# A REVIEW ON ANTIMONY TRISULFIDE THIN FILMS

**Ho Soon min**
Center for American Education, INTI International University, Putra Nilai, 71800, Negeri Sembilan, MALAYSIA.
*Corresponding author: Tel: +6067982000, email: soonmin.ho@newinti.edu.my

***ABSTRACT:*** *Antimony trisulfide thin films have been shown as promising materials for applications in the optoelectronic device, thermoelectric cooling technology, television cameras, photoconductive target type, microwave devices, diodes, and solar cell applications. Because of unique physical, electrical and optical properties. The aim of this work is a systematic review of researches on the properties of $Sb_2S_3$ thin films by using different deposition methods. In this work, several electronic databases including SCOPUS, Science Direct, DOAJ, Google Scholar, and EBSCO were used to search previous research findings and related information. The keywords employed for the search engine including thin films, deposition methods, antimony trisulfide, solar cell, and binary compounds. The databases from 2001 until the year 2020 were searched. There are many reports available on the preparation and characterization of $Sb_2S_3$ thin films by using different deposition methods. These materials have band gap values in the range of 1.6 eV to 2.46 eV and a high absorption coefficient. The conductivity observed was of p-type. The obtained thin films could be used as top sub-cell absorber material in tandem solar cell applications and power conversion efficiency was about 2.4%.*

**Keywords**: antimony trisulfide, thin films, semiconductor, solar cell, bandgap

## INTRODUCTION:

Thin films could be described as a very thin layer of a substance deposited onto various types of supporting materials such as indium tin oxide coated glass [1], microscope glass slide [2], fluorine-doped tin oxide coated glass [3], soda-lime glass [4] and molybdenum glass substrate [5]. Nowadays, a variety of binary [6], ternary [7], quaternary and penternary films have been synthesized by using different deposition techniques. These deposition methods could be classified into physical and chemical deposition methods [8]. Researchers highlighted that the obtained thin films could be used in wide application such as solar cell [9], photoconductor, holographic recording media, an infrared detector, light-emitting diode [10], hydrogen generation [11], laser screen, sensor device [12] and thin-film transistors [13].

Antimony trisulfide ($Sb_2S_3$) thin films are of the binary V-VI compounds [14]. The constituent elements of antimony (Sb) and sulphur (S) are earth-abundant and environment friendly [15]. They have emerged as a potential candidate in solar cell applications, thermoelectric cooling technology, television cameras, photoconductive target type, microwave devices, diodes, high-reflecting dielectric film [16], Hall-effect devices, switching devices [17], photocatalysts, Infrared detector, microelectronic, solar energy storage cells, switching devices and various optoelectronic devices. Because of their tunable electrical, optical, and structural properties. Table 1 showed the production of antimony worldwide in 2016-2019 by country [18]. In 2019, China, Russia, and Tajikistan's antimony production amounted to approximately 100000, 30000 and 16000 metric tons, respectively. Table 2 indicates the global sulfur production by country 2019. China is the world's largest producer, produced 17.4 megatonnes of sulfur [19].

**Table 1: Major countries in worldwide antimony mine production from 2016 to 2019 (in metric tons)**

| | 2016 | 2017 | 2018 | 2019 |
|---|---|---|---|---|
| China | 100000 | 98000 | 89600 | 100000 |
| Russia | 9000 | 14400 | 30000 | 30000 |
| Tajikistan | 8000 | 14000 | 15200 | 16000 |
| Bolivia | 4000 | 2700 | 3100 | 3000 |
| Turkey | 2500 | 2000 | 2400 | 3000 |

**Table 2: Sulfur production worldwide in 2019 by country (in 1000 metric tons)**

| | |
|---|---|
| China | 17400 |
| United States | 8800 |
| Russia | 7100 |
| Saudi Arabia | 6600 |
| Canada | 5300 |

In this work, the preparation of antimony trisulfide thin films was described. The properties of these films will be discussed as reported by many researchers via published results.

