Structural and optoelectrical properties of single phase SnS_2 thin films at various substrate temperatures by Spray Pyrolysis

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Abstract. Thin films of SnS_2 were prepared, as the absorber layer in solar cells, using an aqueous solution of $SnCl_4$ and thiourea by spray pyrolysis technique. Effect of the Substrate temperature on the properties of these thin films was studied. Investigation via XRD showed the formation of polycrystalline SnS_2 along (001) in all layers; there was no sign of other unwanted phases. With increasing of substrate temperature from 325 to 400 ^{0}C, the crystallinity of the sample was improved, after that, it deteriorated the crystallinity. Layers had granular morphology and Valley-Hills topography. UV-VIS spectra revealed that the transmittance of all layers was lower than 40% in the visible region and the band gap reduced from 2.8 to 2.55 eV with increment in temperature from 350 to 400 ^{0}C. Photoluminescence spectra of the prepared film, which was formed at 400 ^{0}C showed a dominant peak at 530 nm, caused recombination of excitons. The least electrical resistivity of the SnS_2 thin film prepared at 400 ^{0}C in dark and light environment were 4.6×10^{-3} Ωcm and 0.65×10^{-3} Ωcm, respectively; which demonstrated 400 ^{0}C was the optimum temperature in point of optoelectrical properties in the SnS_2 thin film.

Keywords: Spray pyrolysis, Chalcogenide, Thin films, Tin disulfide

1.INTRODUCTION

Considering the remarkable demand for clean energy all over the world, much attention has been paid to high efficiency solar cells with economic costs during recent years. Synthesizing an absorbent layer, which is compatible with solar spectra, via simple and economic methods, is a proper way to optimize solar cell performance. As an absorber layer, many chalcogenides such as MgSe, Bi_2S_3, CdSe, In_2S_3, and $CuBiS_2$ have been synthesized on silicon based- solar cells. The advantage of these compounds is the wide and controllable band gap range. It is notable that chalcogenides semiconductors as an absorbent layer, have absorbing wavelength range which matches well with solar radiative spectra; on the other hand, they have high absorption coefficient to obtain the most available energy from photons. Multicomponent such as CuInSe (CIS) and $Cu(In,Ga)Se_2$ (CIGS) have a profound influence on solar cells efficiency[1] , but the excessive cost of indium and toxicity of cadmium beside high expenses of deposition operation and the necessity for complicated equipment, restrict utilization of them [2] .

During recent years, binary chalcogenides compounds of IV-VI groups such as SnS_2 have aroused much interest due to their proper band gap in the visible range, high absorption coefficient and potential as absorber layers [3]. Components of Sn-S are non- toxic and abundant in nature, e.g. SnS, Sn_2S_3, Sn_3S_4, SnS_2[4, 5]. These compounds show a wide band gap from 2.35 to 3 eV. The absorption coefficient of latter compounds is high enough for being absorber layers (10^4 cm^{-1}) [3].

SnS_2 thin films, as one of the most stable phases of Sn-S, have been prepared by various methods such as chemical bath deposition (CBD) [6], successive ionic layer adsorption and reaction (SILAR)[7], vacuum thermal evaporation [8] and spray pyrolysis[9]. Among the mentioned methods, spray pyrolysis is a simple and cost - effective technique, which is easy to control and suitable for large area production [10]. In this method, a solution of intended precursors is atomized and sprayed on a hot substrate; high temperature of the substrate leads to pyrolysis reaction on the surface. Usage of solution precursor makes this method appropriate even for doping thin films, for example, Cu doped SnS thin film[11]. Different parameters such as the substrate temperature, concentration of precursor solution, precursors proportion, type of solvent and spray rate have an impact on the structural, optical and electrical properties of thin

films; among them, substrate temperature is the most effective parameter. Up to now, SnS_2 thin films have been investigated by researchers such as Imen Bouhaf Kherchachia et al. and I. G. Orletskii et al.[12-14]. In this work, thin films of tin disulfide were prepared to study the effect of substrate temperature on the structural, morphological, topographical, optical and electrical properties, to obtain maximum absorption and electrical conductivity for solar cell absorbent layer applications.

