



# Growth, structure, optical and optoelectrical characterizations of the $\text{Cu}_2\text{NiSnS}_4$ thin films synthesized by spray pyrolysis technique

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## Abstract

Earth-abundant Kesterite materials are very important to fabricate low-cost solar cells. Here, good quality  $\text{Cu}_2\text{NiSnS}_4$  (CNSS) thin films were successively manufactured on a glass substrate at 350 °C using a simple spray pyrolysis system. The structural characterization of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films was examined by the FE-SEM and XRD techniques. X-ray diffraction patterns indicate that the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films are single phase and having polycrystalline structure. The elemental composition analysis of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films confirmed that the  $\text{Cu}_2\text{NiSnS}_4$  film is near stoichiometric in compound. Our optical observations indicate that the refractive index ( $n$ ) of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films was increased by increasing the film thickness. Moreover, the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films exhibit a direct optical transition and the magnitudes of the energy gap have been decreased from 1.28 to 1.14 eV with the increase of thickness. The optoelectrical parameters of the  $\text{Cu}_2\text{NiSnS}_4$  films, like optical conductivity, optical mobility, optical resistivity, optical carrier concentration and relaxation time were estimated with different thickness. Additionally, the nonlinear optical parameters of the  $\text{Cu}_2\text{NiSnS}_4$  films were estimated. The fabricated CNSS/n-Si heterojunction achieved a conversion efficiency of 11.34%.

## 1 Introduction

Kesterite thin films of the structure  $\text{Cu}_2\text{-M-Sn-X}_4$  (M = Zn, Cd, Mn, Co and X = S, Se) attracted a great deal of attention in the current articles owing to they have a high absorption coefficient, a promising energy gap, the low-cost element and high earth abundant of all elements [1–4]. The  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) is one of the important Kesterites that utilized as absorber layer in the solar cell. CZTS thin film solar cell was fabricated via vacuum and non-vacuum procedures. The efficiency of the CZTS solar cell reaches to about 9.6% by thermal evaporation process [5] and reaches to 5.1% by spray pyrolysis technique [6]. The substitution of Zinc in the CZTS thin film with other transition metals like Nickel, cobalt and iron will produce some new materials like  $\text{Cu}_2\text{NiSnS}_4$ ,  $\text{Cu}_2\text{CoSnS}_4$ ,  $\text{Cu}_2\text{FeSnS}_4$  suitable for the PV devices [7].

$\text{Cu}_2\text{NiSnS}_4$  has a similar structure to the  $\text{Cu}_2\text{ZnSnS}_4$  material. The  $\text{Cu}_2\text{NiSnS}_4$  is an important p-type Kesterite

material which has a high absorption coefficient (large than  $10^4 \text{ cm}^{-1}$ ) and a promising band gap in the 1.14–1.3 eV range [8]. Several preparation methods were utilized to manufacture the  $\text{Cu}_2\text{NiSnS}_4$  thin films like solvothermal method [9], hydrothermal [10], hot injection [11], spin coating method [12], electrodeposition [13], and dip coating [14] techniques.

The previous articles on the  $\text{Cu}_2\text{NiSnS}_4$  films were focused on some linear optical properties as the band gap and the absorption coefficient. Chen et al. [13] shows that the  $\text{Cu}_2\text{NiSnS}_4$  thin films exhibit a high absorption coefficient and a suitable band gap. Krishnaiah et al. [14] demonstrates that the magnitudes of energy gap were decreased with increasing the dipping time. On the other hand, the studies on the other optical parameters of the  $\text{Cu}_2\text{NiSnS}_4$  thin films like, refractive index, extinction coefficient, optoelectrical parameters and nonlinear optical parameters were not presented in the articles so, in the present work, special focus is set on the optoelectrical parameters, linear and nonlinear optical parameters of the  $\text{Cu}_2\text{NiSnS}_4$  films.

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## 2 Experimental section

### 2.1 Thin film synthesis

High quality  $\text{Cu}_2\text{NiSnS}_4$  films were fabricated on cleaned glass substrates via an inexpensive spray pyrolysis deposition method  $350^\circ\text{C}$ . The  $\text{Cu}_2\text{NiSnS}_4$  precursor solution composed of 0.1 M copper nitrate dehydrate, 0.05 M nickel nitrate dehydrate, 0.05 M stannic chloride dehydrate and 0.2 M thiourea. A mixture of methanol to water ratio of 1:2 ml has been used for solution preparation. The pH of the solution set at 9. The final  $\text{Cu}_2\text{NiSnS}_4$  solution was sprayed into a heated glass substrate held at  $350^\circ\text{C}$ . The spray process occurred at different spray times 10, 20, 30 and 40 min. A digital temperature controller joined with a thermocouple was used to control the substrate temperature. After the preparation, thin films were cooled at ambient temperature. The sprayed  $\text{Cu}_2\text{NiSnS}_4$  films were uniform and adherent to the substrates.

### 2.2 Fabrication of Ag/n-Si/CNSS/Au heterojunction

Firstly, the n-type single crystal silicon wafer subjected to etching processing using a  $\text{CP}_4$  solution consists of 5  $\text{HNO}_3$ : 3 HF: 3  $\text{CH}_3\text{COOH}$  to clear any oxide layer from the surface of the silicon wafer, thereafter the silicon wafer was cleaned with ethyl alcohol and deionized water respectively. Then, Ag electrode has been deposited onto the back surface of the Si substrate by thermal evaporation technique to form the bottom ohmic contacts. The CNSS thin film of thickness 461 nm was sprayed on the top of the n-Si wafer by spray pyrolysis method. The top ohmic electrode was formed by evaporating of Au metal onto CNSS films. The Ag/n-Si/CNSS/Au heterojunction device has been represented in Fig. 1.

### 2.3 Characterization of the $\text{Cu}_2\text{NiSnS}_4$ thin films

The thickness of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films was estimated by using alpha step D 500 stylus profilometer. The structural characterization of the  $\text{Cu}_2\text{NiSnS}_4$  thin films was analyzed by Philips X' pert diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.540 \text{ \AA}$ ). The surface morphology of the  $\text{Cu}_2\text{NiSnS}_4$  thin films were studied by field emission scanning electron microscope (FE-SEM) type (type FESEM, Quanta FEG 250, and FEI, USA). The optical, optoelectrical and nonlinear optical properties of the  $\text{Cu}_2\text{NiSnS}_4$  thin films were evaluated by measuring both of transmittance and reflectance for the  $\text{Cu}_2\text{NiSnS}_4$  thin films in the range of 400–2500 nm via spectrophotometer (type JASCO Corp., V-570). The current–voltage characterization of the

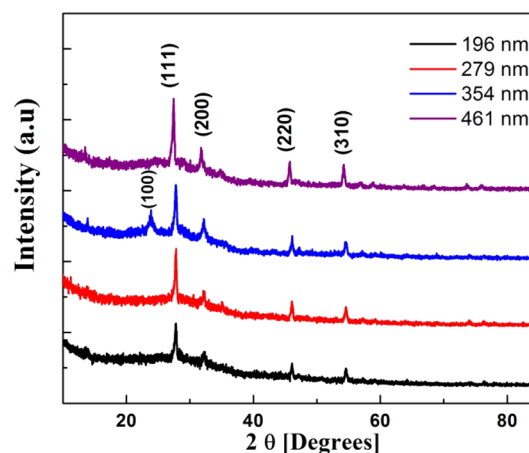


Fig. 1 X-ray diffraction spectra for the  $\text{Cu}_2\text{NiSnS}_4$  thin films

Ag/n-Si/CNSS/Au heterojunction was recorded by high impedance electrometers (Type Keithley 614). A halogen lamp with intensity of  $100 \text{ mW/cm}^2$  has been used to illuminate the Ag/n-Si/CNSS/Au heterojunction.

