International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.2, pp 1038-1044, 2014-2015

ICONN 2015 [4th - 6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Characterization of $ZnIn_2S_4$ AND In rich-$ZnIn_2S_4$ Films By Spray Pyrolysis Method

S.Hemalatha[1]*, J.Tamil Illakkiya[1], Rachel Oommen[1], P.Usha Rajalakshmi[1],

[1]Department of Physics, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore-641 043, India.

Abstract : Using the Spray pyrolysis method, Zinc thioindate ($ZnIn_2S_4$) and In rich-Zinc thioindate thin films were deposited on a glass substrate with the molar ratio of Zn/In = 4.6, 3.1 respectively using $ZnCl_2$, $InCl_3$ and $SC(NH_2)_2$ as precursor material with substrate temperature of 350˚C. From XRD analysis, the position of the peak was shifted with increasing the Zn/ In molar ratio which is well agreed with the Raman spectrum. Optical study shows the maximum transparency of nearly 80% in NIR region. Absorbance shows the maximum for ZIS thin film compared to In rich film. The absorbance edge of ZIS and In rich ZIS film were observed to be around 462 nm and 750 nm respectively. The E_g value of stoichiometric and In rich ZIS film were calculated as 2.1eV and 2.3eV. Morphology has great impact on the molar ratio revealing flower like morphology was observed for ZIS film. Composition of the film was observed using the EDAX spectrum. The presence of Indium rich in ZIS film was confirmed by EDAX analysis.
Keywords: $ZnIn_2S_4$, In rich $ZnIn_2S_4$ thin films, spray pyrolysis, XRD, UV-Vis-NIR, Raman, FE-SEM with EDAX.

Introduction

Wide band gap semiconductor materials have been the center of various studies in the last decade, owing to their physical properties and numerous applications including solar cell.Polymorphism of inorganic materials has attracted extensive interest in many applications. Different types of polymorphs usually exhibit different properties. Zinc indium sulphide is a ternary chalcogenide which belongs to AB_2X_4 (A=Zn, Cd, Hg, B=Al, Ga, In, X=S, Se, Te) exhibited different polymorphs[1].Several layered ternary intermediate phases are formed in the ZnS-In, S, system with the general formula $Zn_mIn_2S_{3+m}$ (*m* = 1,2,3, ...) and that a fairly large variety of polytypic forms exists for each of these phases[2]. $ZnIn_2S_4$ is a ternary chalcogenide with two distinct polymorphs: hexagonal and cubic. According to recent studies physical and electronic properties of these compounds could play a crucial part in the establishment of new devices $ZnIn_2S_4$ has been part of many recent experimental works[3,4]. due to its possible uses in areas such as photo-catalysis[5,6], thermoelectricity[7], photoconduction[8], Charge storage[9]. The indirect band gap (1.8– 2.1 eV) of $ZnIn_2S_4$ is comparable to the solar spectrum and is thus suitable for energy conversion applications[10], $ZnIn_2S_4$ thin film prepared by various deposition condition such as hydrothermal method[11], electro deposition[12], atomic layer deposition[13],spin coating method[14],microwave-assisted synthesis equipment[15], MOCVD[16], magnetron sputtering[17], CBD method[18], facile solvothermal[19], spray pyrolysis[20,21], Successive ionic layer adsorption and reaction (SILAR)[22], solvothermal method[23]. Among these methods, the spray pyrolysis technique has several advantages simplicity, safety and low cost of the apparatus and raw materials. In this spray pyrolysis method has specific conditions such as the preparation of composite thin films can easily achieved by adjusting the composition of spray solution. Also have various deposition parameters such as the optimum distance between the nozzle and the nebulizer spray pyrolysis apparatus, substrate temperature, gas and solution flow rates, doping concentration of the precursor in the starting solution, deposition time etc. The investigation has been made by varying the concentration of In ratio in $ZnIn_2S_4$ precursor during spray pyrolysis using X-ray diffraction analysis, optical and morphological, raman spectrum and photoluminance study.

