology of the films is sensitive to the S/In molar ratio. Indeed, it can be seen that the films are formed by grains separated by depressions. Owing to the



**Fig. 3** (a) 2D and 3D NC-AFM images of thin films for S/In molar ratios equal to 1, 2 and 4. (b) Grain size distribution histogram of thin films for S/In molar ratios equal to 1, 2 and 4.





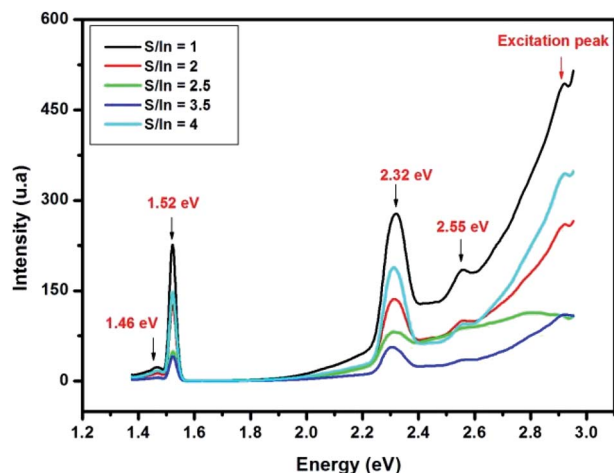


Fig. 4 Photoluminescence spectra of  $\text{In}_2\text{S}_3$  thin films for different S/In molar ratios.

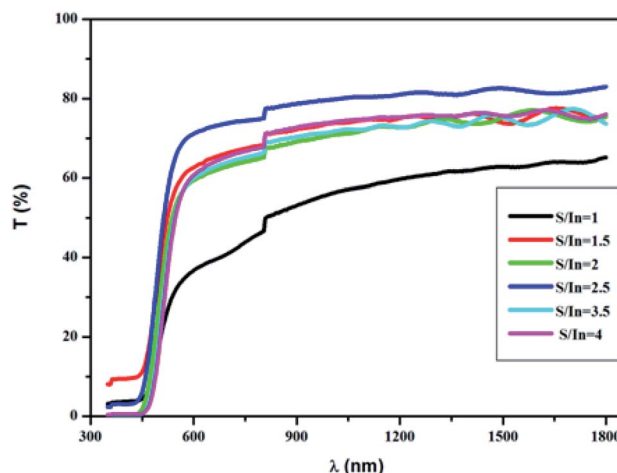


Fig. 5 Transmittance spectra with different S/In molar ratios.

coalescence phenomenon, it appears that the grain size along the surface of the film increases with S/In ratio. Furthermore, we can note also that the films show spherical grains, indicating the polycrystalline nature of these films. This finding agrees with the XRD results. The root mean square roughness (RMS) values decrease from 20 to 6 nm with increasing molar ratio (Table 2). This behavior can be attributed to the increase of crystallite size, and the surface morphology becomes uniform and more compact.

In order to evaluate the average grain size, a statistical count of grain size was performed on the AFM images using Image-J software. Grain size distribution histograms for the different films are shown in Fig. 3b. The average grain size of samples is found to lie in the nanometer range (44–86 nm).

### 3.4. Optical characterization

**3.4.1. Photoluminescence.** The photoluminescence (PL) analysis was performed out for all the deposited  $\text{In}_2\text{S}_3$  thin films at the excitation wavelength  $\lambda = 655$  nm to investigate the defect state emission in the films.

Room temperature photoluminescence spectra of  $\text{In}_2\text{S}_3$  at different S/In molar ratios are exhibited in Fig. 4. PL spectra reveal a peak at 1.46 eV, 1.52 eV, 2.32 eV and 2.55 eV.

The red emission at 1.45 is due to S and In vacancies in the host lattice.<sup>46</sup> The emission at 1.52 eV and green emission (at 2.32 eV and 2.55 eV) are attributed to transitions from the excited states of the sulfur vacancy ( $V_s$ ) to the In vacancy ( $V_{\text{In}}$ ) level.<sup>46–48</sup> Mathew *et al.*<sup>22</sup> reported a green emission from  $\text{In}_2\text{S}_3$  which was attributed to the donor level formed by indium interstitials. The PL emission intensity is found stranger for sample at S/In = 1 than other samples, which proved the presence of higher defect concentration.<sup>49</sup> Thus, the emission intensity decreased indicated the reduction of defects in films. The low emission intensity is obtained for sample at S/In = 3.5, which the crystallinity is the best one. The same result was reported by Ajili *et al.*<sup>50</sup>