## 3 Results and discussion

### 3.1 Structural analysis

#### 3.1.1 XRD diffraction

Figure 1 represents the results of X-ray diffraction patterns for the  $\text{Cu}_2\text{NiSnS}_4$  films fabricated at various thicknesses 196 nm, 297 nm, 354 nm and 461 nm. As illustrated in the figure, the presence of sharp peaks confirms the polycrystalline nature of the  $\text{Cu}_2\text{NiSnS}_4$  thin films. It is clear that the  $\text{Cu}_2\text{NiSnS}_4$  films are single phase with a cubic structure, which confirmed by good coincidence of  $d$ -values of observed peaks with  $\text{Cu}_2\text{NiSnS}_4$  phase in Standard JCPDS file no. 260552, as well the absence of any extra planes that reveal the existence of any secondary phases. The presence of (100) peak for the  $\text{Cu}_2\text{NiSnS}_4$  film of thickness 354 nm was related to  $\text{Cu}_2\text{NiSnS}_4$  and this peak could be attributed to the presence of disorder in the hot plate temperatures during the film deposition.

The interplanar spacing  $d_{hkl}$  of the given Miller indices  $h$ ,  $k$  and  $l$  magnitudes of the  $\text{Cu}_2\text{NiSnS}_4$  thin films were evaluated via Bragg's law [15]:

$$2d_{hkl} \sin \theta = n\lambda, \quad (1)$$

where  $n$  represents the order of diffraction ( $n = 1$ ) and  $\lambda$  is the wavelength of X-ray. The lattice parameters of the tetragonal structure of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films were evaluated from the (111) plane using the following relation [16]:

**Table 1** The structure parameters for the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films

Film thickness (nm)	D (nm)	$\epsilon \times 10^{-3}$	$\delta \times 10^{-4} (\text{nm})^{-3}$
196	38.54	9.39	0.673
279	41.92	8.63	0.569
354	45.78	7.91	0.477
461	49.13	7.36	0.414

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

The estimated values of the unit cell volume and the lattice parameters of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films are recorded in Table 1 and they are in agreement with the JCPDS magnitudes.

The magnitudes of the grain sizes (D), the lattice strain ( $\epsilon$ ) and the dislocation density ( $\delta$ ) of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films were calculated by the presented formulas [17–19]:

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (3)$$

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

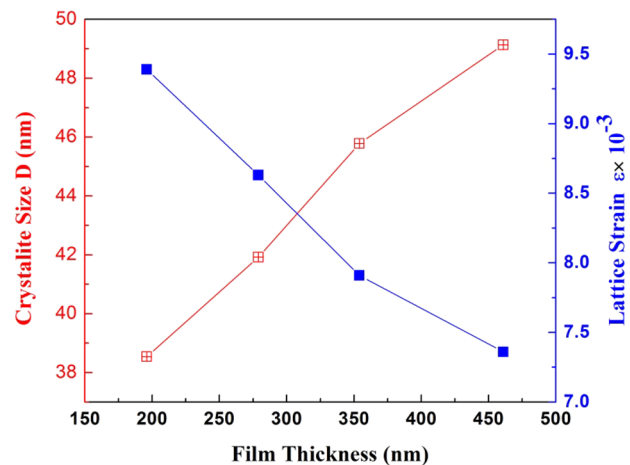
$$\delta = \frac{1}{D^2} \quad (5)$$

where  $\beta$  represents the full-width at half maximum of the peak (in radian) and  $\theta$  represents the corresponding Bragg's diffraction angle at the peak position,  $\lambda$  represents the X-ray wavelength ( $\lambda = 1.540 \text{ \AA}$ ).

The calculated values of the dislocation density ( $\delta$ ), the lattice strain ( $\epsilon$ ) and the grain size (D) of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films were noted in Table 1. It is observed from Table 1 that the increase of the film thickness is attended with an increase in the grain size D and decrease in the lattice strain, and the dislocation density. The dependence of the crystallites size (D) and the strain ( $\epsilon$ ) on the film thickness for the  $\text{Cu}_2\text{NiSnS}_4$  films were presented in Fig. 2. By increasing the film thickness the crystallites size (D) increases and the strain ( $\epsilon$ ) decreases.

### 3.1.2 Field emission scanning electron microscope (FE-SEM)

The microstructural of the  $\text{Cu}_2\text{NiSnS}_4$  thin films has been investigated via field emission scanning electron microscope (FE-SEM). The FE-SEM photograph of the  $\text{Cu}_2\text{NiSnS}_4$  thin

**Fig. 2** The crystallite size and lattice strain as a function of the  $\text{Cu}_2\text{NiSnS}_4$  film thickness

film of thickness 461 nm displays that the film consists of a spherical grains and surface of the film seems to be uniform and homogenous. The EDX pattern of the  $\text{Cu}_2\text{NiSnS}_4$  thin film of thickness 461 nm approves the presence of copper, nickel, tin and sulfur. The atomic ratio of Cu, Ni, Sn and S in the  $\text{Cu}_2\text{NiSnS}_4$  thin film is near 2:1:1:4 so the  $\text{Cu}_2\text{NiSnS}_4$  thin films are near stoichiometric in composition (Fig. 3).

## 3.2 Linear optical properties

### 3.2.1 Transmittance and reflectance analysis

The spectral spreading of optical reflectance and transmittance of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films of thickness 196 nm, 297 nm, 354 nm and 461 nm as a function of wavelength was represented in Fig. 4a and b. From these curves, the reflectance values increase with the increasing the thickness while the transmittance values decrease with the increasing the film thickness of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films.

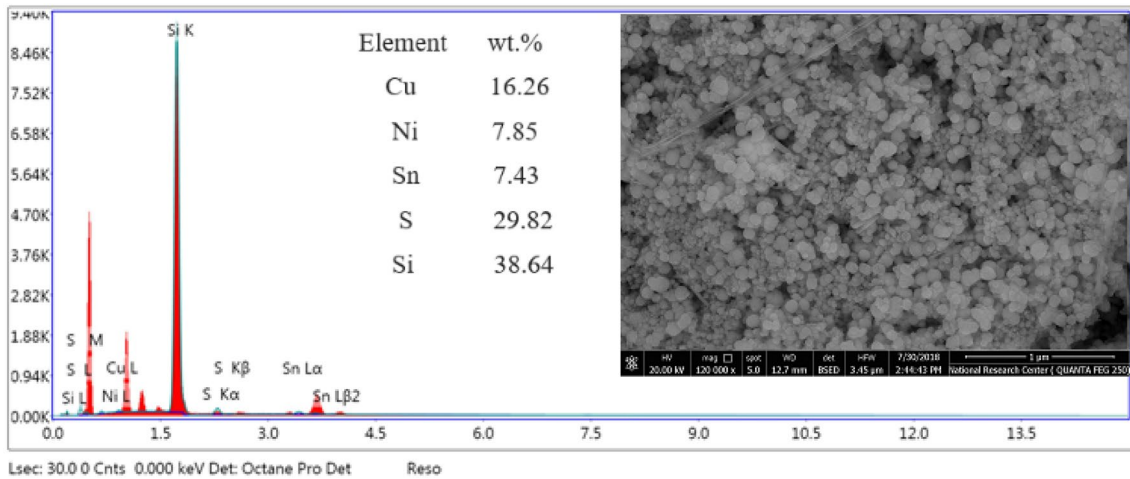
### 3.2.2 Absorption coefficient and optical band gap analysis

