Tuijin Jishu/Journal of Propulsion Technology
ISSN: 1001-4055
Vol. 44 No. 4 (2023)

Chemically synthesized Cu-doped SnS thin films for PV applications.

[1]Kesava Vamsi Krishna V. [2] P. Yamuna, [3]A. Gurusampath Kumar, [4]*Ravindharan Ethiraj
[1]Research Scholar, Department of Physics, Rayalaseema University, Kurnool
[2,3]Dept. of Physics, Malla Reddy Engineering College, Secunderabad
[4] Dept. of Physics, Osmania University
* Corresponding author: mrecphysics@gmail.com

Abstract: As the concern towards the sustainable and eco-friendly development increased in the recent times, research is being done on lesser toxic and abundant materials that can be used for Photovoltaic (PV) applications. SnS seems to be a promising solution in this direction. The suitability of pure and doped SnS thinfilms as absorber layer in a solar cell is experimented and verified widely in the recent past. In this paper, the suitability of Copper (Cu)-doped SnS thin films deposited through Chemical Bath Deposition (CBD) is verified for which the structural, optical, electrical properties in addition to the composition of the synthesized thin films are studied. An increasing trend was observed in the crystallinity with the Cu-doping concentration up to 5 at%. The range of optical band gap variation was observed between 1.193eV to 1.25 eV. The electrical resistivity decreased while the charge carrier concentration increased. The lowest value of $2.12x10^{-2}$ ohm-cm for electrical resistivity and the highest value of $4.68x10^{19}$ cm^{-3} for carrier concentration were recorded by 5 atomic % Cu-doped SnS thin films.

Keywords: Cu-Doped SnS thin films, Orthorhombic structure, Structural Properties, Optical band gap, Hall mobility.

1. Introduction

Relatively lesser toxicity, higher earth abundance, apposite band gap, higher absorption coefficient and pertinent conversion efficiency coinciding with the theoretical value of >25% made SnS a viable alternative fora very important layer called absorber layer in thin film solar cells. In fact, SnS emerged as a reliable alternativeto replace and restrict the usage of highly toxic CdTe and CIGS PV absorbers [1,2]. Compared to theanticipated theoretical efficiency, SnS thin film solar cells of efficiency as low as 4.36% was recorded in the recent times [3]. The contributing factors for this lower efficiency were identified as defects, unusual crystallinity, insufficient diffusion length, resistivity, lattice mismatch and band discontinuities etc. In particular,the band discontinuities like conduction band discontinuity besides the valence band discontinuity observed in SnS heterojunction constrained the performance of the SnS solar cells. These band discontinuities gave rise to energy spikes in the conduction band that confined the carrier transport across the junction.

The interface recombination is yet another considerable factor owing to which negative conduction band discontinuity is formed that in turn results in minimizing the efficiency of SnS thin films [4-6]. A reliable solution to address all these issues is to dope SnS with an apposite element that can significantly modify theband gap and the band positions. This band modification might decrease the negative conduction band discontinuity and may possibly turn it to positive as well [7]. Doping also addresses the valence banddiscontinuity. Doping at the Sn-vacant sites results in greatly changing the acceptor density and the resistivity. Thus, by limiting the doping concentration, the required density of 10^{15} – 10^{19} cm^{-3} can be easily achievedwhich influences the solar cell performance. Hence the need to optimize the doping concentration arises in order to obtain the required acceptor density in SnS thin films. Researchers reported encouraging changes inthe opto-electrical properties of SnS thin films by doping with Bismuth [8], Lead [9], Indium [10,11], Aluminum [12] and Silver [13-16]. The authors opted to verify the aptness of Copper (Cu) as a potential dopant to enhance the charge collection in SnS.

