



## STRUCTURAL, OPTICAL AND PHOTSENSING PROPERTIES OF SPRAY PYROLYZED SnSSe THIN FILMS

Anitha Ezhil Mangaiyar Karasi A<sup>1\*</sup>, Seshadri S and Amalraj L<sup>2</sup>

<sup>1\*</sup> Department of Physics, SIGC, Trichy, Tamilnadu

<sup>2</sup>Department of Physics, VHNSN College, Virudhunagar, Tamilnadu

### ARTICLE INFO

#### Article History:

Received 12<sup>th</sup> December, 2018

Received in revised form 23<sup>rd</sup>

January, 2019

Accepted 7<sup>th</sup> February, 2019

Published online 28<sup>th</sup> March, 2019

#### Key words:

SnSSe thin films, Spray Pyrolysis, XRD, SEM, Band gap, Hall effect, Photosensitivity, Photoluminescence

### ABSTRACT

Tin Sulpho Selenide (SnSSe) thin films were prepared by chemical spray pyrolysis technique. Cleaned non conducting glass slides were used as substrates. The precursors used were Stannous chloride, Thiourea and Selenourea for deposition. Various parameters to synthesize the SnSSe thin films were the surface temperature, distance between surface nozzle and substrate heater and the pressure were optimized initially out of which substrate temperature was kept constant at 325 °C + 5 °C, distance between spray nozzle and heater was kept 29 cm. The as deposited thin films of SnSSe were annealed in the nitrogen atmosphere for half an hour before characterization. The nitrogen annealed thin SnSSe films were studied for structural, optical, morphological, electrical, Photo sensing and Photo luminescent properties. X-ray diffraction studies show that the films are polycrystalline in nature with orthorhombic crystal structure. Crystallite size of the film was found to be 292 nm. Optical absorption study reveals a band gap of 0.9 eV. Present investigation describes the effect of increase in incident intensity of light on the SnSSe thin films. The light intensity was varied by using the incandescent bulb, maximum photosensitivity of SnSSe thin films was found to be 40000. In Photoluminescence study the peaks observed in were in close agreement with the reported peaks of the photoluminescence spectra for SnSSe thin films. The blue shift observed in PL emission spectra corresponds to nanocrystalline effect. This indicates that the nitrogen annealed SnSSe thin films Show the best photosensitivity as well as photo luminescent in nature.

Copyright©2019 Anitha Ezhil Mangaiyar Karasi A, Seshadri S and Amalraj L. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

### INTRODUCTION

Stannous Sulphide (SnS) and Stannous Selenide (SnSe) are becoming an emerging prominent materials in recent years because of their potential technological importance. The synthesis of binary metal chalcogenide of II-VI semiconductors in thick film, thin film and nanocrystalline form has been rapidly growing area in the material research due to their important non-linear optical, photo luminescent and other physical and chemical properties [1]. It is found that the band gap of Stannous Selenide material is 1.1 eV where as of Stannous Sulphide is 1.8 eV, both these are suitable for solar spectrum. This feature makes these materials useful for solar energy conversion in photovoltaic form [2]. These materials can be synthesized in thin film form from several methods like Thermal evaporation [3, 4], Sputtering, ion, Chemical bath deposition[5], Flux Techniques [6], Molecular beam epitaxy [7], Spray Pyrolysis[8].etc., Out of these, Spray Pyrolysis is the most promising for producing inexpensive thin films of good quality with various dopants over a large area.

Here the efforts were taken to synthesize the ternary material of Stannous sulpho selenide by altering the concentration of sulphur and selenium component for the study of effect of the concentration for the change in energy gap and its effect on photosensing and photoluminescent performance of the material. SnSSe is ternary compound has recently attracted much interest in solar energy conversion because of the bandgap in tailoring effected by incorporation of S in SnSe. The two compounds SnS and SnSe form a continuous series of mixed crystals with a minimum melting point of 1128 K. The crystals are all p-type with hole concentration of about  $10^{18} \text{ cm}^{-3}$ . The band edge absorption is found to be allowed indirect transitions. The band gap of SnS and SnSe at 573 K was found to be 1.08 and 0.9 eV respectively. The bandgap of mixed crystals SnSSe varies linearly with the x composition.