**Literature survey:**

Chemical bath deposition was used to prepare $Sb_2S_3$ films due to relatively simple, low-temperature process and suitable for inexpensive large area deposition. Antimony (III) chloride and sodium thiosulphate were provided $Sb^{3+}$ ions and $S^{2-}$ ions, respectively. Ethylenediamine tetraacetic acid plays a role as a complexing agent, helps for obtaining $Sb^{3+}$ ions in an acidic medium during the deposition process. The colour of the solution was found to be changing from milky white to lemon yellow, dark yellow, orange, representing the formation of films. X-ray diffraction (XRD) patterns for the films obtained at room temperature, show peak around $2\theta$=45.7°, orientation along (440) direction. Because of the cationic and anionic ions to be deposited get adsorbed over the nuclei and begin growing into a crystal [20]. Further, the formation of poly crystallinity of films could be observed as the deposition time was increasing. The influence of bath temperature was studied. Researchers conclude that for the films prepared at a temperature greater than room temperature, the random motion of species ($Sb^{3+}$ and $S^{2-}$ ions) because of thermal energy, leading to growth in a different orientation. For the films prepared at 60 and 80 °C, the diffraction peak of $Sb_2O_3$ could be seen. The bandgap values obtained in the range of 1.9 - 2 eV, indicating these materials are suitable for photovoltaic applications. Chemical bath deposited $Sb_2S_3$ films were produced in the absence of the complexing agent. The films prepared in 180 minutes, showed very few identifiable peaks and poor crystallinity if compared to other deposition times. Optical investigation shows these films have very strong absorption at the wavelength range from 400-500 nm. However, the absorbance value was reduced with wavelength and has relatively low values in the Infrared area [21]. Bandgap values were calculated by using the Tauc plot. Bandgap reduced from 2.3 to 1.6 eV as the deposition time was increased from 1 to 3 hours. Post-treatment of chemical bath deposited $Sb_2S_3$ films was studied. Annealed film (at 300 °C, 60 minutes, and 300 mTorr) showed higher intensity and bigger crystallite size if compared to the films treated with nitrogen plasma at 3 Torr for 1 hour. Chemical composition indicated the decrease in antimony and sulfur content after plasma treatment, and the thermal annealing process, respectively [22]. The morphology in annealed films (small grains had coalesced) and plasma-treated (surface is uniform and smooth) was significant changes. A higher bandgap for plasma-treated (1.83 eV) if compared to thermally annealed films (1.75 eV).

Thermal evaporation was used to prepare $Sb_2S_3$ films due to it is simple and very convenient. During the deposition process, the glass substrate was heated at 240 °C and pressure of $10^{-6}$ torr. Amorphous films could be detected as shown in XRD data. The explanation was the non-availability of sufficient thermal energy for the diffusion of adatoms on the substrate surface for the nucleation [23]. The grain size and surface roughness were found to be 42 and 5.5 nm, respectively based on the atomic force microscopy (AFM) results. Optical investigation revealed that obtained films have high absorption co-efficient value in the visible and near-infrared region. On the other hand, thermally evaporated $Sb_2S_3$ thin films were treated at 350 °C. The disorders and defects present in the amorphous change as a result of heat treatment because of the transition from amorphous to crystal state [24]. The crystalline size was about 64 nm. The atomic percentage of S:Sb was maintained at 60.07:39.93 as indicated in energy dispersive X-ray (EDAX) analysis [25]. The low value of activation energy (25 mV) and the transmittance value was obtained.

Spray pyrolysis method was used to prepare $Sb_2S_3$ thin films at 250 °C, nitrogen as a carrier gas, solution, and gas glow rates was kept constant at 2 mL/min and 4 L/min, respectively. XRD analysis indicated the obtained films were partially amorphous, match well with the orthorhombic phase, and showed strong intensity for (130) plane. $Sb_2S_3$ sprayed films grown parallel to the glass substrate, indicating could be used as a buffer layer in the photovoltaic solar cell [26]. The grain size and surface roughness was 52 nm and 55 nm, respectively. There are several peaks that could be detected in Raman spectroscopy ,including 109.3 and 145.7 $cm^{-1}$ (formation of crystalline phase), 280.8, and 303.9 $cm^{-1}$ (symmetric vibration of $SbS_3$), 460 $cm^{-1}$ (S-S vibration). The direct bandgap was about 1.7 eV.