2. Materials and experimental

Tin disulfide thin films were deposited on soda lime glass substrates. The solution was prepared from $SnCl_4.5H_2O$ (Sigma-Aldrich-10026-06-9) and thiourea ($CS(NH_2)_2$) (Merck-62-56-6) as precursors and double distilled water as the solvent. The tin ionic solution was provided by dissolving 0.2M tin (IV) pentahydrate in 25 cc double distilled water. The same volume of 0.4 M aqueous solution was prepared from thiourea to provide Sulfur in the precursor. For complete dissolution, two solutions were well mixed on a magnetic stirrer at the rate 300 rpm for 15 minutes. Finally, they were mixed together. 1.5×1.5 mm^2 glass substrates were washed and degreased with double distilled water and ethanol, then ultrasonically cleaned. Nozzle to substrate distance was set vertically at 35 cm, the solution flow rate was kept at 5 ± 1 cc/min for spray duration of about10 minutes and carrier gas pressure was constant at 4 bar. The substrate temperature varied from 325 ^{0}C to 425^{0}C in steps of 25^{0}C to reach optimum temperature. To avoid cracking, thin films were allowed to cool slowly at ambient temperature after deposition.

The crystallinity of the deposited samples were studied using a PANalytical system, model X'Pert PRO MPD, by means of a Cu anode (λ K_α=1.54A^0) as the radiation source, Ni filter, 40kV voltage and 30 mA current in the 2θ angle range of 5 to 80^0. To analyze the Infrared spectra (IR) of the film, Fourier transform infrared spectroscopy (FTIR) was used, by Perkin system, model Elmer spectrum 400. Morphology and topography of the deposited films surface were investigated by the TESCAN Vega Model scanning electron microscope and the Park Scientific Instrument CP Auto probe-contact mode atomic force microscope, respectively. Elemental composition of the film was determined by the energy

dispersive analysis by X- rays (EDAX), model Sirius SD. The UV-VIS NIR spectroscopy was performed to investigate the optical properties of thin layers in the range 300- 1100 nm wavelength with a Perkin Elmer spectroscope, model lambda 25 with a probing speed of 60 nm/min. The thickness of deposited thin films was determined via spectrometer model Avaspec 3648. Also, photoluminescence spectra (PL) was inspected using a Cary Eclipses spectrometer at ambient temperature, applying 320 nm wavelength as the exciting wavelength. The electrical resistance of tin disulfide layer was measured via two-probe keithley power supply system, model 2400 source meter in the light and darkness.

3. Results and discussion:

Appearance of the thin films is demonstrated in figure 1. Films appeared in golden color at lower temperature and became darker with increasing in temperature. The thickness of the thin films increased from 646 nm to 673 nm as substrate temperature increased from 350^0 C to 400^0 C. Increase in the thickness of formed thin films, made them darker in color[15].Besides, change in the color of the prepared films is a sign of change in optical properties and band gap[16].

All the sprayed films at temperature below 325 ^{0}C were unstable and inadhesive to the substrate, due to insufficient temperature for pyrolyzing; consequently, they were peeled off. On the other hand, in the temperature interval of 325- 425 ^{0}C all films were stable and adhered to the substrate, exhibiting favorable temperature range for depositing SnS_2 thin films. Above the temperature 425 ^{0}C, light brown spots were observed on the surface of the formed films, probably due to complete thermal decomposition of the droplets before landing on the substrate caused by overheating [17].

