

## DETERMINATION OPTIMUM Ni CONCENTRATION IN Zn<sub>2</sub>SnO<sub>4</sub>/Ni-DOPED Sb<sub>2</sub>S<sub>3</sub> THIN FILMS WITH DIFFERENT Ni CONCENTRATIONS USING INCIDENT PHOTONS TO CURRENT EFFICIENCY (IPCE) AND CURRENT DENSITY (J) - VOLTAGE (V) MEASUREMENTS

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In this present study, Ni-doped Sb<sub>2</sub>S<sub>3</sub> thin films with different Ni concentrations were synthesized on Zn<sub>2</sub>SnO<sub>4</sub> coated with FTO conductive glasses by CBD method at room temperature using Ni as the dopant material. The concentration of Ni to be doped during the experiment was determined as 0.25%, 0.5%, 0.75%, and 1%. In the first stage of this study, incident photons to current efficiency (IPCE) and current density (J) - voltage (V) measurements were conducted to investigate the photovoltaic properties of Zn<sub>2</sub>SnO<sub>4</sub>/Ni-doped Sb<sub>2</sub>S<sub>3</sub> thin films with different Ni concentrations for the first time. The main reason for performing IPCE and J-V measurements is to determine Ni-doped Sb<sub>2</sub>S<sub>3</sub> thin film with optimum Ni concentration with the best solar cell performance. It was found that Sb<sub>2</sub>S<sub>3</sub>:Ni(0.75%) thin film has the highest IPCE (%) and power conversion efficiency values compare to other Ni concentrations.

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### 1. Introduction

The constant increase in population causes energy shortage and environmental pollution in the world [1]. Reduction of natural resources such as oil, coal, and gas due to demand-supply imbalance has led people to investigate alternative energy sources [2]. Hydrogen, wind, tidal and sunshine are among the alternative energy sources [3-4]. Compared to other sources, solar energy is considered to be an inexpensive and non-consumable alternative [5]. In the photovoltaic technology where solar energy is used as a source, the sunlight is captured by an absorber material [6]. Organic solar cells [7], dye-sensitized solar cells [8], concentrator solar cells [9] and quantum dot sensitized solar cells [10] are the most advanced configurations of solar cells available today. Cost and efficiency are two key concepts that the solar cell industry focuses on [10]. Thin-film solar cells with the advantages of low cost, easy manufacturing, and low material usage, provide an efficiency of 19% [11].

In thin film technology, there has recently been an increased interest in the V-VI group of semiconductor materials [12-13], which have appropriate optical and electrical properties. Among them, antimony trisulfide (Sb<sub>2</sub>S<sub>3</sub>) in the stibnite phase has been used in different application areas such as optoelectronics and switching devices [14]. Sb<sub>2</sub>S<sub>3</sub> with high absorption coefficient and a refractive index has an energy band gap ranging between 1.5 and 2.2 eV [15] and is used as a good absorber in photovoltaic applications. Sb<sub>2</sub>S<sub>3</sub> has been used for solar cell structures such as Ag Sb<sub>2</sub>S<sub>3</sub>:C/CdS/ITO [16], Pt- Sb<sub>2</sub>S<sub>3</sub>[17] and n- Sb<sub>2</sub>S<sub>3</sub>/p-Ge [18] and the average efficiency has been calculated as 7.4%.

One of the ways to improve the optical and electrical properties of semiconductors and their solar cell efficiency is to be doped them with the appropriate material [19]. Transition metals

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such as manganese (Mn) [20], nickel (Ni) [21], cobalt (Co) [22], iron (Fe) [23], chromium (Cr) [24] and copper (Cu) [25] have been used as dopants in many different studies. In our previous studies, photovoltaic properties of solar cell structures such as  $\text{TiO}_2 / \text{Fe}: \text{ZnS}$  [26]  $\text{TiO}_2 / \text{Cr}: \text{CdS}$  [24],  $\text{Zn}_2\text{SnO}_4/\text{Mn}: \text{ZnS}$  [27] have been investigated and it has been reported that the doped devices have better solar cell performance than un-doped devices. Thus, it can be said that the doping plays a significant role to boost the efficiency of semiconductor-based solar cells.