In addition, the last peak at 2.55 eV is relative to the  $E_g$  values estimated from Tauc formula in earlier work by Bouguila *et al.*<sup>44</sup>

**3.4.2. Transmittance spectra.** Fig. 5 gives the variation of the transmittance ( $T$ ) spectra of  $\text{In}_2\text{S}_3$  films. It is clear from Fig. 5 that the transmittance is improved with S/In molar ratio and it exceeds 80% in the visible and near infrared regions. Its increase until S/In = 2.5 may be related to the crystallinity improvement. Besides, we obtained a low transmittance at the molar ratio S/In = 1. This can be explained by two reasons: the high surface roughness and the stoichiometric deviation. Indeed, the transmittance is highly sensitive to the distribution of grains and their height variation on the layer surface.<sup>51</sup> We notice out the presence of interference fringes in the transmittance spectra, showing the good uniformity and homogeneity of these films. In addition, we observe a sharp signal drop near the band edge due to the presence of direct transitions in the samples,<sup>52</sup> also, this result is obtained in a previous publication by Bouguila *et al.*<sup>44</sup> Besides, two regions in the transmittance spectra are clearly noted: the first region, of a strong absorption ( $\lambda < 570$  nm), is the fundamental absorption in the film due to the interband electronic transition. This region allows us to obtain the energy gap ( $E_g$ ). The second region is of high transparency ( $\lambda > 570$  nm). One can also observe that all the films are opaque in UV region. Therefore, these films can be used as UV detectors.

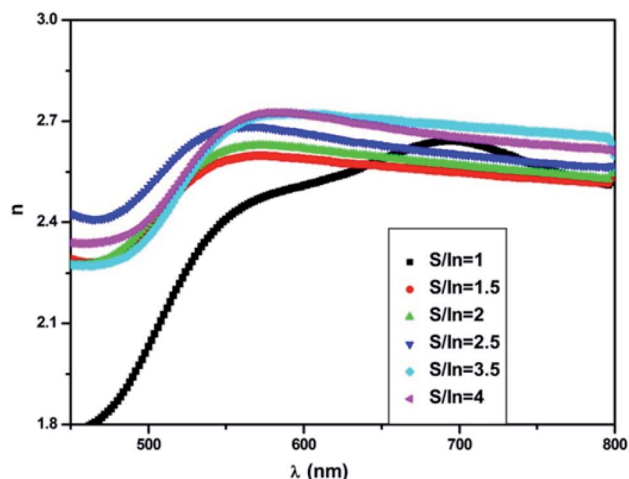
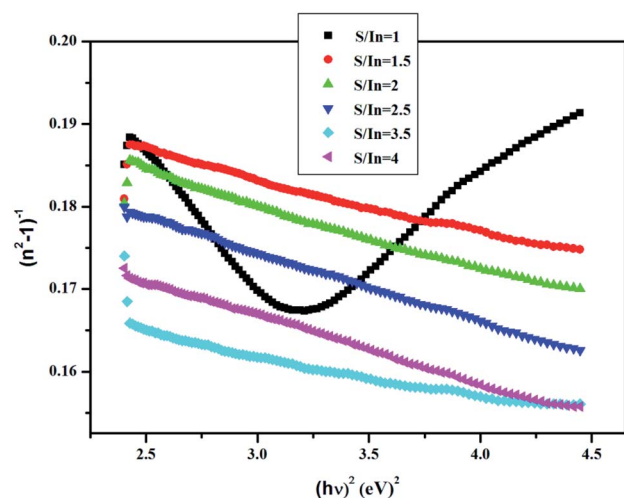
**3.4.3. Refractive index.** The refractive index ( $n$ ) is given by:<sup>53</sup>

$$n = (N + (N^2 - n_0^2 n_1^2)^{1/2})^{1/2} \quad (2)$$

Table 3 Calculated values of  $n$ ,  $\beta$  and Cauchy parameters for different S/In molar ratios

S/In	$n$	$B$	$C$ ( $\mu\text{m}^2$ )	$\beta$ (eV)
1	2.40	3.14	−1.0	0.16
1.5	2.06	2.68	−0.3	0.29
2	2.10	2.73	−0.3	0.26
2.5	1.87	2.79	−0.4	0.27
3.5	2.11	2.81	−0.2	0.31
4	2.03	2.84	−0.4	0.26