The absorption coefficient ( $\alpha$ ) of the  $\text{Cu}_2\text{NiSnS}_4$  films was calculates via the following expression [20]:

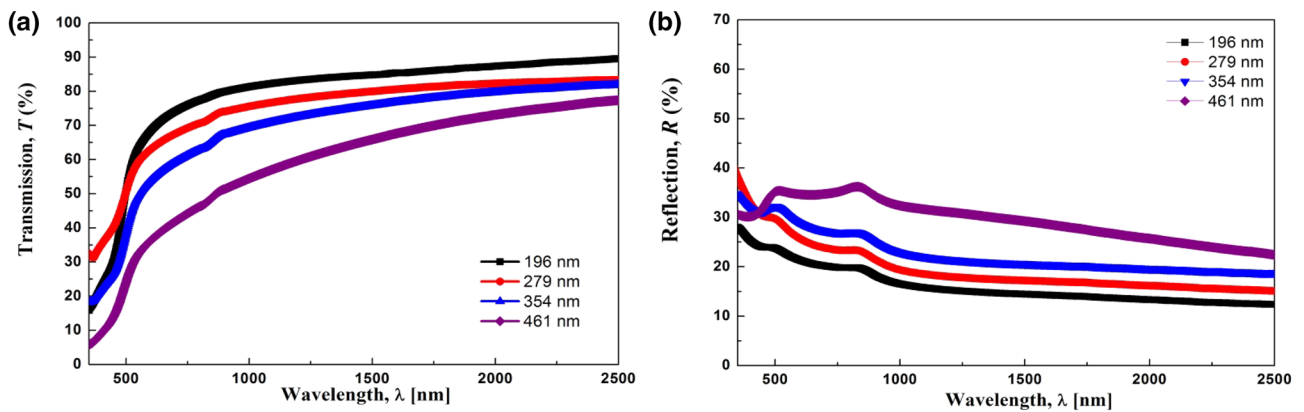
$$\alpha = \frac{1}{t} \ln \left[ \frac{(1-R)^2}{2T} + \left( \frac{(1-R)^4}{4T^2} + R^2 \right)^{1/2} \right] \quad (6)$$

where  $t$  represents the value of film thickness and  $K$  represents the extinction coefficient of the  $\text{Cu}_2\text{NiSnS}_4$  thin films.

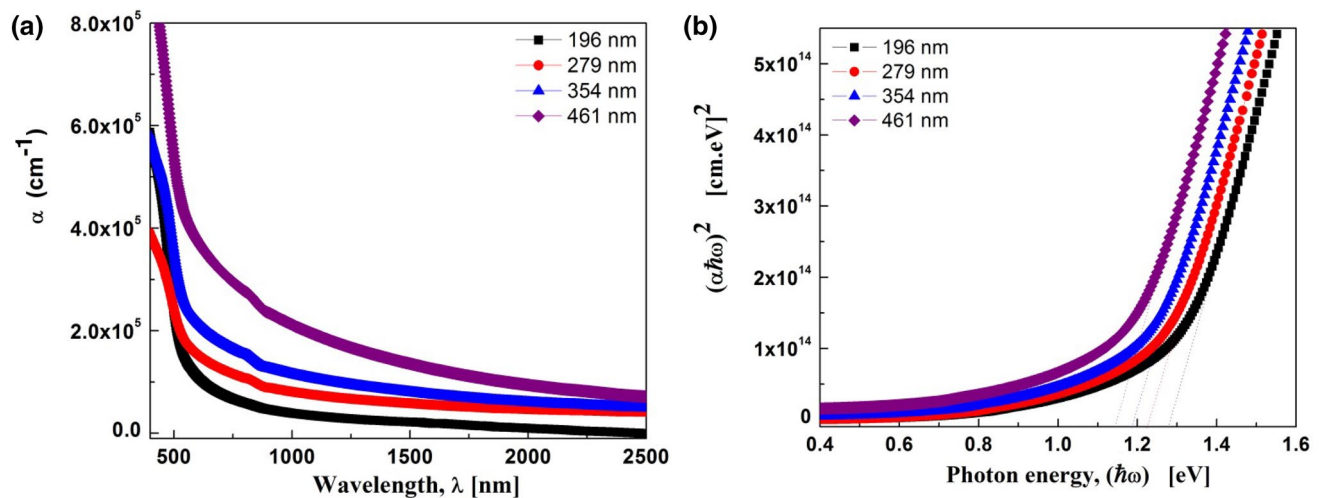
The absorption coefficient,  $\alpha$  of the  $\text{Cu}_2\text{NiSnS}_4$  thin films was presented in Fig. 5a. It is appeared from this plot that the



**Fig. 3** FE-SEM micrographs and EDX analysis of the  $\text{Cu}_2\text{NiSnS}_4$  thin film with thickness 461 nm



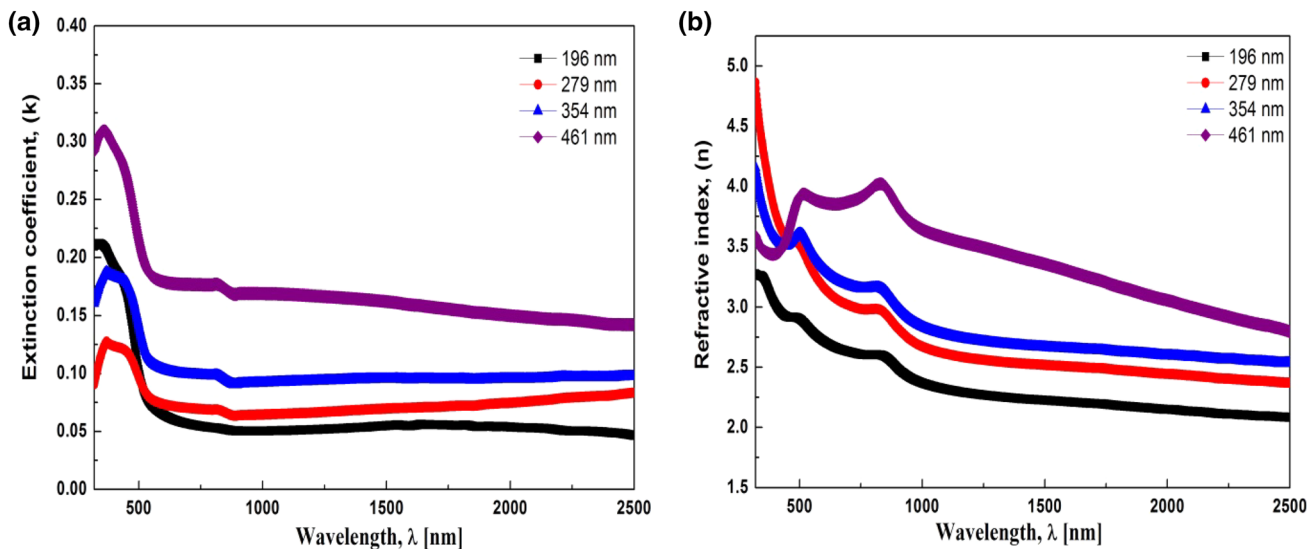
**Fig. 4** **a** The transmittance spectra of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films under investigation and **b** the reflectance spectra of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films