The pulse electrodeposition method was used to prepare $Sb_2S_3$ thin films. Starting materials were $SbCl_3$ and $Na_2S_2O_3$. The deposition was carried out at pH (3,4), in a conventional three-electrode cell. Cyclic voltammetry studies revealed there are several cathodic peaks that could be observed such as -0.82 V versus saturated calomel electrode (deposition of antimony), -0.07 V (reduction of thiosulfate to sulfur), -0.54 V (addition of $Na_2S_2O_3$ to Sb (III)). The as-deposited films are amorphous. The annealed films (250 and 275 °C) indicated orthorhombic stibnite. The films annealed at 300 °C indicated the presence of oxide [27]. XRD analysis showed a reduction in microstrain (1.7 $x10^{-3}$ to 1.1 $x10^{-3}$ ε), and crystallite size increases (39-44 nm) with annealing temperature from 250 to 300 °C. Transmission electron microscopy (TEM) micrograph of films annealed at 300 °C displayed well-defined lattice fringes and measured d-spacing of the crystallographic plane was about 0.305 nm. X-ray photoelectron spectroscopy (XPS) analysis shows no obvious impurities are found. The obtained peaks from Sb (4d, 3d, 3p, 3s, and Sb Auger) and S (2p and 2s) are detected. The atomic concentration of Sb:S was 42.8 % and 57.2 %, which is close to stoichiometric composition.

The $Sb_2S_3$ films were prepared using the RF magnetron sputtering method onto a glass substrate, at substrate temperatures (200 - 350 °C). XRD data confirmed that the films prepared without post-treatment are amorphous [28]. Polycrystalline films could be obtained after annealing at 300 °C, 30 minutes, and under $N_2$-S conditions. The broadband (as-deposited films) and well defined sharp bands (annealed films) confirmed the transformation from amorphous to polycrystalline based on Raman spectroscopy. The morphology of films was strongly dependent on the substrate temperature. For example, a combination of features dissimilar in shape and size for the films prepared at 200 °C, smaller grains coalesce to produce bigger grains for the films prepared at 250 °C, uniform surface, free of voids and leading to an increase in film density for the film prepared at 350 °C. Composition analysis revealed that the S/Sb ratio reduced from 1.9 (200 °C) to 1.5 (at 350 °C). All the obtained films exhibit *p*-type conductivity and photoresponse. Table 3 showed the antimony sulphide thin films have been prepared by many researchers via various deposition methods. Highlighted experimental results were described based on published articles.

**Table 3: Properties of antimony sulphide thin films prepared by using different deposition techniques**

| Deposition method | Highlighted results |
|---|---|
| • Thermal vacuum evaporation | • Thin films prepared at substrate temperatures less than 473 K showed an amorphous structure [29].<br>• Thin films produced at 498 K indicated the polycrystalline phase based on XRD data.<br>• Bandgap increased from 1.62 to 1.78 eV as the substrate temperature reduced from 473 K to 300 K.<br>• The activation energy and dark electrical resistivity decreased with increasing the substrate temperature. |
| • Thermal vacuum evaporation | • XRD data showed that the amorphous structure (as-deposited film) changed to polycrystalline during heat treatment above 500 K.<br>• Different band gap value in as-deposited films (2.46 eV) and heat annealed films (2.4 eV)<br>• SEM image indicated that the grain size about 1.05 µm in annealed films [30]. |
| • Chemical bath deposition | • SEM images showed the particle size increased from 20 nm to 100 nm with increasing deposition time [31]. |