Deposition techniques like Chemical Bath Deposition (CBD) [15], atomic layer deposition [18], two-step process [17], spray pyrolysis [14], pulse electrodeposition [19], and Thermal evaporation [13] were used to deposit doped SnS thin films. Cost effective and relatively simpler deposition method among them is the

CBD technique. This paper reports the synthesis of Cu-doped SnS thin films with an intention to utilize it for the Solar cell applications. Also, the characterization outcomes are discussed in this paper.

2. Experimental section:

2.1 Materials and methods

A cost effective and relatively simpler deposition technique called CBD was employed to deposit undoped and Cu-doped SnS thin films. The Cu-doping concentration was calculated using the following equation [20] and maintained in the range of 0 – 5 at%.

$$\text{Cu-doping concentration (at\%)} = \frac{[Cu]_{Sol}}{[Sn]_{Sol}} \quad [\because [Cu]_{Sol} << [Sn]_{Sol}] \qquad (1)$$

Analytical Reagent Grade Stannous chloride ($SnCl_2.2H_2O$), Copper Chloride ($CuCl_2$), and Thioacetamide (CH_3CSNH_2) were used. The substrates used in the deposition process were of Corning 7059 type. Glass slides were cleaned using the following procedure. The glass slides were cleaned, applying soap water and rinsed thoroughly with deionised water. These slides were then immersed in a beaker consisting of Potassium dichromate solution for about 24 hours. After cleaning these slides with deionised water, they were dried and then immersed in a beaker consisting of Methanol. This beaker was placed in an Ultrasonicator and the slides were subjected to Ultrasonic agitation. Finally, the slides were taken out of the beaker and both the surfaces were dried using hot air gun. These slides were further mounted on substrate holder.

Figure 1 shows the schematic representation of the experimental setup used to grow Cu- doped SnS thin films on glass substrates. 5ml of Acetone was collected in a beaker and 1.13gm of $SnCl_2.2H_2O$ was added. The mixture was stirred well using a magnetic stirrer. 15 ml of Tri Ethanol Amine (TEA) was added to this solution, which acted as a complexing agent. In order to reduce the turbidity, another 3 – 4 ml of Acetone was added to the mixture. Stirring was continued for another 5 minutes. 0.375gm of Thioacetamide was added to 10 ml of deionised water in another beaker and stirred for about 2 minutes. This solution was transferred to the first beaker that consisted of Stannous chloride, Acetone and TEA mixture. 8ml of NH_3 buffer solution was added to the solution while the stirring process was continued. The amount of deionised water required to make up the solution to 50 ml was added. The solution started slowly turning to Pale yellow and then dark brown colour as soon as

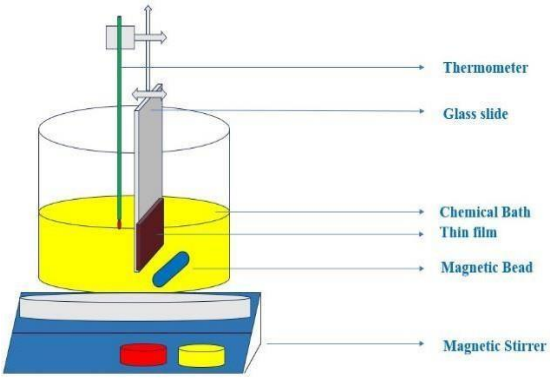

Fig 1 Experimental arrangement for CBD

the water was added. Suitable amount of $CuCl_2$ was added to achieve the doping levels in the range of 0 - 5 at%. The bath temperature was maintained at 70^0 C. The glass substrates cleaned thoroughly were arranged vertically in the reaction bath. The stirring was continued till two hours and fifteen minutes. As a result, pinhole free Cu-doped SnS thin films were deposited on the glass slides. These glass slides were gently rinsed with deionised water. These slides were then allowed to dry under nitrogen flow.