It is possible to synthesize semiconductor thin films by applying many different techniques. In previous different studies [17, 28],  $\text{Sb}_2\text{S}_3$  thin films have been synthesized by chemical bath deposition (CBD) method. One of the main reasons for using this technique is low cost. It was also emphasized that the desired  $\text{Sb}_2\text{S}_3$  thin films were synthesized without the need for intensive laboratory conditions.

In this present study, Ni-doped  $\text{Sb}_2\text{S}_3$  thin films with different Ni concentrations were synthesized on  $\text{Zn}_2\text{SnO}_4$  coated with FTO conductive glasses by CBD method at room temperature using Ni as the dopant material. The concentration of Ni to be doped during the experiment was determined as 0.25%, 0.5%, 0.75%, and 1%. In the first stage of this study, incident photon to electron conversion efficiency (IPCE) and current density (J)- voltage (V) measurements were conducted to investigate the photovoltaic properties of  $\text{Zn}_2\text{SnO}_4 / \text{Ni-doped } \text{Sb}_2\text{S}_3$  thin films with different Ni concentrations for the first time. The main reason for performing IPCE and J-V measurements is to determine Ni-doped  $\text{Sb}_2\text{S}_3$  thin film with optimum Ni concentration which shows the best solar cell performance.

After determining the optimum Ni concentration, the structural, optical and elemental properties of Ni-doped  $\text{Sb}_2\text{S}_3$  thin films with this concentration were investigated, respectively.

## 2. Experimental part

### 2.1 Synthesis of $\text{Zn}_2\text{SnO}_4$ nanoparticles

The method used for the synthesis of nanoparticles is the hydrothermal technique. 50 ml of zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) aqueous solution and 50 ml of tin chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) aqueous solution was stirred at room temperature. The stirring process was continued until to get a homogeneous mixture. Then, sodium hydroxide (NaOH) solution was dropped on the mixture. The obtained white slurry precipitation was transferred into 200 ml Teflon coated autoclave. The autoclave was kept at  $180^\circ\text{C}$  for 12 h in an oven. The product was filtered washed and dried in a hot air oven. Thus, the formation of  $\text{Zn}_2\text{SnO}_4$  nanoparticles was obtained.

To be formed  $\text{Zn}_2\text{SnO}_4$  coated on fluorine alloyed tin oxide (FTO,  $13\Omega \cdot \text{sq}^{-2}$ ) conductive glasses The  $\text{Zn}_2\text{SnO}_4$  paste was coated on the FTO substrates using the doctor blade method, then sintered at  $450^\circ\text{C}$  for 45 minutes.

### 2.2 Synthesis of $\text{Zn}_2\text{SnO}_4 / \text{Sb}_2\text{S}_3$ thin films

In a typical CBD method, 0.65g of antimony chloride ( $\text{SbCl}_3$ ) was dissolved in 10 ml of acetone. 25 mL of 1 M aqueous solution of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) was added to a solution containing  $\text{SbCl}_3$ . The total volume of the mixture was made 100 mL by adding an appropriate amount of de-ionized water. After obtaining a homogeneous mixture,  $\text{Zn}_2\text{SnO}_4$  coated on FTO substrate was vertically left into  $\text{Sb}_2\text{S}_3$  solution for the certain time. Afterward, the substrate was removed from the chemical bath, washed well with de-ionized water and dried in air. The glass substrate was annealed at  $350^\circ\text{C}$  for 1 h under  $\text{N}_2$ .

### 2.3 Synthesis of $\text{Zn}_2\text{SnO}_4 / \text{Ni-doped } \text{Sb}_2\text{S}_3$ thin films with different Ni concentrations

For preparing  $\text{Zn}_2\text{SnO}_4 / \text{Ni-doped } \text{Sb}_2\text{S}_3$  thin films with different Ni concentrations, the different concentrations of nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were added 0.65g of  $\text{SbCl}_3$  solution and then followed the same procedure mentioned above.

### 3. Characterizations

Incident photons to current efficiency (IPCE) and current density (J)- voltage (V) measurements were performed by using PCE-S20 with a monochromatic light source consisting of a 150-W Xe lamp and a monochromator. Structural properties of the thin film were characterized by x-ray diffraction on a Rigaku X-ray diffractometer with Cu  $K_{\alpha}$  ( $\lambda = 154,059$  pm) radiation. Optical characterization was performed by ultraviolet-visible on a Perkin-Elmer Lambda 2. The elemental analysis was studied by energy dispersive x-ray measurement (JEOL JSM 5800).