**Fig. 5** **a** The absorption coefficient as a function of wavelength for the  $\text{Cu}_2\text{NiSnS}_4$  thin films, **b** plot of  $(\alpha h\nu)^2$  versus the photon energy  $h\nu$  for the  $\text{Cu}_2\text{NiSnS}_4$  thin films

**Table 2** The optoelectrical and nonlinear optical parameters for the Cu<sub>2</sub>NiSnS<sub>4</sub> films

Film thickness (nm)	$E_g^{dir}$ (eV)	$\epsilon_L$	$N_{opt}$ ( $\times 10^{14}$ )	$\tau$ ( $\times 10^{-26}$ )	$\mu_{opt}$ ( $\times 10^{-14}$ )	$\rho_{opt}$ ( $\times 10^{18}$ )	$\chi^{(3)}$ ( $\times 10^{-12}$ ) [esu]	$n_2$ ( $\times 10^{-11}$ ) [esu]
196	1.28	3.36	33.17	6.18	4.65	7.43	5.89	0.98
279	1.22	3.1	33.98	5.45	3.79	7.17	7.87	6.97
354	1.19	2.81	35.74	4.76	3.24	4.03	10.31	12.56
461	1.14	2.47	36.67	4.48	2.98	3.71	11.48	14.24



**Fig. 6** **a** The extinction coefficient as a function of wavelength for the sprayed Cu<sub>2</sub>NiSnS<sub>4</sub> films, **b** the refractive index as a function of wavelength for the sprayed Cu<sub>2</sub>NiSnS<sub>4</sub> films under study

absorption coefficient of the Cu<sub>2</sub>NiSnS<sub>4</sub> films was decreased as the wavelength increase and increase with increasing the thickness of the Cu<sub>2</sub>NiSnS<sub>4</sub> films.

The relation between the absorption coefficient ( $\alpha$ ) and incident photon energy ( $h\nu$ ) in the high absorption region of semiconductor can be used to evaluate the kind of optical band transition relating to Tauc’s formula [21]:

$$\alpha h\nu = B(h\nu - E_g)^n \tag{7}$$

where  $h\nu$  represents the photon energy,  $E_g$  represents the optical band gap,  $B$  is complex parameter depending on temperature and photon energy and  $n$  is a number determines the type of optical transition process. The magnitudes of  $n$  are 1/2, 2, 3/2 and 3 for a direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively. It was found that the best linear fit for  $n$  values were at  $n$  equal 1/2, which reveal a direct optical transition. In this study, the value of  $n=2$  did not give any linear relation. The values of  $(\alpha h\nu)^2$  as a function of the photon energy ( $h\nu$ ) for the Cu<sub>2</sub>NiSnS<sub>4</sub> thin films is represented in Fig. 5b. The plot gave a straight line and the value of band gap is obtained by

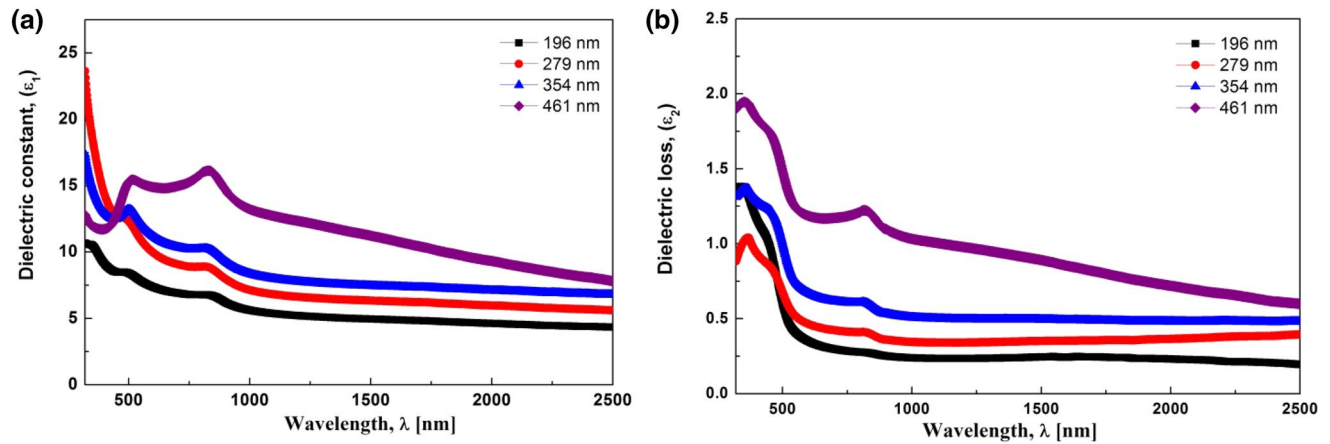
extend this straight line to intercept  $x$ -axis at zero absorption. The values of a direct energy gap of the Cu<sub>2</sub>NiSnS<sub>4</sub> thin films were listed in Table 2. It can observe from this table that the evaluated direct energy gap were decreased from 1.28 to 1.14 eV by increasing the thickness of the Cu<sub>2</sub>NiSnS<sub>4</sub> films this behavior is attributed to many factors, like the increase of grain size, increase of disorders and the variations in barrier height at the grain boundaries through increasing thickness of the sprayed Cu<sub>2</sub>NiSnS<sub>4</sub> films [22].

### 3.2.3 Extinction coefficient and refractive index analysis

For evaluating the magnitudes of the extinction coefficient  $K$  of the Cu<sub>2</sub>NiSnS<sub>4</sub> thin films we have used the following expression [23]:

$$k = \frac{\alpha \lambda}{4\pi} \tag{8}$$

The variation of the extinction coefficient of the sprayed Cu<sub>2</sub>NiSnS<sub>4</sub> thin films with the wavelength was illustrated in Fig. 6a. It can observe from figure that the magnitudes of



**Fig. 7** **a** The variation of the real dielectric constant as a function of wavelength for the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films, **b** the variation of the imaginary dielectric constant as a function of wavelength for the sprayed  $\text{Cu}_2\text{NiSnS}_4$  film

the extinction coefficient  $K$  were increased with increasing the thickness of the  $\text{Cu}_2\text{NiSnS}_4$  films and decreases with the increase in wavelength  $K$ .