Experimental Procedure

The ($ZnIn_2S_4$) Zinc thioindate film deposited on glass substrates using spray pyrolysis. The atomization of the desired chemical solution into a spray of fine droplets is effected by the spray nozzle, with the help of compressed air as carrier gas. The set up consists of a hot plate with thermocouple attached digital controller and compressed motor, the carrier gas presser mainted 1 bar fixed. Substrate temperature is measured with the help of thermocouple. Standard commercial glass slides (7.5 cm X2.5 cm) were cut in to (2.5 cm X 2.5 cm) can be used as substrates, which were previously cleaned well using chromic acid and deionized water dried before depositing the film process. The precursor solutions of Zinc chloride, indium chloride and thiourea were dissolved separately in a solution containing deionized water. Equal volume of these three solutions were mixed together. A few drops of ethanol were added for complete dissolution and stirred 5 to 10 mins continuously . The molarities of Zinc chloride (0.3180 M), Indium chloride (1.4868 M) and thiourea (0.0682M) respectively. The Zn/In ratios varied in the range of 4.6 and 3.1. The total volume of prepared spray solution is 56 ml. The substrate temperature and distances from spray nozzle to substrate were maintained at 350°C and 5cm respectively. As the precursor droplets arrive on the heated substrate, a pyrolytic decomposition process occurs and high quality ZIS ($ZnIn_2S_4$), In rich $ZnIn_2S_4$ film were deposited. The homogeneous yellow colour ZIS, In-ZIS film were deposited.

Characterization

The structural properties of the nebulized-sprayed ZIS films were studied by X-ray diffraction XPERT-PRO analytical, X-ray diffractometer using Cu-Kα radiation (1.5406Å) and the applied current, accelerating voltage was 30 mA and 45 kV respectively. Surface morphology, composition for films was characterized via high resolution scanning electron microscopy and energy dispersive analysis by X-rays (EDAX) equipped in FESEM by OXFORD X-act tescan instrument. The optical studies of the films were done with an Ultra Violet–visible-Near Infra-Red (UV–Vis-NIR) spectro- photometer (ModelJASCO-V-670) in the range from 300to 2500nm. Raman spectra of the film were taken by HORIBA-LABRAM HR-800 equipment. Photoluminance of the film characterized by Horiba JobinYvon Fluoromax-4 spectrofluorometer.

Result and Discussion

Structural Properties

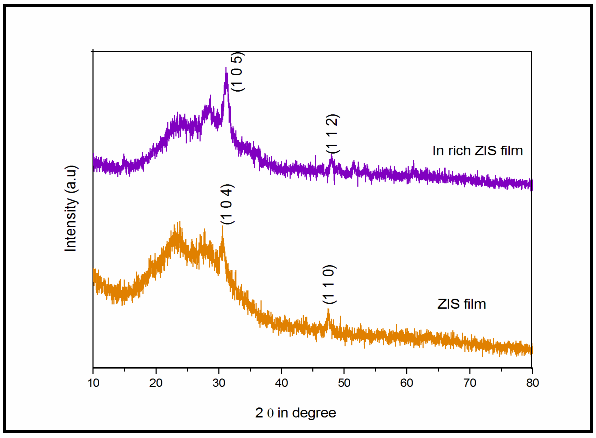


Fig .1 X-RAY diffraction of the $ZnIn_2S_4$, In rich $ZnIn_2S_4$ thin films

The X-ray diffraction spectra of both ZIS, In rich films are shown in the Fig.1.The peaks absorbed for ZIS, In rich film 2θ = 30.6° (1 0 4), 47.4° (1 1 0), 31.1° (1 0 5), 47.9° (1 1 2). ZIS film shows hexagonal phase, at 2θ = 30.6° (1 0 4) plane, the other peaks observed in the X-ray diffractogram are (1 1 0) at 2= 47.4°. The 2θ values were compared with the standard JCPDS data card (72073). When Indium ratio increases, In rich ZIS film peak intensity was high compared to ZIS ($ZnIn_2S_4$) film peak intensity in addition to this, shift occurred to higher angle side. The impurities such as binary sulphides such as ZnS, other binary compound were not presented. The lattice constant of $ZnIn_2S_4$ film shows a = 3.850 Å and c = 24.680 Å. Partical size of the ZIS ($ZnIn_2S_4$), In rich $ZnIn_2S_4$ was 15.54 nm, 21.74 nm. Partical size of the film calculated by scherrer formula such as-

$$D = \frac{K\lambda}{\beta \, \mathrm{Cos}\, \theta}$$

where, K = 0.9 is the shape factor, λ is the X-ray wavelength of Cu Kα radiation at a wavelength (1.5406Å), θ is the Bragg's angle and β is the full width at half maximum of the peak. Where is the full width at half maximum (FWHM) of the peak corrected for instrumental broadening is the wavelength of the X-rays, and *K* is the Scherrer constant, which generally depends on the crystallite shape. The pure phase of ZIS film was can be confirmed not only XRD. The XRD results agree with the Raman spectroscopy which is also used to make further phase identification.