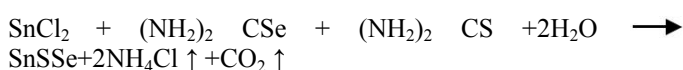
Structural properties of the material play a vital role in the performance of the devices and a knowledge of the influence of the deposition parameters on the structural properties [11-12]. The mixed crystals of composition SnSSe have the same crystal structure as SnS and SnSe. The unit cell contains eight atoms, placed in position about the scaled coordinates. The atoms are arranged in two adjacent double layers orthogonal to the largest cell dimensions [13-14].

\*Corresponding author: Anitha Ezhil Mangaiyar Karasi A  
Department of Physics, SIGC, Trichy, Tamilnadu

The aim of this work is to produce SnSSe thin films of equal sulphur and selenium concentration by spray pyrolysis and to study the Crystal structure, Structural, Optical, Electrical, Photo sensing and Photo luminescent properties.

## EXPERIMENTAL MATERIALS AND METHODS

The SnSSe films were prepared by spraying equimolar mixture of aqueous solutions of Thiourea as source of Sulphur, Selenourea as source of Selenium and Stannous chloride  $\text{Sn}(\text{Cl}_2)$  each of 0.05M as starting solution in deionized water. The proportions of the precursors are maintained such that Stannous precursor is 50% of the composition and remaining 50% composition is of equal parts of sulphur and selenium precursors. The substrates used were insulated microscopic plane glass slides of area 7.5 cm x 2.5 cm, were heated at the optimized temperature of  $325 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$ . The following reaction was taken place at the surface of heated substrate for synthesis of SnSSe thin film by spray Pyrolysis.



The as deposited thin films were annealed at  $500 \text{ }^\circ\text{C}$  in nitrogen atmosphere for 30 minutes.

The major preparatory parameters in the spray pyrolytic process are substrate temperature, the concentration and molar ratios of starting solutions. The spray rate was 1 ml/min and the distance between the spray nozzle and substrate was 29 cm. After deposition, the films were first cooled to room temperature. The texture of the films was observed under Epignost microscope. The films were observed to be quiet uniform and free from pinholes throughout the sample.

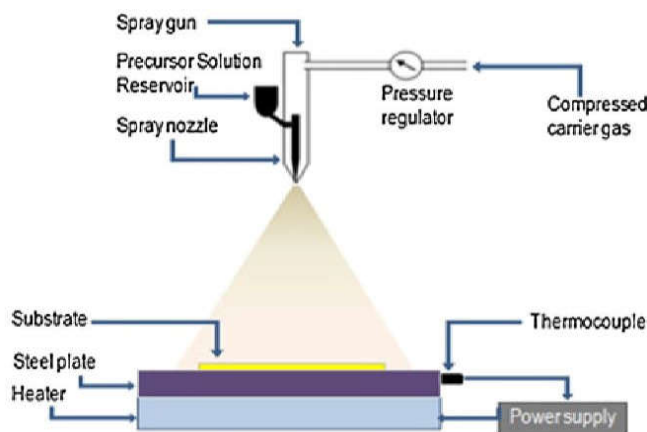


Fig 1 Experimental Set up of Spray pyrolysis technique

## RESULTS AND DISCUSSION

### Structural properties

The ternary compound has recently attracted much interest in the field of solar energy conversion because of the bandgap tailoring effected by the incorporation of SnSSe. Preparation and properties of mixed crystals of  $\text{SnS}(1-x)\text{Se}$  have been already reported [15].