2.2 Characterization

The pure SnS and Cu-doped SnS thin films prepared as per the procedure discussed in the previous sub section were analysed using the appropriate characterisation techniques. VG Multilab 2000 X-ray Photoelectron spectrometer with Kα radiation (1486.6 eV) as the exciting source was employed to study the stoichiometry and the chemical state of the elements in the Cu-doped SnS thin films. The crystal structure was verified with Seifert3003TT X-ray diffractometer with Cu Kα radiation (λ = 1.542 Å). Perkin Elmer Lambda 950 UV-VIS-NIR Spectrometer was used to study the optical properties of these thin films. Lastly, the electrical properties of the grown films were studied using ECOPIA HMS – 3000VER Hall measurement system.

2.3 Growth mechanism

Restricted release of Sn^{2+} and S^{2-} ions in the solution will support acceptable condensation of these ions on the properly mounted substrates by ion-by-ion process. The ionic product of $Sn^{2+}$and S^{2-} must be greaterthan the solubility product of SnS so that SnS thin films can effectively be deposited. Tartaric acid, TEA etc arereliable complexing agents that help in proper deposition of SnS thin films by gradually releasing Sn^{+2} ionsand maintain soluble species of Sn^{+2} in aqueous medium. In this deposition process, TEA was used as complexing agent. The possible growth mechanism in this deposition process is explained based on the Classical nucleation theory.

$$CH_3CSNH_2 + H_2O \leftrightarrow CH_3CONH_2 + H_2S \quad (2)$$

$$H_2S + H_2O \leftrightarrow H_3O^+ + HS^- \ (K_0 = 10^{-7}) \quad (3)$$

$$HS^- + H_2O \leftrightarrow H_3O^+ + S^{-2} \ (K_1 = 10^{-17}) \quad (4)$$

Tri Ethanol Amine (TEA) represented as (T) in the following chemical equations helps in complexing Sn^{+2} ions in the Sn salt and Cu^{+2} ions in Cu dopant.

$$SnCl_2 + T \leftrightarrow [Sn(T)]^{+2} + Cl^- \quad (5)$$

$$CuCl_2 + T \leftrightarrow [Cu(T)]^{+2} + Cl^- \quad (6)$$

$$[Cu(T)]^{+2} \leftrightarrow Cu^{+2} + T \quad (7)$$

The complex ions slowly permit free Sn^{+2} ions in a well-controlled manner. The hydrolysis of thioacetamide results in S^{-2} which then combines with the free Sn^{+2} to form SnS.

$$[Sn(T)]^{+2} + S^{-2} \rightarrow SnS + T \ (K_{sp} = 1 \text{ X } 10^{-26} \text{ at } 25^0C) \quad (8)$$

3. Results and discussion

3.1 XPS analysis

The global scan XPS spectra of the pristine, 1% Cu doped, 3% Cu doped and 5% Cu doped Sns thin films is illustrated in the figure 2, in the binding energy ranging from (0 – 1000 eV). The reflections in the XPS spectrum were calibrated to the carbon C 1s peak (284.6 eV). The XPS spectra of pristine SnS thin films illustrated peaks from various elements like Sn 4d, Sn 3s, S 2p, Sn 3p, C 1s, O1s, and double Sn 3d. Similar peaks were observed in the scan of the Cu-doped SnS thin films, besides double 2p peak of Cu. Presence of Cu in the films was confirmed by this Cu 2p peak. The C 1s peak belonged to the contaminants on the surface of the film. O 1s is yet another peak belonged to such contaminants. Apart from these, no other peak representing any other contaminant was present in the XPS spectra [21 - 24].