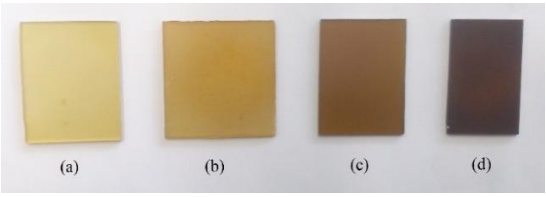

Fig1. Effect of temperature on color of films at a) 350^0 C b) 375^0 C c) 400^0 C d) 425^0 C

3.1 Structural studies

Figure 2 shows XRD patterns of the thin films prepared in the temperature range 325 - 425^{0}C. Based on

the results, the film prepared at 325^0 C is almost amorphous. However, with increasing the temperature and thickness, the intensity of this peak increases and reaches to its maximum at 400^0C. Wondeok Seo et al. observed an improvement in crystallinity as the thickness of SnS_2 thin films increased[16]. When the substrate temperature reaches to 425^0C, the intensity of peaks decreases, which shows the reduction of crystallinity. It was found that tin disulfide thin films have been formed in hexagonal structure (SnS_2-β). Dominant peaks of tin disulfide are located at $2\theta= 15.13^0$, $2\theta= 28.44^0$ and $2\theta= 32.37^0$ in agreement with card JCPDS: 01-075-0367; which are along with crystal (100) plan, (002) plan and (001) plan, respectively. Imen Bouhaf Kherchachi et al. reported similar results about SnS_2 thin film growth along plan (001), using $SnCl_2.2H_2O$ as precursor [14]. They also found the dominant peak at $2\theta=15.02^0$. L. Amalraj et al. observed similar orientation using $SnCl_4.5H_2O$ [9]. Considering figure 2, there was no evidence of other compounds such as SnS, Sn_2S_3, oxidation or sulfur impurities. Texture study of layers showed (001) plane is preferred oriented plane in all thin films. The intensity of the main peak reaches to its maximum at 400^0C; with further increasing the temperature, it decreases again. Rise in the substrate temperature provides more mobility for precipitated ions on the surface, and makes them able to order in places with higher surface energy, which consequently leads to more discipline in structure; but, excess heat energy leads to evaporation of sulfur from the lattice, left behind a rather amorphous phase[18]. S.A. Mahmoud deposited Bi_2S_3[19] and observed the strongest peak at T= 400^0C, then the intensity decreased with further increasing the substrate temperature.

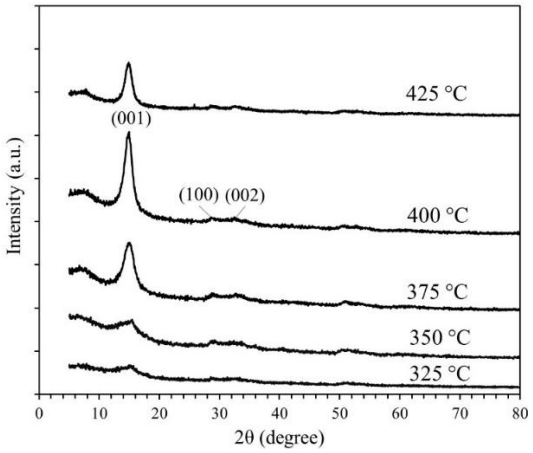

Fig 2. XRD-diffraction patterns of SnS_2 thin films at different substrate temperatures

Mean size of nano crystallites was calculated via Scherrer's formula [6]:

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

Which D is the average crystallite size, K is the constant value 0.9, λ is the wavelength of Cu-K anode (λ=1.54 A^0), β is the full width at half maximum (FWHM) in radian and θ is the Bragg's angle in degree. The mean crystallites size of deposited tin disulfide layers increased from 8 to 38 nm as the temperature raised from 325 to 400^{0}C, which was caused by crystallite growth and the elimination of lattice defects such as micro strains and dislocations [20]. P. Gopalakrishnan deposited tin disulfide in the temperature range of 473 - 573 ^{0}K and reported the same trend in crystallite size [21]. As the substrate temperature reached to 425^{0}C, mean crystalline size reduced to 26 nm, because at higher temperature, the vapor pressure of S is much higher than Sn and as a result, sulfur vaporizes and migrates from the lattice, so lack of sulfur weakens the crystalline quality [22].