Structural properties of the material play a dominant role in the performance of the devices and a knowledge of the influence of various deposition parameters of thin films is essential before the application of these materials in the devices. The mixed crystals of composition of Tin Sulpho Selenide have the

same crystal structure of SnS and SnSe. The unit cell contains eight atoms placed in position by the scaled coordinates + or - and  $(u, 1/4, v)$  and + or -  $(1/2, u, 1/4, 1/2, v)$ . The atoms are arranged in two adjacent double layers orthogonal to the largest cell dimensions as shown in figure [16,17]. Within either double layer, each atom has three nearest atoms lies in the other double layer and provides the bond between the double neighbours and the two next neighbours. The resulting highly layered structure, typical of all orthogonal chalcogenide crystals, causes a strong anisotropy of the physical properties of these compounds [16].

X-ray diffraction method is one of the best methods for the estimation of the crystallographic parameters. Figure 2 represents the XRD pattern of SnSSe thin film [18]. It was observed that the diffraction peak corresponding to (111) orientation was the predominant. The unit cell dimensions of the orthorhombic SnSe lattice was calculated as  $a=4.444 \text{ \AA}$ ,  $b=11.496 \text{ \AA}$  and  $c=4.151 \text{ \AA}$ . These dimensions compared to the low temperature phase orthorhombic structure of SnSe. The peak intensities are high and the narrow width indicated larger grain sizes. This observation was supported by the larger grain sizes are seen in SEM micrographs [17].

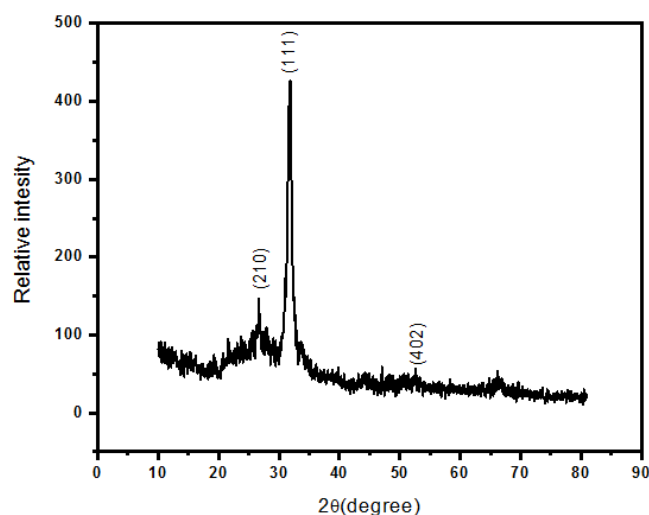


Fig 2 XRD pattern of SnSSe thin film deposited at  $325 \text{ }^\circ\text{C}$

As there are only few reports available on SnSSe in the literature to our knowledge. Patel *et al* [ 24 ] prepared SnSSe thin films by flash evaporation on NaCl crystal as well as on glass substrates. Thin films deposited at 300 K were poor crystalline and fine grained in nature, which is attributed in electron beam heating, whereby electron charge or thermal gradient is set up in the poorly conducting beam where subjected to electron beam. Therefore all the beams are examined under low beam current. The d-spacing values (interplanar distance) calculated from the electron diffraction pattern were fairly agreement with the XRD obtained from bulk SnSSe. The electron diffraction patterns revealed that (111) orthorhombic plane is highly preferred orientation. It was also observed that SnSSe films grown are single phase polycrystalline in nature.