The refractive index ( $n$ ) of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films was evaluated by the Fresnel relation depending on the extinction coefficient  $K$  and reflectance  $R$  as follows [24]:

$$n = \frac{(1+R)}{(1-R)} - \left( \frac{4R}{(1-R)^2} - K^2 \right)^{\frac{1}{2}} \quad (9)$$

The variation of the refractive index  $n$  of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  thin films with the wavelength was represented in Fig. 6b. It is obvious from this plot that the refractive index of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films was increased with increasing the film thickness and decreased with the increase in wavelength  $\lambda$ .

### 3.3 Optoelectrical characterization

#### 3.3.1 Dielectric constants

The dielectric constants of the  $\text{Cu}_2\text{NiSnS}_4$  thin films can be determined according to the following expressions [25, 26]:

$$\epsilon_1 = n^2 - k^2 \quad (10)$$

$$\epsilon_2 = 2nk \quad (11)$$

where  $\epsilon_2$  represents the imaginary part of the dielectric constant and the  $\epsilon_1$  represents the real part of dielectric constant for the  $\text{Cu}_2\text{NiSnS}_4$  thin films.

Figure 7 a and b represents the wavelength dependence of real and imaginary part of the dielectric constant for the  $\text{Cu}_2\text{NiSnS}_4$  films. It has been observed that the real and imaginary part of dielectric constant were increased with increasing the thickness of the  $\text{Cu}_2\text{NiSnS}_4$  films and decreases with increasing the wavelength.

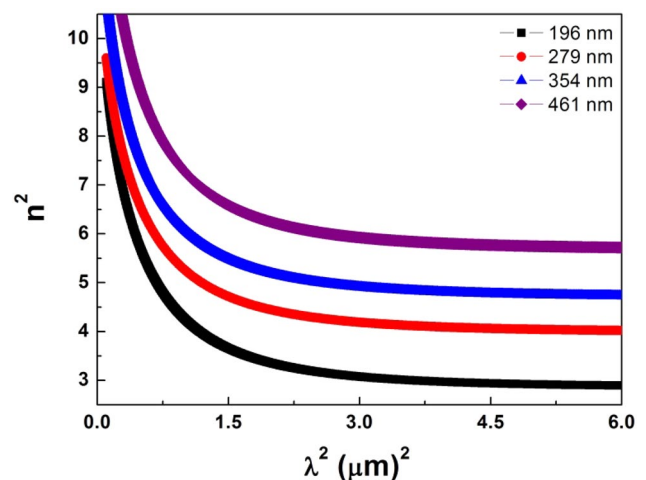
#### 3.3.2 Optical carrier concentration and relaxation time

The ratio of the charge carrier concentrations to the effective mass,  $N_{opt}/m^*$  and the lattice dielectric constant,  $\epsilon_L$ , of the sprayed  $\text{Cu}_2\text{NiSnS}_4$  films have been evaluated using the presented expression [27, 28]:

$$n^2 = \epsilon_L - \left( \frac{e^2}{4\pi^2 c^2 \epsilon_0} \right) \left( \frac{N_{opt}}{m^*} \right) \lambda^2 \quad (12)$$

where  $c$  represents the velocity of light,  $e$  represents the electronic charge.

Figure 8 displays the dependence of  $n^2$  on  $\lambda^2$  for  $\text{Cu}_2\text{NiSnS}_4$  thin films. The values of the  $N_{opt}/m^*$  for the  $\text{Cu}_2\text{NiSnS}_4$  thin films were estimated from the slopes of the graph while the values of  $\epsilon_L$  for the  $\text{Cu}_2\text{NiSnS}_4$  thin films were evaluated from the intercept. The values of  $\epsilon_L$  &



**Fig. 8** The plot of  $n^2$  versus  $\lambda^2$  for the  $\text{Cu}_2\text{NiSnS}_4$  thin films

$N_{opt}/m^*$  estimated via this curves were recorded in Table 2. The obtained values of  $\epsilon_L$  &  $N_{opt}/m^*$  were found to increase with increasing the  $Cu_2NiSnS_4$  film thickness. Moreover, the magnitude of the free carrier concentration  $N_{opt}$  the sprayed  $Cu_2NiSnS_4$  films was estimated by knowledge the value of the effective mass of the free carriers by Shen et al. [29, 30]. relation  $m^* = 0.44m_0$ . The values of  $N_{opt}$  were increased with the increase in film thickness.

The relaxation time,  $\tau$ , of the  $Cu_2NiSnS_4$  thin films was evaluated by the slope of the plot of the  $\epsilon_2$  versus  $\lambda^3$  according to the presented relationship [31, 32]:

$$\epsilon_2 = \frac{1}{4\pi^3\epsilon_0} \left( \frac{e^2}{c^3} \right) \left( \frac{N_{opt}}{m^*} \right) \left( \frac{1}{\tau} \right) \lambda^3 \tag{13}$$

Figure 9 shows the dependence of imaginary dielectric constant  $\epsilon_2$  on  $\lambda^3$  for the  $Cu_2NiSnS_4$  films. The relaxation times,  $\tau$ , of the  $Cu_2NiSnS_4$  thin films was evaluated from the slope of the linear plot and was decreased with increasing the film thickness.

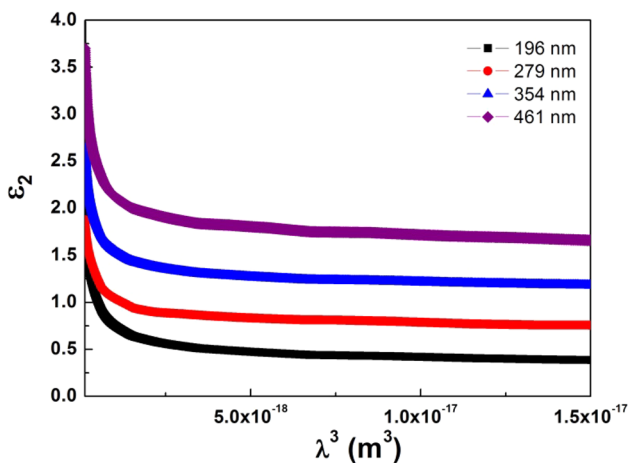
### 3.3.3 Optical mobility and optical resistivity

The optical mobility  $\mu_{opt}$  and the optical resistivity  $\rho_{opt}$  of the  $Cu_2NiSnS_4$  thin films were evaluated according to the below formulas [33–35]:

$$\mu_{opt} = \frac{e\tau}{m^*} \tag{14}$$

$$\rho_{opt} = \frac{1}{e} \mu_{opt} N_{opt} \tag{15}$$

The evaluated values for the optical mobility  $\mu_{opt}$  and the optical resistivity  $\rho_{opt}$  for the  $Cu_2NiSnS_4$  thin films were listed



**Fig. 9** The variation of the imaginary dielectric constant as a function of  $\lambda^3$  for the  $Cu_2NiSnS_4$  thin films

in Table 2. It was found that the optical mobility  $\mu_{opt}$  and the optical resistivity  $\rho_{opt}$  were decreased with increasing the film thickness. This behavior agrees with other previous published data [36, 37]

### 3.3.4 Optical and electrical conductivity evaluation

Optical conductivity ( $\sigma$ ) means the conductance of charge carriers in material due to the optical excitation [38]. The value of optical conductivity depends on the strength of irradiation light. The optical conductivity of the  $Cu_2NiSnS_4$  thin films has been evaluated by below formula [39]:

$$\sigma_{opt} = \frac{\alpha nc}{4\pi} \tag{16}$$

Figure 10a illustrates the variation of optical conductivity with the photon energy for the sprayed  $Cu_2NiSnS_4$  thin films. It is observed from this plot that the optical conductivity increases with increasing the thickness and the photon energy; this behaviour attributed to the increase of electrons excitation via the increase of the incident photon energy.