Lattice constants of tin disulfide thin films were calculated from XRD pattern data using below formula [7]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (2)$$

Which c and a are the lattice parameters of hexagonal structure and d is the distance of adjacent planes (hkl). Table 1 illustrates lattice parameters of tin disulfide thin film prepared at various substrate temperatures. Parameter a decreases from 3.6 to 3.5 A^0 as the temperature rises from 325^{0}C to 425^{0}C, while c increases from 5.77 to 5.94 A^0. Lattice parameters are in close agreement with bulk SnS_2 parameters[23]. Presence of lattice defects such as interstitials and superstitions in the films prepared at temperatures lower than 400^{0}C leads to the formation of stress and tensile strain in the crystalline lattice, which in turn causes slight disparity in lattice parameters of nano-structure and bulk SnS_2 [2]. Increasing the substrate temperature up to 400^{0}C reduced the strains in the lattice, which brought the value of lattice parameters closer to bulk parameters value. Further increase in temperature caused disorder in lattice [15]. It seems the substrate temperature of 400^{0}C is appropriate for preparing single phase SnS_2, while lower

temperatures led to lateral phases such as Sn_2S_3 and SnO_2 [21]. Considering acceptable crystallinity of thin films, which were prepared in the temperature range of 350- 400^{0}C, the properties of thin films will be discussed in this range.

Table1. Mean crystallite size and lattice parameters of SnS_2 thin films at different substrate temperatures

Substrate temperature (^{0}C)	Crystallite size (nm)	Thickness (nm)	Lattice parameter (A^0)	
			a	c
325	8	640	3.609	5.770
350	18	646	3.593	5.852
375	26	667	3.598	5.92
400	38	685	3.580	5.94
425	29	673	3.609	5.77

3.2 FTIR analysis

Removal of organic composition and advancement of pyrolysis reaction in synthesizing of the SnS_2 thin films was studied by Fourier transform infrared spectroscopy. FTIR spectra of SnS_2 thin film prepared at 400^{0}C is shown in figure 3. The peak at 562 cm^{-1} is ascribed to Sn- S bond vibrations, which proves thoroughly pyrolysis reaction. There are two bands at 1396 cm^{-1} and 1620 cm^{-1} attributed to bond vibrations of C-O and C-H, which probably come from thiourea. Ahmad Umar et al. also reported similar results [24].

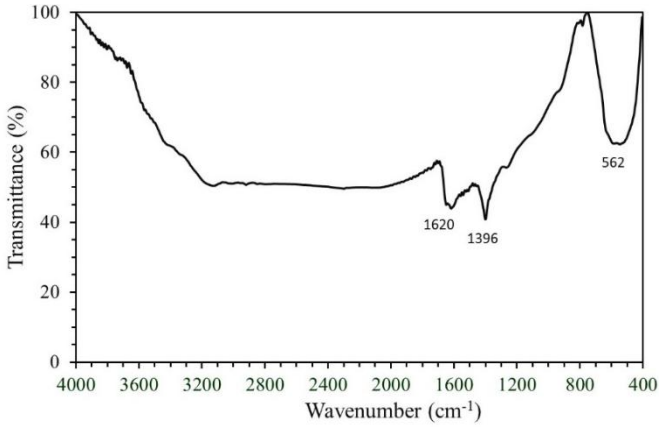

Fig 3. Infrared spectra of SnS_2 thin film prepared at 400^0C.

3.3 Topography

Images of atomic force microscope from SnS_2 thin films prepared at the range 350- 400^0C are illustrated in figure 4. All the films showed hill- valley topography, which was covered all over the surface. The average roughness values of tin disulfide thin films at different substrate temperatures are tabulated in table 2. The film which was synthesized at 350^0C, has a maximum roughness equal to 1.9 nm, while the film prepared at 425^0C shows minimum roughness value of 0.9 nm. The process of grain growth caused by increasing temperature was responsible for the decline in roughness; which resulted in the reduction in the hill- valleys distance.