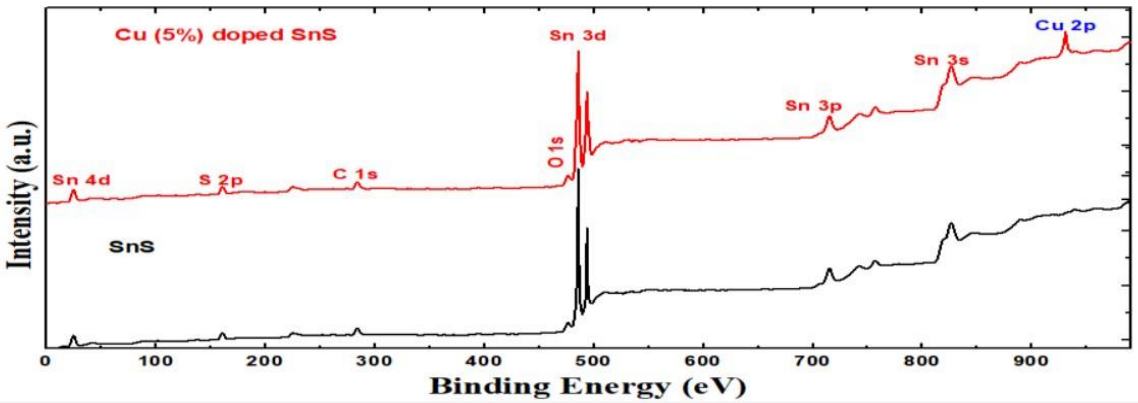

Fig 2: Global scan XPS spectra of undoped and Cu-doped SnS thin films

3.2 Structural properties

SnS thin films were grown, doped with Copper for different [Cu/Sn] concentrations at the bath temperature $T_b = 70^0$C. Figure 3 illustrates the corresponding XRD patterns which hint at orthorhombic structure with polycrystalline nature. XRD peaks were observed at 31.530 ^{0}, 30.665^0, 27.441^0 and 26.076^0 respectively in the case of both pristine and Copper doped thin films. These observed peaks correspond to (111), (301), (021) and (012) planes of SnS, among which (111) appeared as the preferred orientation, in confirmation with the standard values reported [2,25]. At lower doping concentrations of about 1 at%, the structural properties of both pristine and Cu-doped SnS thin films are similar. The reasons may be that either theCu atoms might have accommodated themselves in the Van der waals gaps between the atomic layers of Sulphur and Tin atoms [26] or the Cu atoms might have been absorbed by grain boundaries and hence would not have resulted in any observable structure distortion [27].

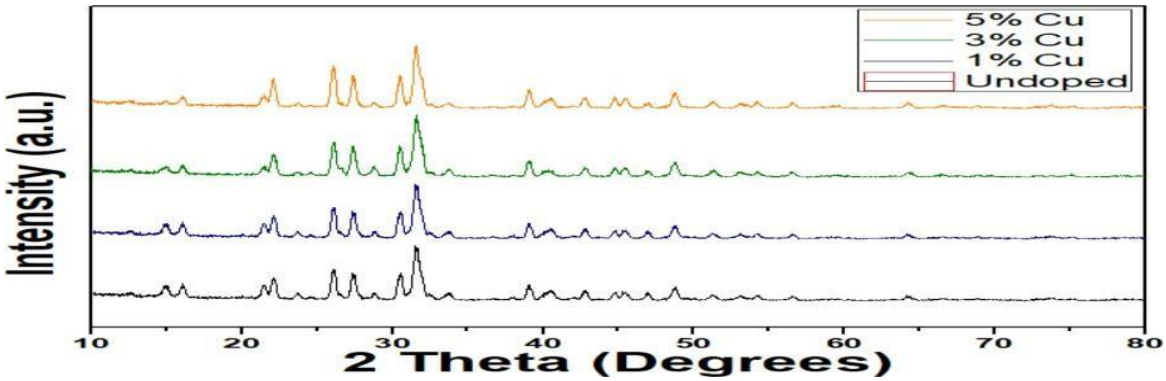

Fig 3: XRD patterns of pristine and Cu-doped (1%, 3% and 5%) thin films

As the Cu-doping concentration increased from 0% to 5% considerable improvement in crystallinity was observed in the as-grown films because the Bragg peaks became sharper and more intense. Cu-atoms might have supported the growth of SnS films, with the formation of new nucleation centres [28].