### 4. Results and discussions

#### 4.1 IPCE and J-V measurements for $Zn_2SnO_4$ /Ni-doped $Sb_2S_3$ thin films with different Ni concentrations

The optimum concentration of Ni content in  $Zn_2SnO_4$  /Ni-doped  $Sb_2S_3$  thin films with different Ni concentrations was determined using the in IPCE and J-V measurements, respectively. The recorded IPCE spectra for  $Zn_2SnO_4$  / $Sb_2S_3$  and  $Zn_2SnO_4$  /Ni-doped  $Sb_2S_3$  with different Ni concentrations are shown in Fig. 1.

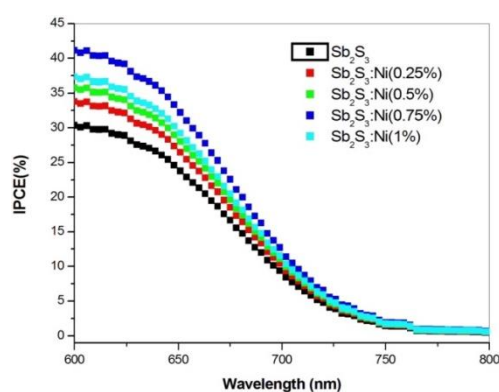


Fig. 1. The recorded IPCE spectra for  $Zn_2SnO_4$  / $Sb_2S_3$  and  $Zn_2SnO_4$  /Ni-doped  $Sb_2S_3$  thin films with different Ni concentrations.

The obtained IPCE (%) values for  $Zn_2SnO_4$  / $Sb_2S_3$  and  $Zn_2SnO_4$  /Ni-doped  $Sb_2S_3$  thin films with different Ni concentrations are given in Table 1.

Table 1. The obtained IPCE (%) values for thin films.

Thin films	The obtained IPCE (%) values at 600 nm
$Sb_2S_3$	30.40
$Sb_2S_3$ : Ni(0.25%)	33.84
$Sb_2S_3$ : Ni(0.5%)	35.59
$Sb_2S_3$ : Ni(0.75%)	41.00
$Sb_2S_3$ : Ni(1%)	37.16

It can be seen clearly, the efficiency of  $Zn_2SnO_4$  / $Sb_2S_3$  thin film shows an enhancement when it is doped with Ni content. The optimum Ni concentration is 0.75% because the obtained maximum the IPCE (%) value efficiency is 41.00 % for  $Sb_2S_3$ : Ni(0.75%) thin film. Consequently, it can be said that the Ni content plays an important role to boost the efficiency of  $Zn_2SnO_4$  /Ni-doped  $Sb_2S_3$  thin films with different Ni concentrations.

J-V measurements were applied to calculate power conversion efficiency values ( $\eta$ ) of synthesized thin films. The power conversion efficiencies of the thin films were calculated using the recorded J-V curve.

Fig. 2 demonstrates the recorded J-V curves for  $\text{Zn}_2\text{SnO}_4/\text{Sb}_2\text{S}_3$  and  $\text{Zn}_2\text{SnO}_4/\text{Ni}$ -doped  $\text{Sb}_2\text{S}_3$  thin films with different Ni concentrations.

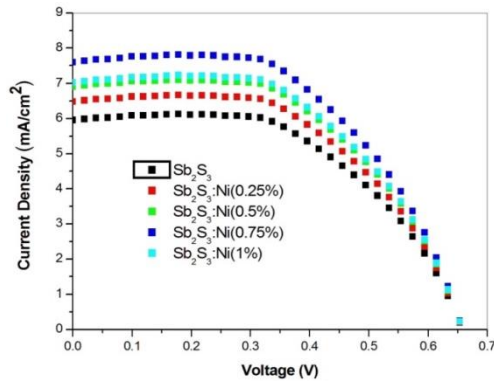


Fig. 2. The recorded J-V curves for  $\text{Zn}_2\text{SnO}_4/\text{Sb}_2\text{S}_3$  and  $\text{Zn}_2\text{SnO}_4/\text{Ni}$ -doped  $\text{Sb}_2\text{S}_3$  thin films with different Ni concentrations.

The obtained short-circuit current density ( $J_{\text{SC}}$ ), open circuit voltage ( $V_{\text{OC}}$ ) and  $\eta\%$  values are given in Table 2.