Raman Spectrum

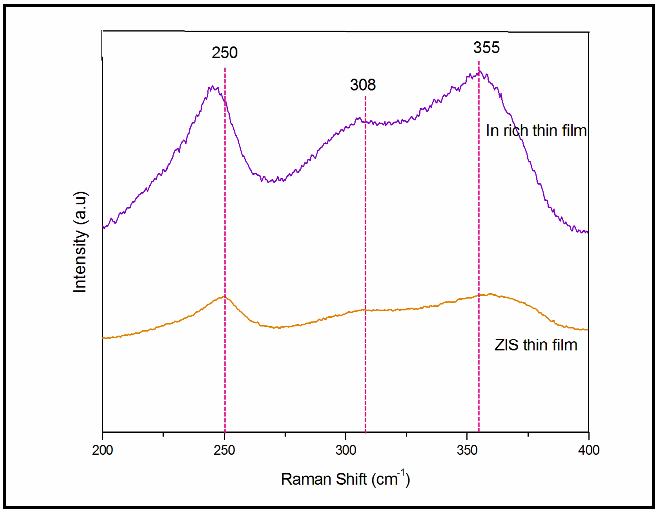


Fig 2. Raman spectrum of the $ZnIn_2S_4$, In rich $ZnIn_2S_4$ thin films.

Raman spectra of the film detect the structural characteristics. Raman spectroscopy is an optical non-contact and non-destructive characterization technique often used to monitor the phases present and their crystal qualities. The phonon energies probed in Raman spectroscopy are strain and composition dependent making it an ideal technique for thin film solar cell absorber characterisation[24,25]. The Raman peaks around 248,308,355 cm^{-1} as deposited ZIS ($ZnIn_2S_4$) film, In rich- Zinc thioindate film. These peaks assigned as a longitudinal mode (LO1), transverse optical mode (TO2) and longitudinal mode (LO2)[14,26]. Broad peaks indicates the crystalinity which was shown in the Fig.2 In rich- ZIS thin film indicates the broad beak compared to ZIS film, the crystalinity of the sample it is well matched with the XRD which is shown in the Fig.1.

Optical Properties

The optical properties of the samples were studied by absorption measurements at room temperature with a UV/Visible/NIR spectrophotometer. Transmittance of the film spectra wavelength range of 200–2400 nm shown in the (Fig .3). Transmittance of the as-deposited $ZnIn_2S_4$ film, In rich $ZnIn_2S_4$ film transmittance is nearly 80% in the NIR region which is agree with the Jianbo Yin et al group.