3.3 Optical properties

It was clear from the figure 4(a) that the absorption coefficient (α) was to the tune of $> 10^6$ cm^{-1} for the as-grown films. It was observed that the absorption edge slightly shifted to higher wavelength region as the doping concentration was increased that obviously resulted in the decrease of optical band gap. The following relation was employed in evaluating the energy band gap of the semiconductor films [29]

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \qquad (9)$$

where the band edge constant is denoted by (A) while direct transition band gap is represented by (E_g). The SnS is considered as more suitable for direct band gap material and hence n = ½ [30]. Figure 4(b) shows the plot between $(\alpha h\nu)^2$ vs Photon energy for undoped and Copper doped SnS thin films. The (E_g) was determined by the extrapolation of the linear portions of the curve to reach the x-axis as α=0. The optical band gap thus determined for the pristine SnS thin films was 1.25 eV while that in the case of Copper doped SnS thin films were 1.2 eV for 1% doping, 1.196 eV for 3% doping and 1.193 eV for 5% doping. Presence of Cu in the SnS lattice was the key reason for the reduction in the optical band gap [29].

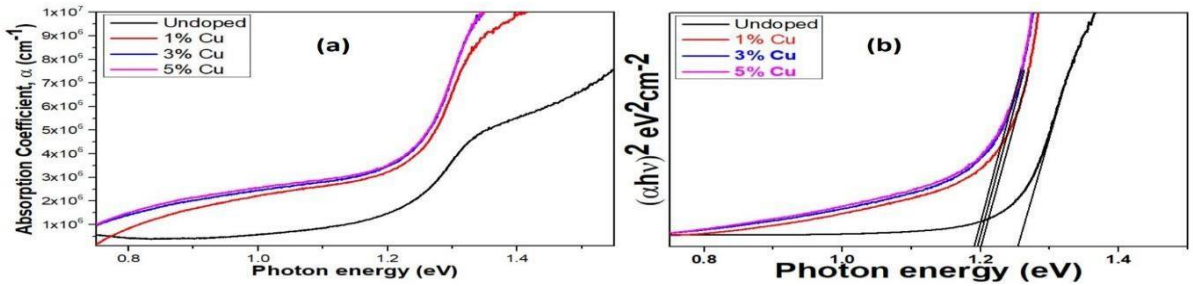

Fig 4: (a) Absorption coefficient (b) $(\alpha h\nu)^2$ Vs Photon energy ($h\nu$) of undoped and Cu-doped (1%, 3% and 5%) SnS thin films.

3.4 Electrical properties

Table 1 lists out the various electrical parameters like resistivity, carrier concentration and Hall mobility for the undoped and Cu-doped (1%, 3% and 5%) SnS thin films. The resistivity of these thin films decreased with the rise in the doping concentration of Cu which might be owing to the replacement of Sn^{2+} by the Cu^{2+} ions which resulted in the increase in the conductivity. From the table 1, the lowest resistivity of $2.12x10^{-2}$ Ω - cm was observed in the case of 5% Cu-doped SnS thin film which represented the better crystallinity. This was confirmed in figure 1 also. Further, it was observed that doping Cu not only increased the carrier concentration but also improved the Hall mobility. Similar observations were reported in the case of Ag doped SnS thin films [16].

Sample	$\boldsymbol{Resistivity}$ $(\boldsymbol{\Omega - cm})$	$\boldsymbol{Carrier\ Concentration}$ $(\boldsymbol{cm^{-3}})$	$\boldsymbol{Hall\ mobility}$ $(\boldsymbol{cm^2/V-S})$
Undoped	6.02×10^{2}	5.74×10^{15}	140.23
1% Cu-doped	5.54×10^{1}	2.46×10^{17}	410.28
3% Cu-doped	3.26×10^{-1}	4.57×10^{18}	520.43
5 % Cu-doped	2.12×10^{-2}	4.68×10^{19}	680.54