Table 2.  $J_{\text{SC}}$ ,  $V_{\text{OC}}$  and  $\eta\%$  values  $\text{Zn}_2\text{SnO}_4/\text{Sb}_2\text{S}_3$  and  $\text{Zn}_2\text{SnO}_4/\text{Ni}$ -doped  $\text{Sb}_2\text{S}_3$  thin films with different Ni concentrations.

Thin films	$J_{\text{SC}}$ (mA/cm <sup>2</sup> )	$V_{\text{OC}}$ (V)	$\eta\%$
$\text{Sb}_2\text{S}_3$	5.98	0.66	3.95
$\text{Sb}_2\text{S}_3:\text{Ni}(0.25\%)$	6.50	0.66	4.29
$\text{Sb}_2\text{S}_3:\text{Ni}(0.5\%)$	6.91	0.66	4.56
$\text{Sb}_2\text{S}_3:\text{Ni}(0.75\%)$	7.63	0.66	5.04
$\text{Sb}_2\text{S}_3:\text{Ni}(1\%)$	6.98	0.66	4.61

It should be noted that there is a significant improvement in the performance of the  $\text{Sb}_2\text{S}_3$  thin film when it is doped with different concentrations of Ni.

As can be seen from Table 2, (1) the  $\eta$  (%) of  $\text{Zn}_2\text{SnO}_4/\text{Ni}$ -doped  $\text{Sb}_2\text{S}_3$  thin films with different Ni concentrations is higher than  $\text{Zn}_2\text{SnO}_4/\text{Sb}_2\text{S}_3$ . The Ni dopant plays an effective role to enhance the performance of the  $\text{Zn}_2\text{SnO}_4/\text{Sb}_2\text{S}_3$ -based solar cells. (2) The  $\eta$  (%) value of  $\text{Sb}_2\text{S}_3:\text{Ni}(0.75\%)$  thin film has the highest value when the  $\eta$  (%) values of the four different Ni concentrations used are compared.

Thus, it was experimentally determined with the data obtained from the IPCE and J-V measurements that  $\text{Sb}_2\text{S}_3:\text{Ni}(0.75\%)$  thin film has better efficiency than both the pure  $\text{Sb}_2\text{S}_3$  and other Ni concentrations used.

#### 4.2 XRD patterns for $\text{Sb}_2\text{S}_3:\text{Ni}(0.75\%)$ thin film

Fig. 3 indicates XRD patterns of  $\text{Sb}_2\text{S}_3:\text{Ni}(0.75\%)$  thin film. The recorded all diffraction patterns for  $\text{Sb}_2\text{S}_3:\text{Ni}(0.75\%)$  thin film can be identified as those of orthorhombic,  $\text{Sb}_2\text{S}_3$ . The diffraction patterns are located at  $2\theta^\circ = 15.48, 17.27, 21.95, 24.64, 28.06, 29.14,$

$32.01, 35.06, 36.68, 39.01, 39.91,$  and  $42.60$  and associate with (020), (120), (220), (130), (230), (211), (221), (301), (231), (430), (141), and (421) planes, respectively, of the orthorhombic  $\text{Sb}_2\text{S}_3$ . Any XRD patterns related to Ni compounds or oxides are not observed. The average size of

the  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film, estimated from the full width at half height of diffraction peaks using the Debye-Scherrer formula, is 51.18 nm.

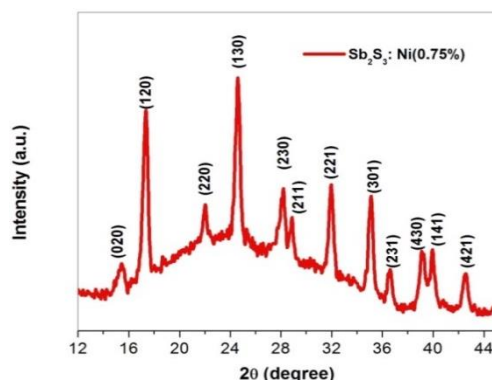


Fig. 3. The recorded XRD patterns of  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film.