### Optical Properties of SnSSe films

The optical absorption of spray pyrolysed SnSSe thin films were obtained in the wavelength range 300 nm to 1200 nm at  $325 \text{ }^\circ\text{C}$ . The spectrum of the Tin sulpho selenide had been shifted towards shorter wavelength exhibited direct bandgap of

0.9 eV, it was found to be in the same order as Bhatt *et al.*, have calculated absorption coefficient upto  $2 \times 10^4 \text{ cm}^{-1}$ . This was attributed to the surface nature of the films. The variation of optical bandgap with thickness of the film was found to be decreased with the increasing thickness. The variation was explained due to the quantum effect. The transmission effect of single crystals of SnSSe was measured at 325 °C. The square root of the absorption coefficient in this region was found to be linear function of photon energy which indicated absorption was due to the direct and indirect transitions of electrons from valence band to conduction band [19]. Optical absorption of flash evaporated SnSSe thin films were obtained in the wavelength of 200 nm to 1500 nm at room temperature [20]. It was noted that the bandgap increased with increasing substrate temperature, which led to an improvement in crystallinity of the films.

For the optical band gap study the square of  $\alpha h\nu$  was plotted against  $h\nu$  for each sample as shown in Fig.3. The extrapolation of the each curve to zero yields an direct character of band gap. The value of band gap ( $E_g$ ) obtained for SnSSe was found to be 0.9 eV which is in agreement with Albers *et al.* [28] indirect band gap of SnSe is 0.90 and Bhatt *et al.* [30] reported it as 0.936. Also according to Yu *et al.* [33] it is 0.923 whereas it is 0.948 as reported by Elkorashy [31]. The observed indirect character of band gap is a common property of orthorhombic IV–VI compounds [26,27] and has been confirmed by band structure calculations for SnSe single crystals [28,29].