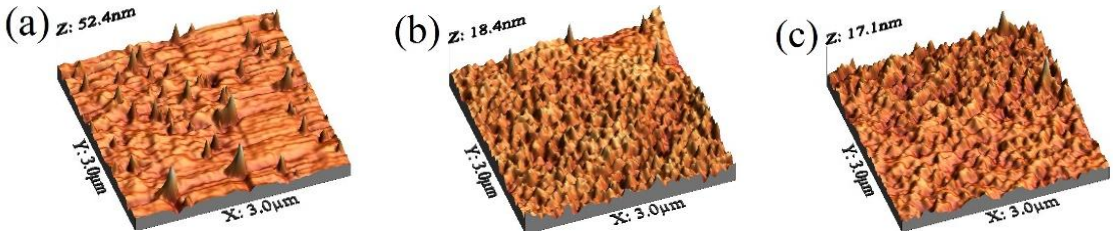

Fig 4. Atomic force microscope images of SnS_2 surface at a) 375^0C b) 400^0C c) 425^0C

Table 2. Effect of substrate temperature on roughness of thin films

Substrate temperature (°C)	**Roughness average (nm)**	**RMS roughness (nm)**
375	1.9	3.1
400	1.1	1.5
425	0.9	1.2

3.4 Morphology

Scanning electron microscopy image of SnS_2 surface prepared at 400^0C is shown in figure 5.a. SnS_2 thin film has granular and homogeneous morphology. SnS_2 grains are spherical in shape, easily distinguishable

and their size lies in the region of 75 to 90 nm. Study of EDS spectra confirmed that tin and sulfur are two dominant elements in the films. Also, EDS image showed peaks of other elements such as O, C and N, which may have been caused by precursor solution and experimental conditions. The S/Sn ratio in the film was calculated to be 2.1, which was near- stoichiometric.

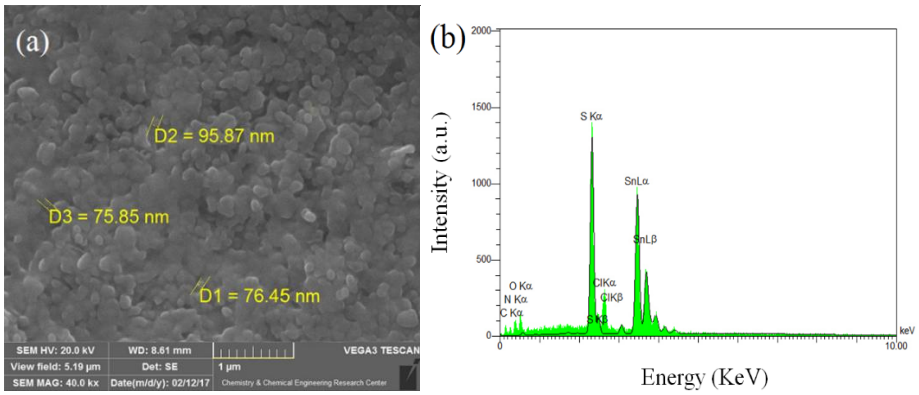

Fig 5. a) SEM image and b) EDS spectra of SnS_2 thin film prepared at 400^0C

3.5 Optical properties

Figure 6 shows UV-VIS transmittance spectra of SnS_2 thin films at different substrate temperatures in the wavelength range of 300 to 1100 nm. With increasing the substrate temperature from 350 to 400^0C, the transmittance of all the deposited films increased in visible and near infrared range; though they remained less than 40% transparent in mentioned wavelengths range. All the samples absorbed the whole wavelengths in the ultraviolet range, due to transmission of excited electrons from the valence band to the conduction band. Band gap variation was calculated from transmittance spectra and Tauc's formula [5]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (3)$$