4. Conclusions

Cu-doped SnS thin films were deposited along with the undoped films using CBD. The properties like structural, optical and electrical are studied and reported in this paper. The existence of copper dopant in the SnS thin films was confirmed from the XPS studies. Improved crystallinity was observed in the case of 5% Copper doped SnS thin films compared to the pristine, 1% and 3% Copper-doped SnS thin films. Further, doping SnS with Copper, reduced the optical band gaps with about 1.193 eV band gap for 5% Cu-doped SnS thin film. Also, the electrical properties were greatly influenced by the Cu-doping with lowest resistivity, highesthall mobility and highest carrier concentration recorded for 5% Copper doped SnS thin films. These observations suggest the appropriateness of Cu-doped SnS thin films in the case of photovoltaic applications.

References

[1] J.J. Loferski, Theoretical considerations governing the choice of the optimum semiconductor for photovoltaic solar energy conversion, J. Appl. Phys. 27 (1956) 777–784.

[2] C. Chen, C. Huang, Effects of silver doping on electromigration of eutectic SnBi solder, J. Alloy. Compd. 461 (2008) 235–241.

[3] P. Sinsermsuksakul, L. Sun, S.W. Lee, H.H. Park, S.B. Kim, C. Yang, et al., Overcoming efficiency limitations of SnS-based solar cells, Adv. Energy Mater. 4 (2014) 1–7.

[4] A. Niemegeers, M. Burgelman, A. De Vos, On the CdS/CuInSe2 conduction band discontinuity, Appl. Phys. Lett. 67 (1995) 843–845.

[5] T. Minemoto, T. Matsui, H. Takakura, Y. Hamakawa, T. Negami, Y. Hashimoto, T. Uenoyama, M. Kitagawa, Theoretical analysis of the effect of conduction band offset of window/CIS layers on performance of CIS solar cells using device simulation, Sol. Energy Mater. Sol. Cells 67 (2001) 83–88.

[6] L. Sun, R. Haight, P. Sinsermsuksakul, S. Bok Kim, H.H. Park, R.G. Gordon, Band alignment of SnS/Zn(O, S) heterojunctions in SnS thin film solar cells, Appl. Phys. Lett.103 (2013) 1–5.

[7] P. Malkeshkumar, R. Abhijit, Magnetron sputtered Cu doped SnS thin films for improved photoelectrochemical and heterojunction solar cells, RSC Adv. 4 (2014) 39343–39350.

[8] A. Dussan, F. Mesa, G. Gordillo, Effect of substitution of Sn for Bi on structural and electrical transport properties of SnS thin films, J. Mater. Sci. 45 (2010) 2403–2407.

[9] V.F. Gremenok, V.Y. Rud, Y.V. Rud, S.A. Bashkirov, V.A. Ivanov, Photosensitive thin- film In/p-PbxSn1−xS Schottky barriers: fabrication and properties, Semiconductors 45(2011) 1053–1058.

[10] M. Reghima, A. Akkari, C. Guasch, N. Kamoun-Turki, Effect of indium doping on physical properties of nanocrystallized SnS zinc blend thin films grown by chemical bath deposition, Renew. Sustain. Energy 4 (1–12) (2012) 011602.

[11] W. Huang, S. Cheng, H. Zhou, Electrical and optical properties of In-doped SnS thin films prepared by thermal evaporation, ECS Trans. 44 (2012) 1295–1301.

[12] S. Zhang, S.Y. Cheng, H.J. Jia, H.F. Zhou, Preparation and characterization of aluminium-doped SnS thin films, Adv. Mater. Res. Trans. Tech. Publ. 418 (2012) 712–716.

[13] M. Devika, N.K. Reddy, K. Ramesh, K.R. Gunasekhar, E.S.R. Gopal, K.T.R. Reddy, Low resistive micrometer-thick SnS:Ag films for optoelectronic applications, J. Electrochem. Soc. 153 (2006)G727–G733.