| | |
|---|---|
| | • The bandgap increased from 2.2 eV to 3.8 eV with reducing the particle size |
| • Chemical bath deposition | • XRD data showed that the obtained films were polycrystalline with an orthorhombic structure [32].<br>• The films deposited onto flexible polymer polyetherimide substrate were rougher if compared to the glass substrate.<br>• The absorption coefficient of about $10^4$ $cm^{-1}$.<br>• The bandgap values were in the range of 1.6 eV to 2.1 eV, strongly depended on the structural defect. |
| • Radiofrequency sputtering | • Amorphous and polycrystalline structures could be observed in as-deposited films and annealed film (500 nm grain, 400 °C), respectively [33].<br>• As-deposited films showed absorption coefficients of $1.8X10^5$ $cm^{-1}$ and a direct bandgap of 2.24 eV.<br>• Annealed films indicated absorption coefficients of $7.5X10^4$ $cm^{-1}$ and a direct bandgap of 1.73 eV. |
| • Radiofrequency magnetron sputtering | • The thin films could be used as top sub-cell absorber material in tandem solar cell applications [34].<br>• The power conversion efficiency about 2.4%. |
| • Chemical bath deposition | • Thin films have been deposited onto the glass substrate at room temperature.<br>• Experimental results showed that the addition of silicotungstic acid improved the photoactivity of films and enhanced the rate of deposition.<br>• The obtained films were highly photo conducting in nature [35]. |
| • The physical vapor deposition method | • XRD data supported the existence of polycrystalline in annealed films.<br>• The conductivity type is p-type.<br>• Researchers point out that each photon was observed to be absorbed in the visible and NIR range [36].<br>• The bandgap values in the range of 1.3 eV to 2.4 eV in both samples. |
| • Chemical spray pyrolysis | • The films prepared with Sb:S: tartaric acid ratio of 1:3:10 at 205 °C showed some properties such as 1 µm thick, orthorhombic stibnite phase, high amount of carbon and oxygen residues [37].<br>• The mean crystalline size reduced (25 nm to 15 nm), increase in oxygen content with increasing deposition temperature from 205 to 355 °C.<br>• The films showed a bandgap of about 1.7 eV. |
| • Aerosol assisted chemical vapor deposition | • XRD data showed that orthorhombic thin films have been prepared using tris(thiobenzoato) antimony(III) complex (as single-source precursor).<br>• The EDX spectra confirmed that the obtained films are antimony rich [38].<br>• The bandgap values are in the range of 1.81 eV to 1.9 eV. |
| • MOCVD | • Preparation of thin films from a single source (antimony thiolate) precursors [39].<br>• XRD data showed these films were orthorhombic structure.<br>• EDAX data exhibited that stoichiometric (Sb2S2.78-3.10).<br>• Different morphologies could be observed for the films deposited onto a silicon substrate (long rod of stacked platelet) and glass substrate (needle morphology).<br>• Bandgap energy was 1.6 eV. |
| • Solvo thermal and hydrothermal method | • The size of the nanorod and morphologies of the sample (dumbbell, sphere) are strongly dependent on the deposition temperature [40].<br>• SEM and TEM analysis confirmed that controlling the size and morphology is very important for solar cell and photocatalytic applications. |
| • Solvo thermal and hydrothermal method | • Thin films have been synthesized using xanthate and dithiocarbamate as a precursor [41].<br>• The films prepared through the solvothermal method indicated near uniform and bigger particles.<br>• The films produced in the presence of xanthate exhibited the ability to form oxide-free thin films. |

## CONCLUSION:

The $Sb_2S_3$ thin films have been prepared by using various deposition techniques. A large number of investigations have denoted to the physical, optical, and electrical properties of $Sb_2S_3$ thin films. The influence of various deposition conditions on the properties of thin films was studied. X-ray diffraction patterns confirmed that existent of amorphous and polycrystalline structure, in as-deposited and annealed films, respectively. The bandgap values are in the range of 1.6 to 2.46 eV. The power conversion efficiency was about 2.4 %.

**Acknowledgments**

This work is supported by INTI INTERNATIONAL UNIVERSITY.

**Conflicts of interests**

The author declared that there are no conflicts of interest.

## REFERENCES

1. Anuar, K., Ho, S.M., Noraini, K., Abdul, H.A. (2010) Influence of the deposition time on the structure and morphology of the ZnS thin films electrodeposited on indium tin oxide substrates. *Digest Journal of Nanomaterials and Biostructures*. **5**, 975-980.