A is a constant and hν shows the photon energy. α is the optical absorption coefficient and E_g is the related energy value of SnS_2 absorption edge. The gap energy of the formed thin films reduced with increment in temperature and thickness until it reaches to the least value of 2.55 eV at 400^0C, with a maximum thickness of 685nm. Sulfur evaporation from the lattice at higher temperature creates local states. These localized states form band tails that extend to energy band gap, result in a decrease in band

gap [25]. M. R. Fadavieslam et al. synthesized SnS_2 thin films in the temperature range of 320 to 470 ^{0} C and reported same decreasing trend in band gap value from 3.05 to 2.55 eV and increasing the thickness from 550 to 600nm [14], they also observed the optimum crystallinity at 370^{0}C, corresponding to band gap 2.7 eV. The calculated band gaps value for SnS_2 thin films in this work are more than the band gap of bulk SnS_2; because nano structure SnS_2 has weaker crystallinity compared to bulk SnS_2, due to more strains and dislocations [26].

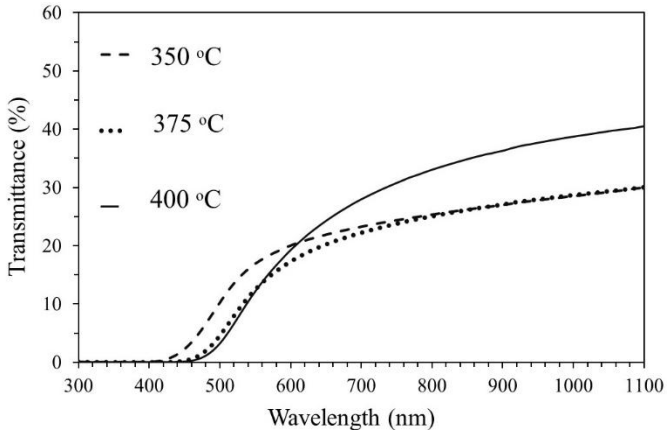

Fig 6. Transmittance plots of SnS_2 thin films at different substrate temperatures

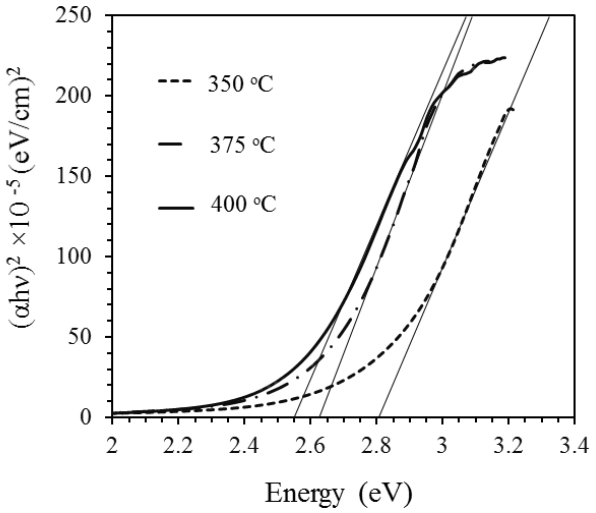

Fig 7. Tauc plots of SnS_2 thin films at different temperatures

Table 3. Band gap values of SnS_2 thin films at different temperatures

Substrate temperature (^{0}C)	E_g (eV)
350	2.80
375	2.62
400	2.55

Photoluminescence (PL) spectra of SnS_2 thin film prepared at 400^{0}C is exhibited in figure 8. The PL spectra were studied to evaluate the quality of the deposited film.