[14] K. Santhosh Kumar, A.G. Manohari, S. Dhanapandian, T. Mahalingam, Physical properties of spray pyrolyzed Ag-doped SnS thin films for opto-electronic applications,Mater. Lett. 131 (2014) 167–170.

[15] M. Reghima, A. Akkari, C. Guasch, N. Kamoun-Turki, Structural, optical, and electrical properties of SnS:Ag thin films, J. Electron. Mater. 44 (2015) 4392–4399.

[16] Sreedevi Gedi, Vasudeva Reddy Minnam Reddy, Tulasi Ramakrishna Reddy Kotte, Soo-Hyun Kim, Chan-Wook Jeon, Chemically synthesized Ag-doped SnS films for PV applications, Ceramics International 42 (2016) 19027 – 19035.

[17] C. Lilia, C. Triana, P.B.G. Gordillo, Preparation and characterization of SnS:Bi thin films, Braz. J. Phys. 41 (2011) 15–20.

[18] P. Sinsermsuksakul, R. Chakraborty, S.B. Kim, S.M. Heald, T. Buonassisi, R.G. Gordon, Antimony- doped tin(II) sulfide thin films, Chem. Mater. 24 (2012) 4556–4562.

[19] Y. Yongli, C. Shuying, Preparation of SnS∶Ag thin films by pulse electrodeposition, J. Semicond. 4177 (2008) 1–5.

[20] M. Kilani, B. Yahmadi, T. Kamoun, M. Castagne, Effect of Al doping and deposition runs on structural and optical properties of In2S3 thin films grown by CBD, J. Mater. Sci. 46 (2011) 6293– 6300.

[21] G. Sreedevi, M. Vasudeva Reddy, P. Chinho, J. Chan-Wook, K.T. Ramakrishna Reddy,Comprehensive optical studies on SnS layers synthesized by chemical bath deposition,Opt. Mater. 42 (2015) 468–475.

[22] A. GuruSampath Kumar, Xuejin Li, Yu Du, Youfu Geng, Xueming Hong, UV- photodetector based on heterostructured ZnO/(Ga,Ag)-co-doped ZnO nanorods by cost-effective two-step process, Applied Surface Science 509 (2020) 144770.

[23] GuruSampath Kumar A., Sofi Sarmash T., Obulapathi L., Jhansi Rani D., Subba Rao T., Asokan K, Structural, optical and electrical properties of heavy ion irradiated CdZnO thin films, Thin Solid Films 605 (2016) 102–107

[24] L. Obulapathi, A. GuruSampath Kumar, T. Sofi Sarmash, D. Jhansi Rani, G.V.V. Bhaskara Rao, and T. Subba Rao, Effect of film thickness on physical properties of CuCrO2 thin films, Journal of The Australian Ceramic Society Volume 52, (2016) 102 – 105.

[25] M. Vasudeva Reddy, G. Sreedevi, P. Babu, Z. Guillaume, K.T. Ramakrishna Reddy, P. Chinho, Influence of different substrates on the properties, Sci. Adv. Mater. 7 (2015) 1–5.

[26] T.H. Patel, R. Vaidya, S.G. Patel, Growth and transport properties of tin monosulphoselenide single crystals, J. Cryst. Growth 253 (2003) 52–58.

[27] I. Lefebvre-Devos, J. Olivier-Fourcade, Lithium insertion mechanism in SnS2, Phys. Rev. B 61 (2000) 3110–3116.

[28] J. Morales, E. Andrade, M. Miki-Yoshida, Influence of Al, In, Cu, Fe and Sn dopants in the microstructure of zinc oxide thin films obtained by spray pyrolysis, Thin Solid Films 366 (2000) 16–27.

[29] Kumar, AG., Sarmash, T.S., Obulapathi, L. Rani, D.J., Rao, T.S., Asokan, K., Structural, optical and electrical properties of heavy ion irradiated CdZnO thin films, Thin Solid Films., 605 2016: pp.102–107.https://doi.org/10.1016/j.tsf.2015.12.02