2. Soonmin, H. (2016) Preparation and characterization of nickel oxide thin films: a review. *International Journal of Applied Chemistry*, **12**, 87-93.
3. Lucky, I.I., Okoli, D.N., Ekpunobi, A.J. (2019) Influence of pH on tin doped zinc selenide (SnZnSe) via electrochemical deposition technique. *International Journal of ChemTech Research*. **12**, 200-211.
4. Jeha, K., Lee, C., Vinaya, K., Kim, S., Lee, W., Chung, Y. (2020) Role of hydrazine in the enhanced growth of zinc sulphide thin films using chemical bath deposition for Cu(In, Ga)$Se_2$ solar cell application. *Materials Science in Semiconductor Processing*. 105, https://doi.org/10.1016/j.mssp.2019.104729.
5. Zeng, L., Guo, Y., Zhao, F., Nie, C., Li, H., Shi, J., Liu, X. (2020) Effect of film thickness and evaporation rate on co-evaporated SnSe thin films for photovoltaic applications. *RSC Advances*, **10**, 16749-16755.
6. Ho, S.M. (2016) Power conversion efficiency in thin film solar cell: a review. *International Journal of Chemical Sciences*, **14**, 143-151.
7. Kassim, A., Ho, S.M., Saravanan, N., Tan, W.T., Atan, M., Abdullah, D., Jelas, M. (2009) Effect of deposition period and pH on chemical bath deposited $Cu_4SnS_4$ thin films. *Philippine Journal of Science*, **138**, 161-168.
8. Ho, S.M. (2019) Raman investigations of metal chalcogenide thin films (a short review). *Oriental Journal of Chemistry,* **35**, 1-7.
9. Soonmin, H (2015) Chalcogenide thin films prepared using chemical bath deposition method. *Research Journal of Applied Sciences, Engineering and Technology,* **11**, 1058-1065.
10. Masashi, O., Mai, U., Kiba, T., Midori, K., Kim, K., Abe, Y (2020) Characterization of Ag/ZnS/Ag multilayered film as transparent electrode for organic light emitting diode. *Thin Solid Films*, 704, https://doi.org/10.1016/j.tsf.2020.137999.
11. Prado, E., Garcia, C., Oliva, J., Alvarado, J., Torres, D., (2020) Enhancing the solar photocatalytic hydrogen generation of ZnS films by UV radiation treatment. *International Journal of Hydrogen Energy*, **45**, 12308-12317.
12. Ali, A., Sarkar, D., Das, M. (2020) Room temperature ammonia sensing by CdS nanoparticle decorated polyaniline (PANI) nanorods. *Sensors and Actuators A: Physical*, **310**, https://doi.org/10.1016/j.sna.2020.112071.
13. Ventura, M., Rao, M., Davila, M., Ochoa, J., Bon, R. (2020) PVP $SiO_2$ and PVP $TiO_2$ hybrid films for dielectric gate applications in CdS based thin film transistors. P*olymer*, 191, https://doi.org/10.1016/j.polymer.2020.122261.
14. Marquina, R.G.S., Mathew, X., Mathews, N.R., Sanchez, T.G. (2017). Vacuum coated $Sb_2S_3$ thin films: thermal treatment and the evolution of its physical properties. *Materials Research Bulletin*, **90**, 285-294.
15. Zhang, L., Zhuang, D., Zhao, M., Gong, Q., Guo, L., Ouyang, L., Sun, R., Wei, Y., Peng, X., Lyu, X. (2017). $Sb_2S_3$ thin films prepared by vulcanizing evaporated metallic precursors. *Materials Letters*, **208**, 58-61.
16. Shaji, S., Garcia, L.V., Loredo, S.L., Krishnan, B., Martinez, J.A.A., Roy, T.K.D., Avellaneda, D.A. (2017). Antimony sulfide thin films prepared by laser assisted chemical bath deposition. *Applied Surface Science*, **393**, 369-376.
17. Ubale, A.U., Deshpande, V.P., Shinde, Y.P., Gulwade, D.P. (2010). Electrical, optical and structural properties of nanostructured $Sb_2S_3$ thin films deposited by CBD technique. *Chalcogenide Letters*, 7, 101-109.
18. Garside, M. (2020a) Major contries in antimony mine production 2015-2019. https://www.statista.com/statistics/264958/antimony-production/ [Accessed on 25 JULY 2020]
19. Garside, M. (2020b) Global sulfur production by country 2019. https://www.statista.com/statistics/1031181/sulfur-production-globally-by-country/ [Accessed on 25 JULY 2020]
20. Anil, N.K., Prasad, M.B.R., Ingle, R.V., Habib, M.P., Gaber, E.E., Mu, N., Patil, R.S. (2015). Structural and optical properties of nanocrystalline $Sb_2S_3$ films deposited by chemical solution deposition. *Optical Materials*, **46**, 536-541.
21. Asogwa, P.U., Ezugwu, S.C., Ezema, F.I., Osuji, R.U. (2009). Influence of dip time on the optical and solid state properties of as-grown $Sb_2S_3$ thin films. *Chalcogenide Letters*, **6**, 287-292.
22. Calixto, M., Martinez, H., Pena, Y., Flores, O., Ponce, H.E., Juarez, A.S., Reyes, P., Campos, J. (2010). A comparative study of the physical properties of $Sb_2S_3$ thin films treated with $N_2$ AC plasma and thermal annealing in $N_2$. *Applied Surface Science*, **256**, 2428-2433.
23. Aousgi, F., Kanzari, M. (2011). Study of the optical properties of Sn-doped $Sb_2S_3$ thin films. *Energy Procedia*, **10**, 313-322.
24. Rachel, O., Jessy, M.N., Usha, R.P. (2010). Structural and morphological studies of $Sb_2S_3$ thin films. *Journal of Ovonic Research*. **6**, 259-266.
25. Ghrairi, N., Aousgi, F., Zribi, M., Kanzari, M. (2010). Comparative studies of the properties of thermal annealed $Sb_2S_3$ thin films. *Chalcogenide Letters,* **7**, 271-225.
26. Boughalmi, R., Boukhachem, A., Kahlaoui, M., Maghraoui, H., Amlouk, M. (2014). Physical investigations on $Sb_2S_3$ sprayed thin film for optoelectronic applications. *Materials Science in Semiconductor Processing,* **26**, 593-602.
27. Garcia, R.G.A., Avendano, C.A.M., Pal, M., Delgado, F.P., Mathews, N.R. (2016). Antimony sulfide ($Sb_2S_3$) thin films by pulse electrodeposition: effect of thermal treatment on structural, optical and electrical properties. *Materials Science in Semiconductor Processing*, **44**, 91-100.
28. Montes, M.I., Montiel, Z., Mathew, X., Mathews, N.R. (2017). The influence of film deposition temperature on the subsequent pot-annealing and crystallization of sputtered $Sb_2S_3$ thin films. *Journal of Physics and Chemistry of Solids*, **111**, 182-189.
29. Zawawi, I., Abdel, A., Terra, F., Mounir, M. (1998) Substrate temperature effect on the optical and electrical properties of antimony trisulfide thin films. *Thin Solid Films*, **324**, 300-304.