Fig. 6 Spectral distribution of  $n(\lambda)$  for different S/In molar ratios.Fig. 7 Plot of  $(n^2 - 1)^{-1}$  versus  $(h\nu)^2$ .

$$N = \frac{2n_0n_1}{T_{\min}} - \frac{(n_0^2 + n_1^2)}{2} \quad (3)$$

where  $n_0$  is the index of vacuum,  $n_1$  is the glass substrate index and  $T_{\min}$  denotes minimum transmission.

The values of  $n$  are reported in Table 3. It can be observed that this value is minimum at S/In = 2.5, beyond this value it increases slightly. This is related to the variation in packing density of the films.<sup>54</sup>

Fresnel equation<sup>55</sup> was used to evaluate the refractive index  $n(\lambda)$  of the films as given by:

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

Fig. 6 displays the dispersion of  $n$  for different molar ratios. In the high absorption region, the refractive index increases strongly. The sharp onset of  $n$  at the absorption edge is

attributed to Van Hove singularity in the joint density state in the excitation of transition between two bands.<sup>56</sup> Thus, it follows the normal dispersion in the medium and weak absorption regions. This latter phenomenon is ascribed to both light scattering effect and absorbance decrease. From Fig. 6, it can be noticed that  $n$  varies from 2.4 to 2.75 with S/In ratio. The higher values of  $n$  make  $\text{In}_2\text{S}_3$  thin films suitable for use in optoelectronic devices. Indeed, thin films are used for optical containment in waveguides, lasers and light-emitting diodes. The good value of  $n$  depends on the active layer used.

Thus, the increase of  $n$  indicates the better crystallinity of the films. Indeed, the material with amorphous nature has a low refractive index when compared to the polycrystalline one.<sup>57</sup>

The variation of  $n$  along the Cauchy distribution is given by:<sup>58</sup>

$$n = B + \frac{C}{\lambda^2} \quad (5)$$

where  $B$  and  $C$  denote the Cauchy's parameters.

Table 3 represents the values of these constants, which are evaluated from the fitting of  $n(\lambda)$ .

The dispersion energy was also calculated using the single oscillator model as described by Wemple and DiDomenico:<sup>59</sup>

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - E^2} \quad (6)$$

where  $E = h\nu$ ,  $E_0$  is the oscillator energy and  $E_d$  is the dispersion energy.

Fig. 7 represents the linear variation of  $(n^2 - 1)^{-1}$  versus  $(h\nu)^2$  for these films. This permits us to determine both  $E_0$  and  $E_d$  from the slope  $(E_d E_0)^{-1}$  and  $(E_0/E_d)$  from the intercept at the origin for each straight line.

The results are listed in Table 4.

The highest dispersion energy value is obtained at S/In = 3.5, indicating that this film has a more ordered microstructure compared to the other films. The microstructure of  $\text{In}_2\text{S}_3$  thin films varied with S/In ratio. Indeed, the influence of S/In molar ratio on microstructure is related with the nucleation and grows of  $\text{In}_2\text{S}_3$  crystal.<sup>60</sup> Furthermore, sulfur deficiency or sulfur excess would involve the presence of impurities that can affect or destroy the microstructure.<sup>61</sup>

It can also be seen that the values of  $E_0$  vary from 3.8 to 5.6 eV and oscillation energy describes the expressions  $E_0 \approx 1.5E_g$  at S/In = 1 and  $E_0 \approx 2E_g$  for S/In > 1. We can thus conclude that the Wemple–DiDomenico model describes well the behavior of these films.<sup>62,63</sup> The lower value of ratio  $E_0$  is obtained at S/In = 1, this could be attributed to the higher rate of diffusion of

Table 4 Evolution of optical parameters of  $\text{In}_2\text{S}_3$  films with different S/In molar ratios

S/In	1	1.5	2	2.5	3.5	4
$E_0$ (eV)	3.8	5.6	5.1	4.9	5.4	4.8
$E_d$ (eV)	15.5	27.8	25.3	25.5	30	25
$E_g^{\text{WDD}}$ (eV)	1.9	2.8	2.5	2.4	2.7	2.4
$\epsilon_\infty$	9.6	7.5	7.8	7.4	8	7.9
$\omega_p$ (rad s <sup>-1</sup> )	14	8	9	10	8	10
$N/m^*$ (m <sup>-3</sup> )	6	1.5	2	2	1.5	2.4