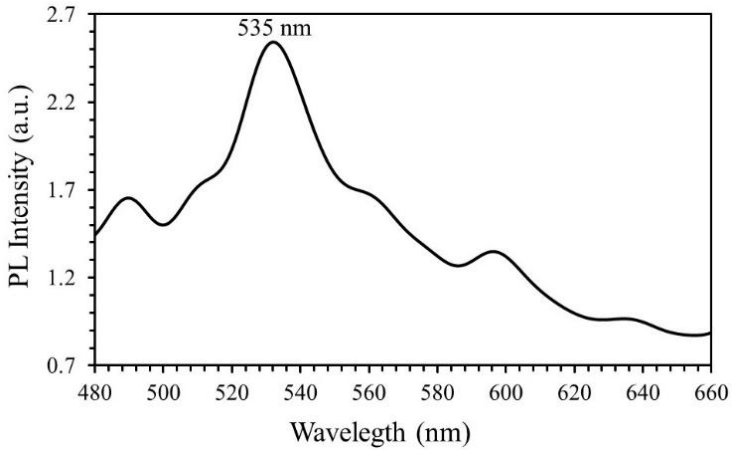

Fig 8. PL spectra of SnS_2 thin film at 400^{0}C

According to figure 8, there is a main peak at 535 nm, indicating recombination of excitons from the conduction band to the valence band. The band gap was calculated from the main PL peak directly, and it was equal to 2.31eV, which is almost in conformity with the one calculated from Tauc plot. Other weak peaks in PL spectra confirm lattice defects and impurities in the thin film lattice. Vijayarajasekaran observed a similar peak at 526 nm, which attributed it to the absorption edge [27].

3.6 Electrical properties

Figure 9 illustrates the plot of current against voltage for SnS_2 thin film prepared at 400^{0}C in the dark and light. The electrical resistance of SnS_2 thin film was calculated from below formula [28]:

$$\rho = \frac{VA}{IL} \quad (5)$$

A is the area between the junction of system and the deposited film, V is the voltage, L is the distance between two junctions and I is the current between two points. The electrical resistivity of the deposited film in dark and light environment were 4.6×10^3 Ωcm and 0.65×10^3 Ωcm, respectively. This result is in good agreement with result that Z. Hadef1 reported [29]. The resistivity of other films was not measured, because they had weaker crystallinity. Increment in the substrate temperature leads to crystallites growth and removal of lattice defects; consequently, electron scattering decreases in the lattice; which in turn results in reduction in resistivity [12]. In addition, M. R. Fadavieslam reported a decrease in electrical resistivity as the substrate temperature and thickness increased [15].

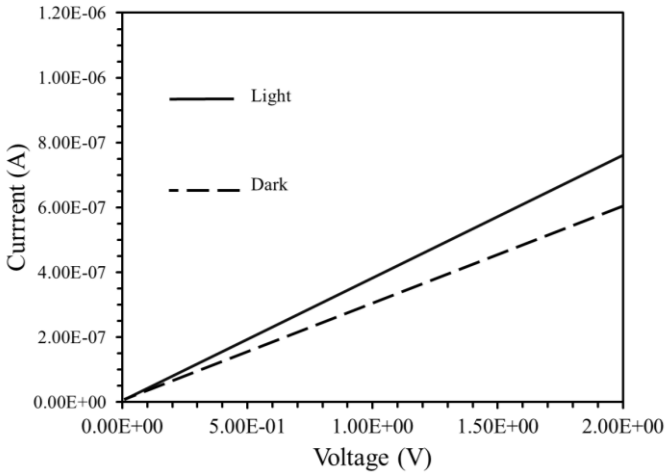

Fig 9. I-V plot of tin disulfide thin film at 400^0 C

4. Conclusion. SnS_2 thin films were prepared by the spray pyrolysis method and influence of the substrate temperature as the most effective parameter on the properties of thin films was investigated. XRD studies revealed that increasing temperature causes improvement in crystallinity of tin disulfide thin films. The best crystallinity of SnS_2 was obtained at 400^0C. All SnS_2 thin films were oriented along (001) plan, indicating preferred orientation of the films is independent of the substrate temperature. FTIR spectra of SnS_2 film prepared at 400^0C proved the formation of Sn- S bonds. AFM images revealed that roughness of the films decreased from 1.9 nm to 0.9 nm as the substrate temperature rised from 350^0C to 400^0C. Study of the optical transmittance spectra indicated elevating temperature from 350^0C to 400^0C reduces the tin

disulfide band gap from 2.8 to 2.55 eV. Also, all the prepared films were less than 40% transparent in the visible range, indicating high absorption in this range. The least electrical resistivity of SnS_2 thin films was measured 4.6×10^3 Ωcm and 0.65×10^3 Ωcm in the dark and light, respectively.

Acknowledgements

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