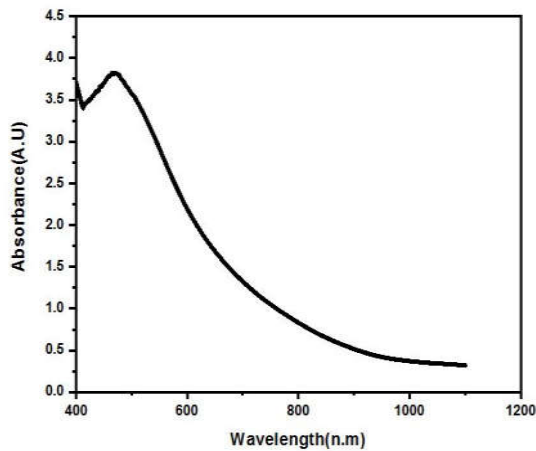


Fig 3 represents absorbance spectra of SnSSe thin films deposited at 325 °C

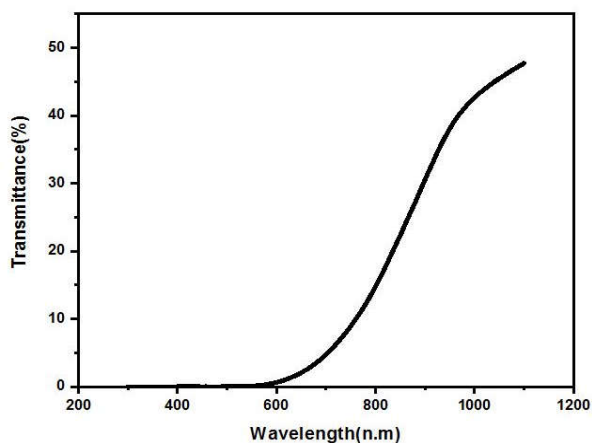


Fig 4 represents transmittance spectra on SnSSe thin films deposited at 325 °C

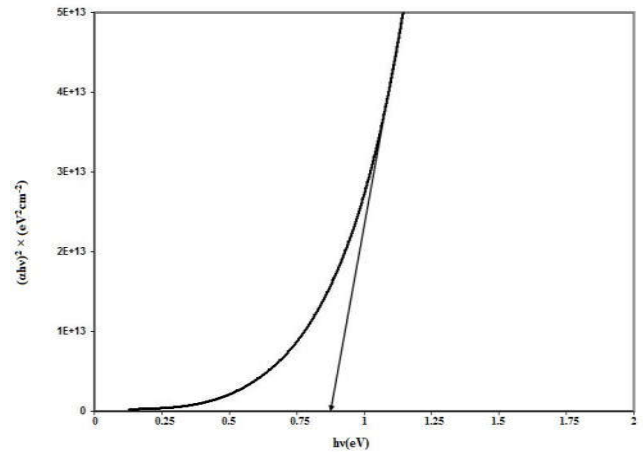


Fig 5 represents band gap of SnSSe thin films deposited at 325 °C

### Electrical Properties

The electrical properties of SnSe films deposited by flash evaporation on glass, mica and KCL substrates are reported [21]. The films deposited at KCL substrates showed a lower resistivity than those deposited on glass and mica substrates. The films were found to be p-type in nature. Single crystals of SnSSe were used for hall voltage and resistivity measurements according to vander pauws method [22]. Good electrical contacts were obtained using silver paint or by welding 100 micro gold wires to the samples. The SnSSe thin films prepared by spray pyrolysis were p-type with a free hole concentration at 325 °C will be  $80 \Omega\text{cm}$ ,  $59 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and  $9.5 \times 10^{16} \text{ cm}^{-3}$ . Hot probe measurements indicated that the films are p-type with a free hole concentration between  $10^{17}$  and  $5 \times 10^{18} \text{ cm}^{-3}$ . The temperature dependance of the hole mobility measured on the cleavage plates of SnSSe showed that at high impurity concentrations, the mobility was observed to decrease drastically at low temperatures.

### Photo Sensing Performance

When light radiations incident on the semiconducting sample, excess electron hole pairs are created in semiconducting materials, thereby results in increase in conductivity. This gives important applicability to the material as sensors of radiations. During present investigation, the samples were illuminated by 100W tungsten filament lamp as source of light. Incident from 12 cm distance from as deposited SnSe thin films, and the photosensitivity was measured by the equation as shown below:

$$\text{Photosensitivity } (P_s) = \frac{I_{\text{illuminated}}}{I_{\text{dark}}}$$

Intensity of the light radiation was varied by dimmerstat. The observations were taken for the intensity of light radiations at 60 V a. c. to 230 V a. c. mains by the step of 10 V a. c.

Light radiations were allowed to incident on SnSSe thin films giving the photosensitivity of the materials. One can customized the photo sensing performance of the thin films by arranging the unimolecular layers of nanostructured materials

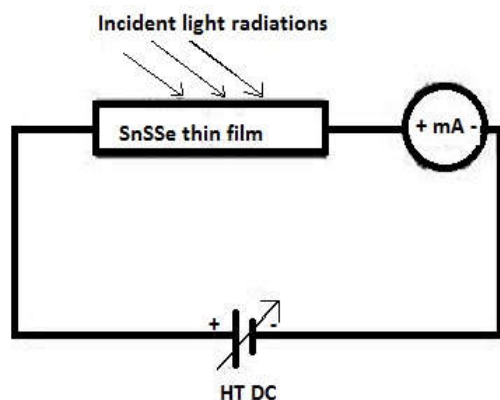


Fig 6 depicts the experimental setup of measurement of photosensitivity.

The photosensitivity performance of the SnS<sub>2</sub> thin film was observed to be maximum, at the 150 Vdc across the film. There are imperfections created in the SnS<sub>2</sub> thin film structure. These imperfections associated with the incorporation of atoms of elements other than the host elements can be termed as impurity imperfections or simply impurities. The imperfections associated with structural deviations from atomic arrangement in the compositions create defects in the semiconducting materials sample. This defect category of the imperfections includes vacancies, interstitial atoms, dislocations, etc. there is increasing experimental evidence that similar electronic defects can be caused by both impurities and defects [9,10].