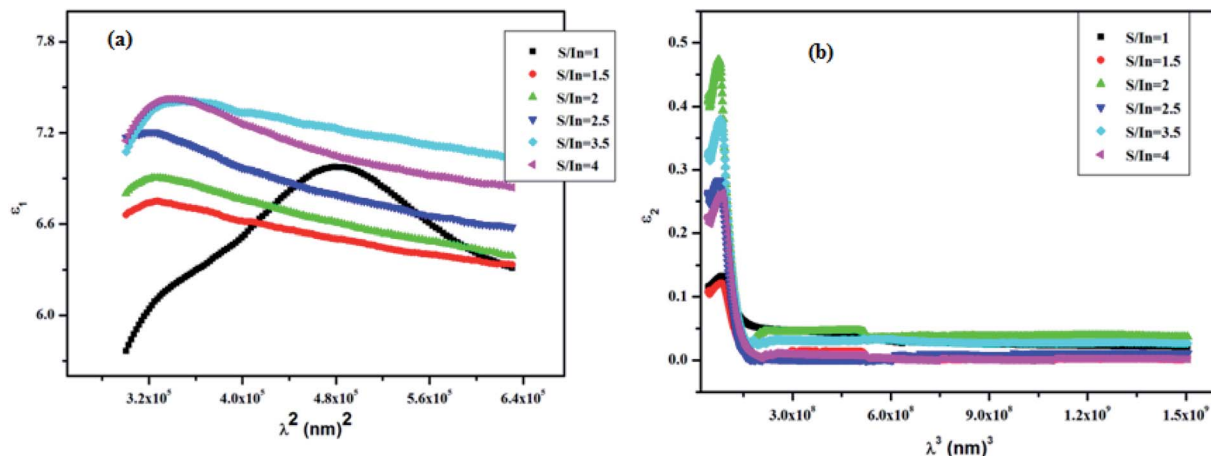


Fig. 8 (a) Plot of  $\epsilon_1$  versus  $\lambda^2$  and (b)  $\epsilon_2$  versus  $\lambda^3$ .

atoms in this film.<sup>64</sup> Furthermore, the change in the values of  $E_0$  and  $E_d$  reveals that the molar ratio S/In is a suitable parameter for the change of refractive index and oscillator parameters. Thus, Tanaka<sup>63</sup> proposed the first approximate value of the optical band gap  $E_g^{\text{WDD}}$  from the Wemple–DiDomenico model using the expression ( $E_g^{\text{WDD}} \approx \frac{E_0}{2}$ ). The  $E_g^{\text{WDD}}$  values are given in Table 4. The small difference between the two methods is ascribed to the calculations in two different regions. Indeed, in the case of Tauc method, the value of  $E_g$  is calculated in the absorption region of the spectrum, while in the Wemple–DiDomenico model the value of  $E_g^{\text{WDD}}$  is acquired in the transparent region of the spectrum.

The following empirical relation for  $E_d$  is established in crystals containing a single anion species:<sup>65</sup>

$$E_d = \beta N_c Z_a N_c \quad (7)$$

where  $\beta$  is a constant,  $N_c$  and  $Z_a$  denote the coordination number of the nearest-neighbor cation and formal anion valency.  $N_c$  represents the effective number of valence electrons per anion. For  $\text{In}_2\text{S}_3$ ,  $N_c$ ,  $Z_a$  and  $N_e$ , are equal to 6, 2 and 8, respectively. In addition,  $\beta$  takes two values:  $0.26 \pm 0.04$  eV (ionic compound) and  $0.37 \pm 0.05$  eV (covalent compound). In our work, the  $\beta$  values vary from 0.16 to 0.31 eV (Table 3). These

values agree with the first condition. Therefore,  $\text{In}_2\text{S}_3$  films are found to be ionic compounds.