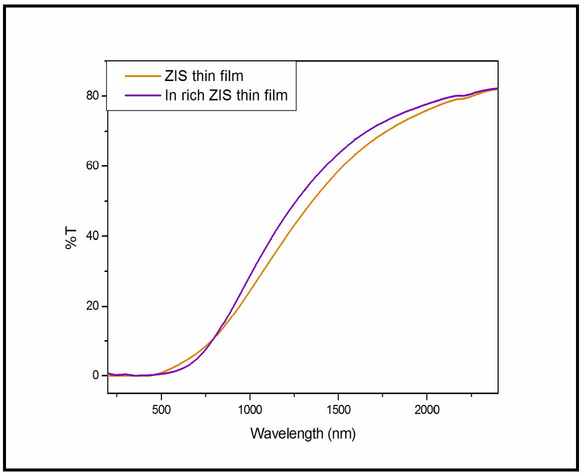


Fig. 3 Transmittance of the thin films

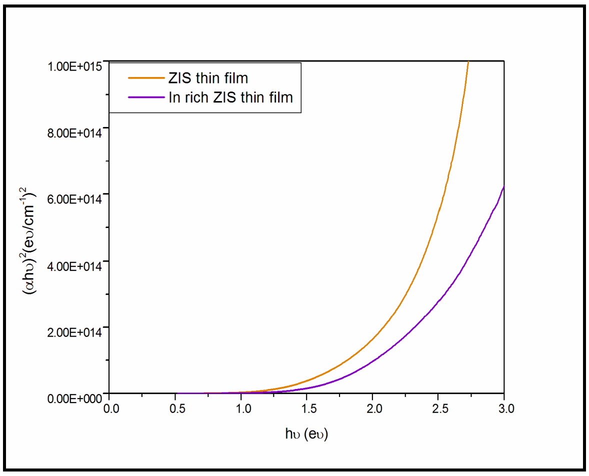


Fig .4 Direct band gap thin films

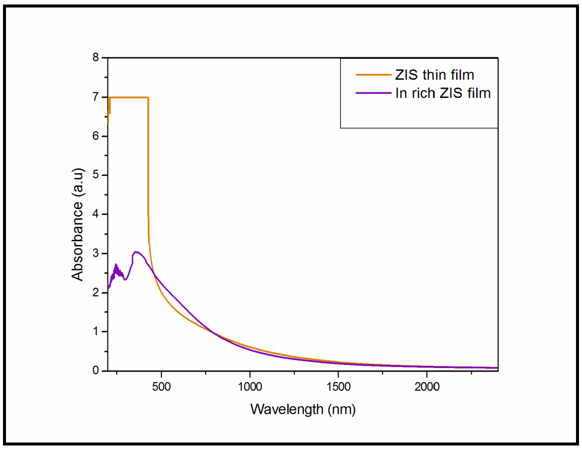


Fig. 5 Absorbance of the thin films

The band positions of a one semiconductor are very important to know the photovoltaic, electrochemical photovoltaic solar cell, etc. applications. The band gap of the film shown in the Fig 4 .The direct optical band gaps (*Eg*) of the sprayed ZIS, In rich ZIS thin films were plotted by extrapolating the linear segment of the plots drawn for $(\alpha h\upsilon)^2$ Vs hυ to obtain the energy axis. The E_g value of stoichiometric and In rich ZIS film were calculated as 2.1eV and 2.3eV respectively. It is clearly show the band gap broadening due to increasing the In ratio which is well agree with composition of the film shown in the Table 1. Absorbance shows the maximum for ZIS thin film compared to In rich film. Pure ZIS films have a steep shape absorption edge in the visible region. The absorbance edge of ZIS and In rich ZIS film were observed to be around 462 nm and 750 nm respectively which was shown in the Fig. 5. Two different absorption edges are clearly seen with increasing the In ratio.

Morphological and Composition of the Film

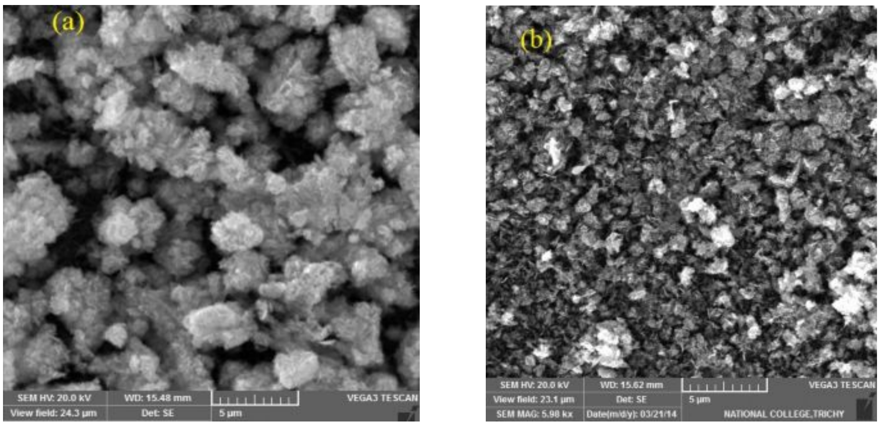
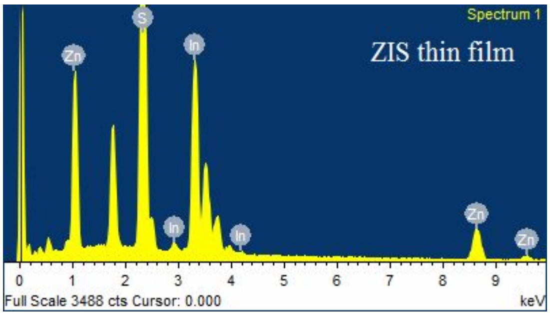


Fig 6. FESEM images of $ZnIn_2S_4$,In rich $ZnIn_2S_4$ films (a) $ZnIn_2S_4$ thin film, (b) In rich $ZnIn_2S_4$ thin film

ZIS,In rich ZIS film were morphological studied by FESEM. The morphlogy of the ZIS film shows the rulless dollops was produced rather than a microsphere[27] which was shown in the Fig.6 ZIS ($ZnIn_2S_4$) thin film (a), In rich ZIS thin film (b). When the increasing the In ratio, the surface of the In rich ZIS film changed.