The electrical conductivity of the sprayed  $Cu_2NiSnS_4$  thin films has been estimated from the absorption coefficient,  $\alpha$  and the optical conductivity  $\sigma_{opt}$  via the presented expression [40]:

$$\sigma_e = \frac{2\lambda\sigma_{opt}}{\alpha} \tag{17}$$

The variation of the electrical conductivity with the photon energy for the  $Cu_2NiSnS_4$  films was illustrated in Fig. 10b. It is observed from this plot that the magnitudes of the electrical conductivity for the  $Cu_2NiSnS_4$  thin films increases with increasing the thickness and decreases with increasing the photon energy.

### 3.4 Nonlinear optical characterization

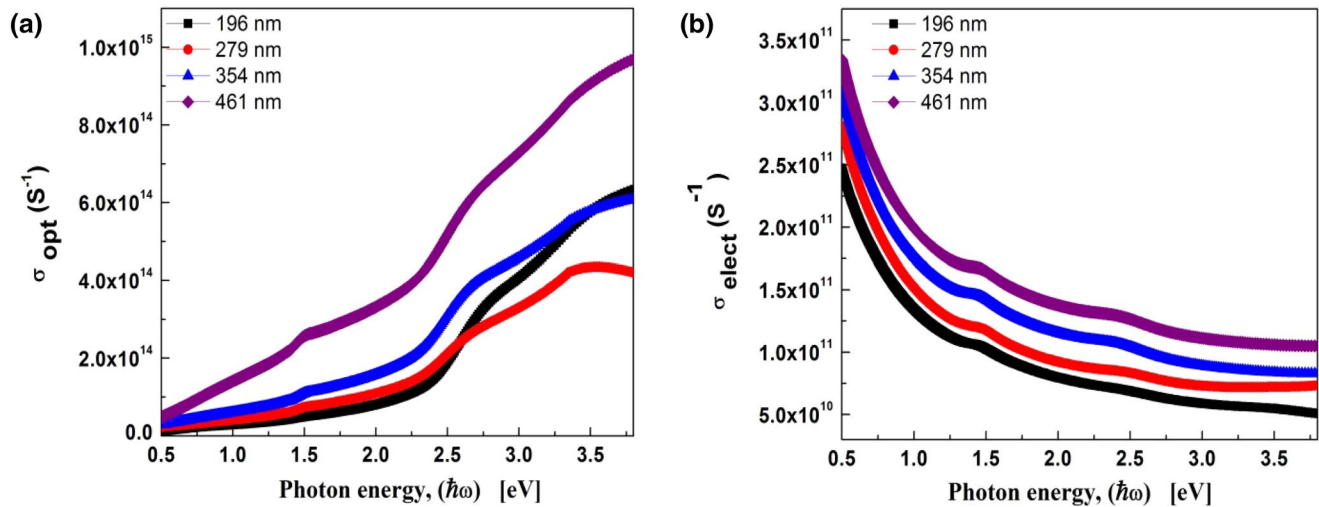
The evaluation of the nonlinear optical constants of the thin film like third-order nonlinear susceptibility  $\chi^{(3)}$  and nonlinear refractive index  $n_2$  is important for several applications like the large capacity communications and optical switching devices. The  $\chi^{(3)}$  of the  $Cu_2NiSnS_4$  films were calculated by the below expression [41]:

$$\chi^{(3)} = B \left[ \frac{n_0^2 - 1}{4\pi} \right]^4 \tag{18}$$

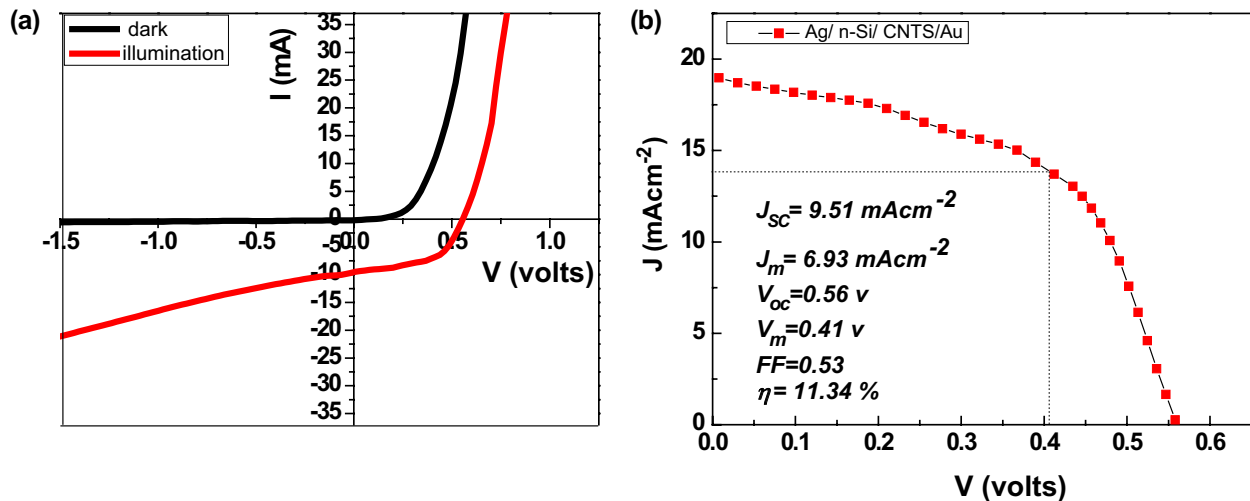
where  $n_0$  represents the values of the static refractive index, B represents a constant factor equal  $1.7 \times 10^{-10}$  esu.

The nonlinear refractive index  $n_2$  of the  $Cu_2NiSnS_4$  thin films has been calculated using the presented formula [42]:

$$n_2 = \frac{12\pi\chi^{(3)}}{n_0} \tag{19}$$



**Fig. 10** **a** The dependence of the optical conductivity on the photon energy of the  $\text{Cu}_2\text{NiSnS}_4$  thin films, **b** the electrical conductivity as a function of photon energy for the  $\text{Cu}_2\text{NiSnS}_4$  thin film



**Fig. 11** **a** The I–V characteristics of the Ag/n-Si/CNSS/Au heterojunction device in dark and under illumination, **b** J–V characteristics for Ag/n-Si/CNSS/Au heterojunction under illumination of  $100 \text{ mW/cm}^2$

The magnitudes of both  $\chi^{(3)}$  and  $n_2$  for the  $\text{Cu}_2\text{NiSnS}_4$  thin films were listed in Table 2. It can be noticed that both parameters were found to increase with increasing the film thickness.