**3.4.4. Dielectric constants.** The real ( $\epsilon_1$ ) and imaginary parts ( $\epsilon_2$ ) of the dielectric constant are related to the wavelength ( $\lambda$ ) by the formulas:<sup>66</sup>

$$\epsilon_1 = \epsilon_\infty - \frac{\epsilon_\infty \omega_p^2}{4\pi^2 c^2} \lambda^2 \quad (8)$$

$$\epsilon_2 = -\frac{\epsilon_\infty \omega_p^2}{4\pi^3 c^3 \tau} \lambda^3 \quad (9)$$

The free carrier concentration-to-effective mass ratio can be obtained from the relation:

$$\omega_p^2 = \frac{4\pi N e^2}{\epsilon_\infty m_e^*} \quad (10)$$

where  $\epsilon_\infty$  is infinite high frequency dielectric constant which is commonly associated with the free carriers and lattice vibration modes of the material dispersion properties,<sup>67</sup>  $\tau$ ,  $e$ ,  $\omega_p$ , and  $N/m_e^*$  denote respectively the relaxation time, electronic charge, plasma frequency and ratio of carrier concentration to the effective mass.

Fig. 8a and b, show that the behavior of  $\epsilon_1$  is similar to the refractive index ( $n$ ). This is due to the smaller value of  $k$  compared to  $n$ . However, the behaviors of  $\epsilon_2$  and  $\alpha$  are the same,

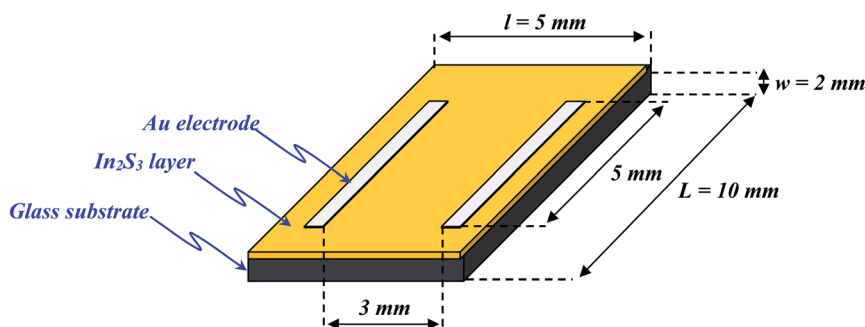


Fig. 9 Shape of  $\text{In}_2\text{S}_3$  photodetector.



because  $\varepsilon_2$  depends on the  $k$  values which are correlated to the variation of absorption coefficient ( $\alpha$ ). We observed high value of  $\varepsilon_1$  at low wavelengths; this is due to the presence of space charge polarization at the grain boundaries, which generates a potential barrier. Thus, a charge accumulation at the grain boundary occurred, which leads to highest value of  $\varepsilon_1$ .<sup>68</sup> However, the real part decreases with the increase of wavelength. This trend is due to the reduction of space charge polarization effect.

From the intercepts and slopes of the  $\varepsilon_1$  plots as a function of  $\lambda^2$  (see Fig. 8a), the values of  $\varepsilon_\infty$  and  $N/m^*$  for the films are estimated and reported in Table 4.

The increase in refractive index induces a rise in the electromagnetic radiation absorption which in turn increases the frequency. In addition, the value of  $n$  becomes high when the radiation frequency corresponds to the electron characteristic frequency. The physical interpretation of the variation of plasma frequency can be ascribed to the variation of the concentration of the charged carriers in  $\text{In}_2\text{S}_3$  thin films. Hence, the high value of  $\omega_p$  at  $\text{S/In} = 1$  might be due to the higher concentration of the charged carriers in this film. This finding confirms the results of optical band gap value at  $\text{S/In} = 1$ . As can be seen, all  $N/m^*$  values are of the order of  $10^{19} \text{ m}^{-3}$ . Bouguila *et al.*<sup>69</sup> reported comparable values for  $\text{In}_2\text{S}_3$  thin films for different thicknesses. The higher value obtained at  $\text{S/In} = 1$ , could be explained by higher defect states in the film.<sup>70</sup> Besides, Nicholas *et al.*<sup>71</sup> reported that the low value of effective mass leads to high carrier mobility. Thus, it is clear from Table 2 that the values of  $N/m^*$  are affected by the  $\text{S/In}$  molar ratio. So, we can say that  $\varepsilon_\infty$  and  $N/m^*$  are assigned to the internal microstructure.<sup>72</sup>

## 4. Photoresponse

Due to absorption in the UV and visible region,  $\text{In}_2\text{S}_3$  is considered here as photodetector. To study the photoresponse of the  $\text{In}_2\text{S}_3$  film ( $\text{S/In} = 2$ ), two rectangular gold electrodes

3 mm long and 3 mm apart were deposited on the film using thermal evaporation technique under high vacuum. The samples obtained have the shape of a parallelepiped, the dimensions of the glass substrate are ( $L = 10 \text{ mm}$ ,  $l = 5 \text{ mm}$ ,  $w = 2 \text{ mm}$ ) and the  $\text{In}_2\text{S}_3$  film thickness is around  $2 \mu\text{m}$  (Fig. 9).