#### Photoluminescence Performance

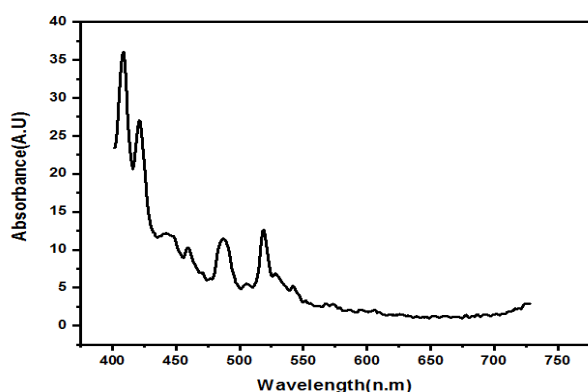


Fig 7 represents Photoluminescence of SnS<sub>2</sub> thin films deposited at 325 °C

Optical excitation and PL emission spectra under 389 nm excitation of thin film recorded at room temperature and indicated in figure 7. Figure shows that there intense band in green region at 521 nm, and less intense in blue region at 485 nm. This is in close agreement of the work of J. P. Singh *et. al* [34] Figure showing the large stokes shift between optical absorption spectrum and PL emission band may be attributed to presence of one deep trapping site and electron hole recombination via trap state or imperfection site (12) Such lattice phenomena is observed in nanomaterials, This predicts the spray deposited SnS<sub>2</sub> thin film in present investigation is nanocrystalline thin film. It is also reported that in nanocrystalline thin films, the deep states are mainly associated with stiochiometric defects or presence of external atoms like oxygen [35]

SnS<sub>2</sub> thin film indicate that photoresponse of the sample which increases gradually with a. c. voltage, (intensity of light radiation) may be attributed to knocking of charge carriers

from the base materials, releasing them from the bulk of the materials and makes available the charge carriers to carry the current independently, which causes to enhance the conductivity of the films. Initially, the sensitivity was observed to increase by negligibly small amount, and then slowly and thereafter the sensitivity increases suddenly with intensity of light radiations. This may be attributed to the creation of EHPs by light agitation. This increases the carrier concentration in the material, which helps in carrying the current, which constitutes the rise of sensitivity.

Photo sensing performance of the SnS<sub>2</sub> thin films shows enhanced photo sensing properties and we can tailor any value of photo sensing property from this material for desired intensity of light. Photo luminescent spectra show the major peak at 485.44 and 511.16, which are in close agreement of the reported peaks of 485nm and 521nm. [14] This indicates that the material has good photo luminescent properties and thus the as formed material is good for phosphor applications.

#### CONCLUSION

Tin sulpho selenide (SnS<sub>2</sub>) thin films were prepared by chemical spray pyrolysis technique using precursor Stannous chloride, Thiourea and Selenourea for deposition kept at optimized temperature 325 °C. X-ray diffraction studies show that the films are polycrystalline in nature with orthorhombic crystal structure. Crystallite size of the film was found to be 292 nm. SEM micrographs revealed larger spherical grains with stoichiometric value. Optical absorption study reveals a band gap of 0.9 eV. Photo sensing properties of the SnS<sub>2</sub> thin films indicates the response of the synthesized material to the incident radiations for equal concentration of sulphur and selenium. A Photoluminescence spectrum shows the peaks in the close agreement of the reported values of SnS<sub>2</sub> material. Thus SnS<sub>2</sub> would very useful for the fabrication of solar cells and phosphor material.