### 3.5 Photovoltaic properties of the CNSS thin films

The photovoltaic properties have been determined by measuring the dark and illuminated current–voltage (I–V) characteristics for the Ag/n-Si/CNSS/Au heterojunction. Figure 11a illustrates the I–V characteristics of the Ag/n-Si/CNSS/Au heterojunction in the dark and illumination conditions. It is

observed from figure that the value of current for CNSS/n-Si heterojunction under illumination is more than the value of current in the dark. This attributed to the light absorbed produces carrier-contributing photocurrent due to the production of electron–hole pairs [43]. Figure 11b displays the J–V plot of Ag/n-Si/CNSS/Au heterojunction with area  $0.5 \times 0.5 \text{ cm}^2$  under illumination of  $100 \text{ mW/cm}^2$ .

The solar efficiency ( $\eta$ ) of the CNSS/n-Si heterojunction can be evaluated via the following formula [44]:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}} \times 100\%, \quad (20)$$



where  $P_{in}$  is the input energy from the sun and  $P_{max}$  is the output energy from the solar cell.

The device parameters estimated for Ag/n-Si/CNSS/Au heterojunction are  $V_{OC}=0.56$  V,  $J_{SC}=18.96$  mAcm<sup>-2</sup>,  $V_m=0.41$  V,  $J_m=13.83$  mAcm<sup>-2</sup>,  $FF=0.53$  and efficiency = 11.34%.

## 4 Conclusion

In this study, spray pyrolysis technique was utilized to deposit Cu<sub>2</sub>NiSnS<sub>4</sub> thin films at different thickness (196, 279, 354 and 461 nm). The XRD analysis of the Cu<sub>2</sub>NiSnS<sub>4</sub> films displays that the as-deposited Cu<sub>2</sub>NiSnS<sub>4</sub> thin films are polycrystalline with a cubic structure. The linear optical properties of the Cu<sub>2</sub>NiSnS<sub>4</sub> thin films have been studied in the spectral range 400–2500 nm. The refractive index of the Cu<sub>2</sub>NiSnS<sub>4</sub> films was found to increase with increasing the thickness. The type of optical transition in the Cu<sub>2</sub>NiSnS<sub>4</sub> thin films was detected to be direct allowed transition. The optoelectrical parameters of the Cu<sub>2</sub>NiSnS<sub>4</sub> films, like optical conductivity, optical mobility, optical resistivity, optical carrier concentration, electrical conductivity and relaxation time were evaluated. The effect of thickness on the non-linear optical parameters has been studied. The Ag/n-Si/CNSS/Au heterojunction has been fabricated using the CNSS film of thickness 461 nm. This device has a solar conversion efficiency of 11.34%.

## References

- S. Siebentritt, S. Schorr, Kesterites—a challenging material for solar cells. *Prog. Photovolt.* **20**(5), 512–519 (2012)
- M. Nakashima, T. Yamaguchi, S. Yukawa, J. Sasano, M. Izaki, Effect of annealing on the morphology and compositions of Cu<sub>2</sub>ZnSnSe<sub>4</sub> thin films fabricated by thermal evaporation for solar cells. *Thin Solid Films* **621**, 47–51 (2017)
- A. Walsh, S. Chen, S.-H. Wei, X.-G. Gong, Kesterite thin-film solar cells: advances in materials modelling of Cu<sub>2</sub>ZnSnS<sub>4</sub>. *Adv. Energy Mater.* **2**(4), 400–409 (2012)
- S.S. Fouad, I.M. El Radaf, P. Sharma, M.S. El-Bana, Multifunctional CZTS thin films: structural, optoelectrical, electrical and photovoltaic properties. *J. Alloys Compds.* **757**, 124–133 (2018)
- A. Ennaoui, M. Lux-Steiner, A. Weber, D. Abou-Ras, I. Kötschau, H.-W. Schock, R. Schurr, A. Hölzling, S. Jost, R. Hock, Cu<sub>2</sub>ZnSnS<sub>4</sub> thin film solar cells from electroplated precursors: novel low-cost perspective. *Thin Solid Films* **517**(7), 2511–2514 (2009)
- X. Zeng, K.F. Tai, T. Zhang, C.W.J. Ho, X. Chen, A. Huan, T.C. Sum, L.H. Wong, Cu<sub>2</sub>ZnSn(S, Se)<sub>4</sub> kesterite solar cell with 5.1% efficiency using spray pyrolysis of aqueous precursor solution followed by selenization. *Solar Energy Mater. Sol. Cells* **124**, 55–60 (2014)
- M.S. Kumar, S.P. Madhusudan, S.K. Batabyal, Substitution of Zn in Earth Abundant Cu<sub>2</sub>ZnSn(S, Se)<sub>4</sub> based thin film solar cells—a status review. *Sol. Energy Mater. Sol. Cells* **185**, 287–299 (2018)
- A. Jariwala, T.K. Chaudhuri, S.P.A. Toshniwal, V. Kheraj, A. Ray, Direct-coated copper nickel tin sulphide (Cu<sub>2</sub>NiSnS<sub>4</sub>) thin films from molecular ink. *Mater. Lett.* **215**, 118–120 (2018)
- T.-X. Wang, Y.-G. Li, H.-R. Liu, H. Li, S.-X. Chen, Flower-like Cu<sub>2</sub>NiSnS<sub>4</sub> nanoparticles synthesized by a facile solvothermal method. *Mater. Lett.* **124**, 148–150 (2014)
- S. Sarkar, B. Das, P.R. Midya, G.C. Das, K.K. Chattopadhyay, Optical and thermoelectric properties of chalcogenide based Cu<sub>2</sub>NiSnS<sub>4</sub> nanoparticles synthesized by a novel hydrothermal route. *Mater. Lett.* **152**, 155–158 (2015)
- A. Kamble, K. Mokurala, A. Gupta, S. Mallick, P. Bhargava, Synthesis of Cu<sub>2</sub>NiSnS<sub>4</sub> nanoparticles by hot injection method for photovoltaic applications. *Mater. Lett.* **137**, 440–443 (2014)
- A. Ghosh, A. Biswas, R. Thangavel, G. Udayabhanu, Photo-electrochemical property and electronic band structure of kesterite copper chalcogenides Cu<sub>2</sub>-II-Sn-S<sub>4</sub> (II = Fe, Co, Ni) thin films. *RSC Adv.* **6**, 96025–96034 (2016)
- H.-J. Chen, S.-W. Fu, T.-C. Tsai, C.-F. Shih, Quaternary Cu<sub>2</sub>NiSnS<sub>4</sub> thin films as a solar material prepared through electrodeposition. *Mater. Lett.* **166**, 215–218 (2016)
- K. Mokurala, S. Mallick, P. Bhargava, S. Siol, T.R. Klein, M.F.A.M. van Hest, Influence of dipping cycles on physical, optical, and electrical properties of Cu<sub>2</sub>NiSnS<sub>4</sub>: direct solution dip coating for photovoltaic applications. *J. Alloys Compds.* **725**, 510–518 (2017)
- A.L. Patterson, The Scherrer formula for X-ray particle size determination. *Phys. Rev.* **56**, 978 (1939)
- A.Y. Shenouda, M.M. Rashad, L. Chow, Synthesis, characterization and performance of Cd<sub>1-x</sub>In<sub>x</sub>Te compound for solar cell applications. *J. Alloys Compds.* **563**, 39–43 (2013)
- T.A. Hameed, I.M. El Radaf, H.E. Elsayed-Ali, Characterization of CuInGeSe<sub>4</sub> thin films and Al/n-Si/p-CuInGeSe<sub>4</sub>/Au heterojunction device. *J. Mater. Sci.* **29**, 12584–12594 (2018)
- Xu Wang, Tilantlan Liu, Hao Guan, Yu. Fangli, Haijun Hou, A comparative study of Cu<sub>2</sub>MnSnS<sub>4</sub> thin films synthesized via different chemical methods. *J. Optoelectron. Adv. Mater.* **9**, 1190–1193 (2015)
- I.M. El Radaf, S.S. Fouad, A.M. Ismail, G.B. Sakr, Influence of Spray time on the optical and electrical properties of CoNi<sub>2</sub>S<sub>4</sub> thin films. *J. Mater. Res. Express* **5**, 046406 (2018)
- M.S. El-Bana, R. Bohdan, S.S. Fouad, Optical characteristics and holographic gratings recording on As<sub>30</sub>Se<sub>70</sub> thin films. *J. Alloy. Compd.* **686**, 115–121 (2016)
- J. Tauc, R. Grigorovici, A. Vancu, Optical properties and electronic structure of amorphous germanium. *Phys. Status Solidi (B)* **15**, 627–637 (1966)
- I.S. Yahia, I.M. El Radaf, A.M. Salem, G.B. Sak, Chemically deposited Ni-doped CdS nanostructured thin films: optical analysis and current-voltage characteristics. *J. Alloy. Compd.* **776**, 1056–1062 (2019)
- T.A. Hameed, I.M. El Radaf, G.B. Sakr, Synthesis and characterization of thermochromic Ag<sub>2</sub>HgI<sub>4</sub> thin films. *Appl. Phys. A* **124**, 684 (2018)
- M.S. El-Bana, G. Mohammed, A.M. El Sayed, S. El-Gamal, Preparation and characterization of PbO/carboxymethyl cellulose/polyvinylpyrrolidone nanocomposite films. *Polym. Compos.* **39**, 3712–3725 (2017)
- M. Fadela, I.S. Yahia, G.B. Sak, F. Yakuphanoglu, S.S. Shenouda, Structure, optical spectroscopy and dispersion parameters of ZnGa<sub>2</sub>Se<sub>4</sub> thin films at different annealing temperatures. *Opt. Commun.* **285**, 3154–3161 (2012)
- I.M. El Radaf, R.M. Abdelhameed, Surprising performance of graphene oxide/tin dioxide composite thin films. *J. Alloy. Compd.* **765**, 1174–1183 (2018)
- M.S. El-Bana, I.M. El Radaf, S.S. Fouad, G.B. Sakr, Structural and optoelectrical properties of nanostructured LiNiO<sub>2</sub> thin films