$I$ - $V$  characteristics measured in dark and under illumination by neon lamp with a bias voltage ranging from  $-10$  to  $10$  volts are shown in Fig. 10a. The linear  $I$ - $V$  curves from the sample confirm the ohmic nature of  $\text{Au/In}_2\text{S}_3$  contacts. This ohmic contact with Au electrodes enables excellent photo-response behaviors. Furthermore, the formation of ohmic contacts between semiconductors and metals serving as electrodes is an important requirement for photodetector device. Indeed, this contact is required to inject the maximum current density across the contact.<sup>73</sup>

The resistance evolution was measured, while the sample was illuminated by reversible switching (ON/OFF) cycles of the neon lamp. The light was ON for 15 min and OFF for 15 min for all cycles. Fig. 10b shows that the resistance of  $\text{In}_2\text{S}_3$  film increases in dark until reaching its equilibrium value and decreases quickly to the baseline value in light. We also observe that repetitive cycles profile reveals the ability of the material to produce the same response, by exhibiting an acceptable reproducibility and reversibility of the response. This evolution suggests that more photons with higher energy are involved in the photon-induced charge-transfer process. This behavior is suitable given the fact that typical absorption is located for wavelength  $< 500 \text{ nm}$ , as shown in Fig. 5. Likewise, the optical excitation allows the generation of electron-hole pairs. The fact that the transit time of the holes is much greater than that of the electrons; a single hole can cause the circulation of several electrons in order to ensure the electrical neutrality of the material, which enhances photocurrent response.<sup>74</sup>

The increase of photocurrent is traduced by the decrease of the resistance. In this context, we have adjusted in Fig. 10b, the resistance curves *versus* time with a bi-exponential equations that have two evolution components in both decaying and rising progress.<sup>74</sup>

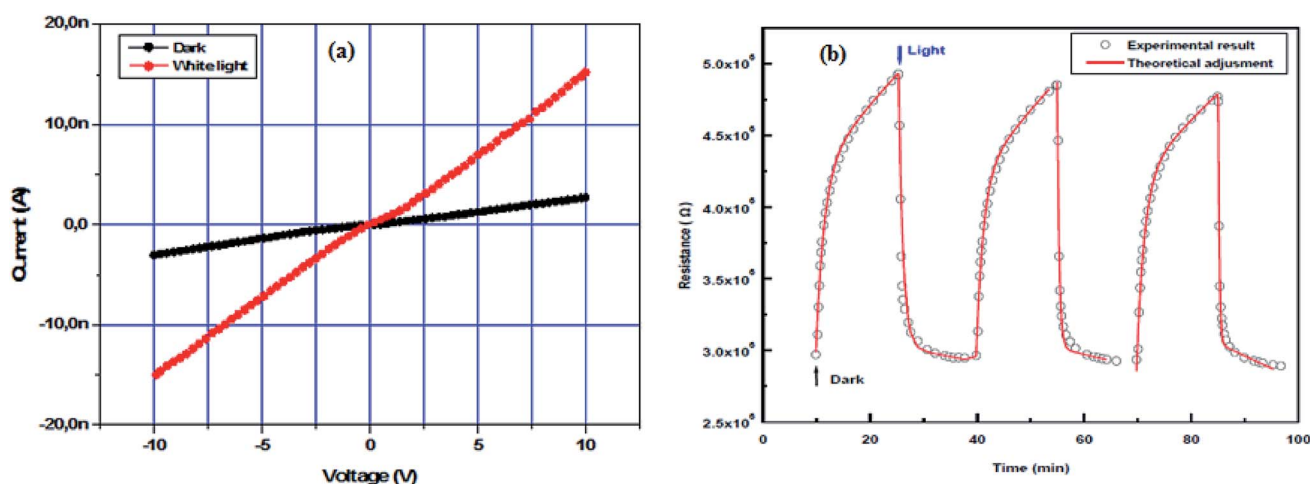


Fig. 10 (a)  $I$ - $V$  characteristics of  $\text{In}_2\text{S}_3$  thin film in dark and under illumination, (b) adjustment of  $\text{In}_2\text{S}_3$  thin film photoresponse with two exponentials evolutions.