#### 4.3 Determination energy band gap value for $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film

UV-Vis spectroscopy was used to study the band structure of  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film. Equation (1), called as Tauc's relation, was used to determine energy band gap value of  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film.

$$\alpha h\nu = C(h\nu - E_g)^n \quad (1)$$

Where  $\alpha$  is the absorption coefficient,  $n=1/2$  or 2 for direct or indirect allowed transition, respectively,  $C$  is the characteristic parameter for respective transitions,  $h\nu$  is photon energy and  $E_g$  is energy band gap.

The recorded optical absorption spectrum and  $(\alpha h\nu)^2$  versus  $h\nu$  curve for  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film was demonstrated in Fig. 4(a-b).

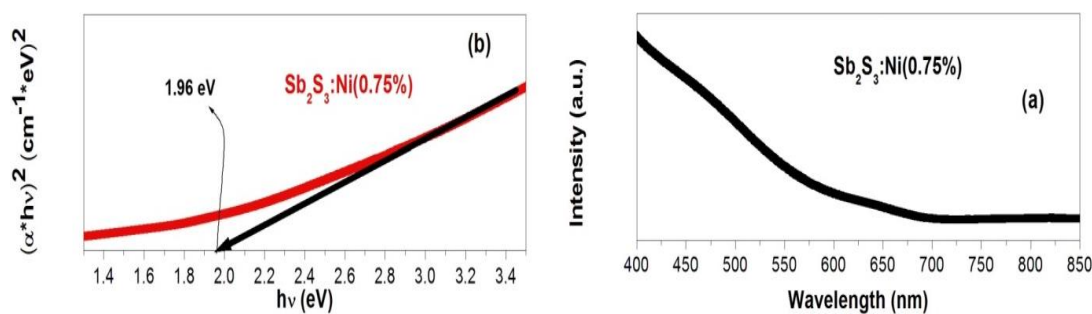


Fig. 4. (a) The recorded optical absorption spectrum and (b)  $(\alpha h\nu)^2$  versus  $h\nu$  curve for  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film.

It was determined that the band gap value for  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film is 1.96 eV whereas the band gap value for un-doped  $\text{Sb}_2\text{S}_3$  thin film is 1.89 eV (is not shown). The obtained the band gap values for thin films show that the absorption wavelength ( $\sim 642.48$  nm) of  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film is shifting to the shorter wavelength compared to pure  $\text{Sb}_2\text{S}_3$  ( $\sim 656.08$  nm). The increase in energy band gap value of  $\text{Sb}_2\text{S}_3$ : Ni(0.75%) thin film in the presence of Ni additive material, may be owing to structural modification. Furthermore, it can be said that the replacement of Ni ion in the  $\text{Sb}_2\text{S}_3$  lattice is a reason for an increase in energy band gap value of  $\text{Sb}_2\text{S}_3$  thin film. As a result, this situation could lead to being formed some additional energy levels in  $\text{Sb}_2\text{S}_3$  energy band gap.

#### 4.4 Determination of real % of nickel in Sb<sub>2</sub>S<sub>3</sub>: Ni(0.75%) thin film

The energy dispersive x-ray (EDX) spectrum was used to confirm the elemental compositions of Sb<sub>2</sub>S<sub>3</sub>: Ni(0.75%) thin film. The elemental percentages for thin film obtained from EDX patterns are 62.17 for Sb, 37.26 for S and 0.57 for Ni. Thus, this result can be an indication that the Ni additive material is successfully incorporated into Sb<sub>2</sub>S<sub>3</sub>.

### 5. Conclusions

We reported that Ni-doped Sb<sub>2</sub>S<sub>3</sub> thin films with different Ni concentrations are synthesized on Zn<sub>2</sub>SnO<sub>4</sub> coated with FTO conductive glasses by CBD method at room temperature. The concentration of Ni to be doped during the experiment was determined as 0.25%, 0.5%, 0.75%, and 1%. In the present study, IPCE and J-V measurements were conducted to investigate the photovoltaic properties of Zn<sub>2</sub>SnO<sub>4</sub>/Ni-doped Sb<sub>2</sub>S<sub>3</sub> thin films with different Ni concentrations for the first time. The main reason for performing IPCE and J-V measurements is to determine Ni-doped Sb<sub>2</sub>S<sub>3</sub> thin film with optimum Ni concentration which shows the best solar cell performance. It was observed that Sb<sub>2</sub>S<sub>3</sub>: Ni(0.75%) thin film has better efficiency ( $\eta\%$ =5.04) than other Ni concentration.

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