- grown by spray pyrolysis technique. *J. Alloy. Compd.* **705**, 333–339 (2017)
28. P. Sharma, M.S. El-Bana, S.S. Fouad, V. Sharma, Effect of compositional dependence on physical and optical parameters of  $\text{Te}_{17}\text{Se}_{83-x}\text{Bi}_x$  glassy system. *J. Alloy. Compd.* **667**, 204–210 (2016)
  29. Q. Shen, K. Katayama, T. Sawada, T. Toyoda, Characterization of electron transfer from CdSe quantum dots to nanostructured  $\text{TiO}_2$  electrode using a near-field heterodyne transient grating technique. *Thin Solid Films* **516**, 5927–5930 (2008)
  30. Q. Shen, T. Toyoda, Characterization of nanostructured  $\text{TiO}_2$  electrodes sensitized with CdSe quantum dots using photoacoustic and photoelectrochemical current methods. *Jpn. J. Appl. Phys.* **43**, 2946 (2004)
  31. A.S. Hassanien, Studies on dielectric properties, opto-electrical parameters and electronic polarizability of thermally evaporated amorphous  $\text{Cd}_{50}\text{S}_{50-x}\text{Se}_x$  thin films. *J. Alloy. Compd.* **671**, 566–578 (2016)
  32. A. Hassanien, A.A. Akl, Influence of composition on optical and dispersion parameters of thermally evaporated non-crystalline Cd 50 S 50-x Se x thin films. *J. Alloy. Compd.* **648**, 280–290 (2015)
  33. M.S. El-Bana, R. Bohdan, S.S. Fouad, Optical characteristics and holographic gratings recording on  $\text{As}_{30}\text{Se}_{70}$  thin films. *J. Alloy. Compd.* **686**, 115–121 (2016)
  34. M.S. El-Bana, S.S. Fouad, Opto-electrical characterisation of  $\text{As}_{33}\text{Se}_{67-x}\text{Sn}_x$  thin films. *J. Alloy. Compd.* **695**, 1532–1538 (2017)
  35. P. Sharma, M.S. El-Bana, S.S. Fouad, V. Sharma, Effect of compositional dependence on physical and optical parameters of  $\text{Te}_{17}\text{Se}_{83-x}\text{Bi}_x$  glassy system. *J. Alloy. Compd.* **667**, 204–210 (2016)
  36. S.S. Fouad, E.A.A. El-Shazly, M.R. Balboul, S.A. Fayek, M.S. El-Bana, Optical parameter studies of thermally evaporated As-Se-Sn glassy system. *J. Mater. Sci.* **17**, 193–198 (2006)
  37. S.S. Fouad, M.S. El-Bana, P. Sharma, V. Sharma, Analysis of chemical ordering and fragility for Ge–Se–In glasses. *Appl. Phys. A* **120**, 137–143 (2015)
  38. S. Gedi, V.R.M. Reddy, C. Park, J. Chan-Wook, K.T.R. Reddy, Comprehensive optical studies on SnS layers synthesized by chemical bath deposition. *Opt. Mater.* **42**, 468–475 (2015)
  39. G.B. Sakr, I.S. Yahia, M. Fadel, S.S. Fouad, N. Romčević, Optical spectroscopy, optical conductivity, dielectric properties and new methods for determining the gap states of CuSe thin films. *J. Alloy. Compd.* **507**, 557–562 (2010)
  40. M. El-Mansy, M. El-Bana, S. Fouad, On the spectroscopic analyses of 3-hydroxy-1-phenyl-pyridazin-6 (2H) one (HPPH): a comparative experimental and computational study. *Spectrochim. Acta, Part A* **176**, 99–105 (2017)
  41. I.M. El Radaf, T.A. Hamid, I.S. Yahia, Synthesis and characterization of F-doped CdS thin films by spray pyrolysis for photovoltaic applications. *J. Mater. Res. Express* **5**, 066416 (2018)
  42. R.M. Abdelhameed, I.M. El Radaf, Self-cleaning lanthanum doped cadmium sulfide thin films and linear/nonlinear optical properties. *J. Mater. Res. Express* **5**, 066402 (2018)
  43. I.M. El Radaf, M.S. Al-Kotb, M. Nasr, I.S. Yahia, Fabrication and electrical characterization of the  $\text{InSbS}_3/\text{n-Si}$  heterojunction. *J. Alloy. Compd.* **788**, 206–211 (2019)
  44. M. Nasr, I.M. El Radaf, A.M. Mansour, Current transport and capacitance–voltage characteristics of an n-PbTe/p-GaP heterojunction prepared using the electron beam deposition technique. *J. Phys. Chem. Solids* **115**, 283–288 (2018)

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