30. Tigau, N., Ciupina, V., Prodan, G., Rusu, G., Vasile, E. (2004) Influence of thermal annealing in air on the structural and optical properties of amorphous antimony trisulphide thin films. *Journal of Optoelectronics and Advanced Materials*, **6**, 211-217.
31. Salem, A., Selim, M., Salem, M (2001) structure and optical properties of chemically deposited $Sb_2S_3$ thin films. *Journal of Physics D: Applied Physics*, **34**, https://doi.org/10.1088/0022-3727/34/1/303.
32. Ameur, S., Duponchel, B., Leroy, G., Meherzi, M., Amlouk, M., Guermazi, H. (2020) Impact of substrate nature and film thickness on physical properties of antimony trisulphide ($Sb_2S_3$) thin films for multifunctional device applications. *Superlattices and Microstructures*, **142**, https://doi.org/10.1016/j.spmi.2020.106473.
33. Matthieu, Y. and Joel, A (2007) Structural and optical properties of amorphous and crystalline antimony sulphide thin films. *Thin Solid Films*, **515**, 7171-7176.
34. Gao, C., Huang, J., Li, H., Sun, K., Lai, Y., Jiang, L., Liu F (2019) fabrication of $Sb_2S_3$ thin films by sputtering and post annealing for solar cells. *Ceramics International*. **45**, 3044-3051.
35. Savadogo, O. and Mandal, K. (1992) Studies on new chemically deposited photo conducting antimony trisulphide thin films. *Solar Energy Materials and Solar Cells*, **26**, 117-136.
36. Ali, N., Ahmed, R, Hussain, A., Shamsuri W, Shaari, A., Abbas S (2016) Antimony sulphide and absorber layer for solar cell application. *Applied Physics A*, **122**, ttps://doi.org/10.1007/s00339-015-9542-0.
37. Kriisa, M., Malle, K., Acik, I., Erki, K., Valdek, M (2015) The effect of tartaric acid in the deposition of $Sb_2S_3$ films by chemical spray pyrolysis. *Materials Science in Semiconductor Processing*. **40,** 867-872.
38. Ghulam, M., Akhtar, M., Malik, A., Brien, P., Neerish, R (2015) Aerosol assisted chemical vapour deposition of $Sb_2S_3$ thin films: environmentally benign solar energy material. *Materials Science in Semiconductor Processing*, **40**, 643-649.
39. Jorge, R., Dale, P., Mary, F., Molloy, K., Laurie, M (2007) Deposition of antimony sulphide thin films from single source antimony thiolate precursors. *Chemistry of Materials*, **19**, 3219-3226.
40. Senthil, T., Kang, M., Muthukumarasamy, N (2014) Study of various Sb2S3 nanostructures synthesized by simple solvo thermal and hydro thermal methods. *Materials Characterization*, **95**, 164-170.
41. Castro, J., Molloy, K., Lai, C., Dong, Z., Tiekink, E., White, T. (2008) Formation of antimony sulphide powders and thin films from single source antimony precursors. *Journal of Materials Chemistry*, **18**, 5399-5405.