#### References

1. H Tributsch, Proceeding, Indian Acad Science, Chem sci, 105, (1993),305Jaspart Singh, Semiconductor Optoelectronic Devices;Physics and Technology,(1995)
2. E S Sabisky, Solar energy materials Solar cells, (1995).
3. H J Hovel, Semiconductors and semi metals, New York (1975).
4. P A Lee, G Said, R Davis and T H Lim, J Phys Chem Solids, 30(1969) 2719.
5. D I Bletskan, I F Kopinets, P P Pogorsh, E N Salkova and D V Chepor Kristallographia, 20 (1978) 1008.
6. V P Bhatt, K Ganesan and F M Desai, Crys Res Technol, 24 (1989) 187.
7. M F Ladd and R A Palmer, Structure determination of X-ray Crystallography. Plenum Press, New york (1964) 71.
8. H E Bennet and J M Bennet in G Hass and E Thund (Eds), Physics of Thin Films Vol 4, Academic press, New York (1967).
9. D Bhattacharya, S Chaudhari, A K Patel and S K Bhattacharya, Vacuum, 42,(1991) 1113.
10. W Albers, C Haas, H Ober, G R Schodder and J D Wascher, J Phys Chem Solids, 23 (1962), 215.

11. R W G Wycoff, Crystal Structure, Wiley New York, (1963). B Subramanian, C Sanjeeviraja and M Jayachandran, J Crystal Growth, 234 ,(2002)421-426,.
12. B Subramanian, C Sanjeeviraja, T Mahalingam and Mary Juliana Chokalingam, Thin Solid Films, 357, (1969),119.
13. F Huiller, , Structural chemistry of layer type phases in (eds), F Ley, D Reichel Dordrecht Holland (1976).
14. B Foutachi, A Katty and O Gorochov, *Journal of Electrochem society*,132, (1985) 2181.
15. R D Engelkan and McCloud, Bulletin of American Chemical Society 29,(1984) , 2806.
16. O H Hausser, H Von Kanel, and F Levy, *Journal of Electro Chem Society*,183,(1985),810.
17. B Foutachi, A Katty and O Gorochov, *Journal of Electro Chem Soc*, 131 (1984) 2806.
18. B Foutachi, A Katty and O Parsons, *Journal of Electro Chem Soc*,183 (1985),303.
19. S Adachi and T Taguchi *Physics Rev B* 43, (1991) 9569.
20. B Subramanian, C Sanjeeviraja, M Jayachandran, S Mohan and Mary Juliana Chokalingam, Proc SPIE International Symposium on Photonics and Applications (ISPA) vol 3896, (1999) 398.
21. S G Patel, S K Arora, R G Patel , Ajay Agarwal ,Thin Film characterization and Applications ,Proceedings of National conference ,S A K Narayanadas.(1996).
22. R D Engelkan, H E McCloud, C Lee, M S layton and A Goreishi, *Journal of ElectroChem Soc*, 134, (1987), 2696. J P Singh and R K Bedi *Thin Solid Films* (1991)
23. P Ambros, D Geralaes, N A Economon, *Phy Chem Solids* ,(1974) 537.
24. M Nikolic, S S Vijitovic, O H Hughes ,C J Stran and J M Chamberlain , Proceedings of the International conference in Physics and Semiconductors (1974).
25. W. Albers, C. Hass, H. Ober, G.R. Schrodder, *Journal of Phys Chem Solids* 23(1962),215
26. V.P. Bhatt, K. Ganesan, G.R. Pandya, *Journal of Crystal growth* 96,(1989),649.
27. A M .Elkorashy, *Journal of Phys Chem Solids*,47,(1986),497.
28. A W Park, G P Srivatsava, *Phys Status Soilidi B* 101,(1980).
29. J C Yu ,A S Yue, O M Staffsud ,*Journal of Crys Growth* 54,(1981),248.
30. J P singh and R K Bedi ,*Journal of Applied physics* 29(1990) 869.
31. J Reichmann and M A Russake, Photo effects of Semiconductor interface,146,(1981)359.

**How to cite this article:**

Anitha Ezhil Mangaiyar Karasi A, Seshadri S and Amalraj L (2019) 'Structural, Optical and Photosensing Properties of Spray Pyrolyzed SnSSe thin Films', *International Journal of Current Advanced Research*, 08(03), pp.18047-18051.  
DOI: <http://dx.doi.org/10.24327/ijcar.2019.18051.3440>

\*\*\*\*\*