**Table 5** Theoretical values of time constants for first and second kinetics of photocurrent cycles

Cycle number	Light		Dark	
	$\tau_1$ (s)	$\tau_2$ (s)	$\tau_1$ (s)	$\tau_2$ (s)
1	48	24 877	90	4361
2	22	20 362	77	4194
3	14	10 223	84	4695

$$r_{\text{light}} = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (11)$$

$$r_{\text{dark}} = A_1 \left(1 - e^{-\frac{t}{\tau_1}}\right) + A_2 \left(1 - e^{-\frac{t}{\tau_2}}\right) \quad (12)$$

where  $\tau_1$  and  $\tau_2$  are the time constants for first and second kinetics of photocurrent cycles, respectively.

The determination of the constants  $A_1$ ,  $A_2$ ,  $\tau_1$  and  $\tau_2$  is not obvious given the nonlinearity of the eqn (11) and (12). As a result, we divide each film response into two parts:

-the first part is dominated by the fast kinetic ( $\tau_1$ ) and corresponds to a significant variation of the resistance.

-the second part is dominated by a slow kinetic ( $\tau_2$ ) and results in a weak variation of the resistance.

We have adjusted the last points of the second domain ( $t \gg \tau_1$ ) by the function  $A_2 e^{-t/\tau_2}$  and we have deduced  $A_2$  and  $\tau_2$  values using the least squares method. Then, the quantity  $A_2 e^{-t/\tau_2}$  is subtracted from the experimental points of the first domain ( $0 < t < \tau_1$ ). The obtained results are similarly adjusted *via* the same technique to determine  $A_1$  and  $\tau_1$ . Several iterations were made in order to adjust precisely the theoretical fit with the experimental results. The fit is constructed correspond to the theoretical function. The  $\tau_1$  and  $\tau_2$  values are regrouped in Table 5.

The results of the theoretical adjustment demonstrate good conformity with the experimental data. The evolution of the resistance under illumination and in dark follows two kinetics: the first is fast, the other is slow. For the fast kinetic, the averages values of  $\tau_1$  are found around 28 s in light and 84 s in dark. We can note that time constants associated in light are relatively small compared to those associated with other in dark. This result is expected because the charge carrier generation time is shorter than the recombination time.<sup>75</sup>

## 5. Conclusion

Using spray pyrolysis technique, we have deposited  $\text{In}_2\text{S}_3$  thin films on a glass substrate at different S/In ratios. We investigated the influence of S/In molar ratios on their structural, morphological and optical properties. The Raman analysis confirms the absence of secondary phase. The RMS roughness decreases from 20 to 6 nm as the molar ratio increases. The PL study shows the presence of two major emission bands. In addition,  $n$  of the films is shown to be dependent on the S/In ratio. The dispersion of the layers is investigated using the Wemple–DiDomenico model. The oscillator energies ( $E_0$ ,  $E_d$ ) are deduced.  $E_0$  can be related to  $E_g$  in close approximation by  $E_0 \approx$

$1.5E_g$  at  $S/\text{In} = 1$  and  $E_0 \approx 2E_g$  for  $S/\text{In} > 1$ . Furthermore, the calculated value of  $\beta$  shows that  $\text{In}_2\text{S}_3$  is an ionic compound. The photoconductive property, the optical transmission and energy gap make it a promising material for optoelectronics applications.

## Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by Tunisian Ministry of Higher Education and Scientific Research, Spanish Ministry of Science and Innovation – FEDER Funds (MODENA Project CTQ2016-79461-R) and Fundación Ramón Areces (Spain, Project CIVP18A3940). NANOMAG group belongs to Galician Competitive Research Group ED431C-2017/22, programme co-funded by FEDER, and AEMAT Strategic Partnership (ED431E-2018/08, Xunta de Galicia, Spain). The authors are grateful to Professor Ibrahim Halidou (Faculté des Sciences et Techniques, Université Abdou Moumouni, Niamey, Niger) for his revision of the manuscript.

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