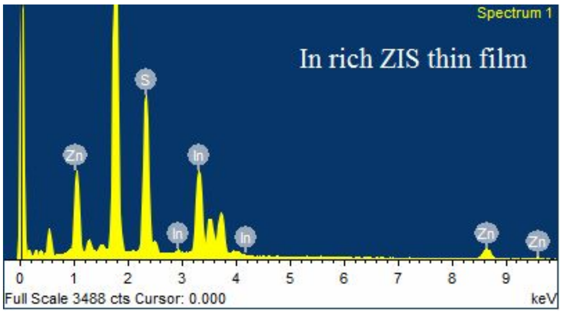


Fig 7. EDAX spectrum of the $ZnIn_2S_4$, In rich $ZnIn_2S_4$ thin film

EDAX is used to measure the ion ratio on the surface of the film. Table 1 shows the EDAX measurements deposited films were carried out at an acceleration voltage of 20 kV. From the EDAX Spectrum three strong peaks corresponding to Zn, In and S were found in the spectrum which confirms the high purity of the $ZnIn_2S_4$ thin films. ZIS, In rich film were composed of zinc, indium and sulfur atoms. The atomic percentages of ZIS film have Zinc (Zn), indium (In) and thiourea(S) nearly comes under the stoichiometric value and the spectrum of the film was shown in the Fig.7. When the indium increases the zinc, sulfur ratio decreases simultaneously which is shown in the Table 1.

Photoluminance Study of The film

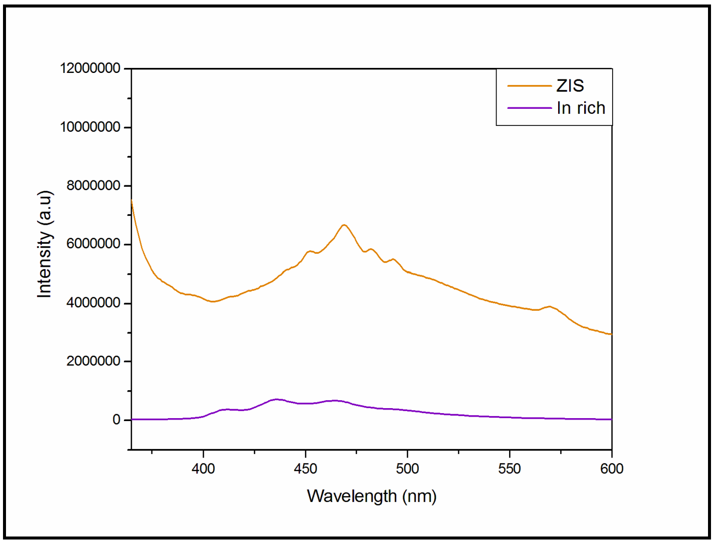


Fig.8 Photoluminance study of the $ZnIn_2S_4$,In rich $ZnIn_2S_4$ film

Fig 8 presents the PL spectra for as-deposited ZIS, In rich ZIs film. The emission peaks located approximately at 474 nm, 495 nm and 560 nm. The emission peak around 560 nm occurred due to band to band transitions[28]. Peak intensity decreases while varying the Zn/In ratio.

Conclusion

Zinc thioindate ($ZnIn_2S_4$),In rich $ZnIn_2S_4$ thin film deposited on a glass substrate using the spray pyrolysis method. Using the spray pyrolysis method molar ratio of Zn/In = 4.6, 3.1 varied respectively. The deposition temperature was mainted 350° C. From XRD result, the peak position was shifted in the higher angle side with increasing the Zn/ In molar ratio which is well agreed with the Raman spectrum. The transmittance of the film of nearly 80% in NIR region. Absorbance shows the maximum for ZIS thin film compared to In rich film. The absorbance edge of ZIS and In rich ZIS film were observed to be around 462 nm and 750 nm respectively. The direct band gap (E_g) of $ZnIn_2S_4$ (Zinc thioindate) and In rich ZIS film were calculated as 2.1eV and 2.3eV.

Morphology of the film show the rulless dollops rather than microspheres for ZIS film when the molar ratio increases .Composition of the film was observed using the EDAX spectrum. In ratio increases in the In rich $ZnIn_2S_4$ film Zn, S (wt %) simultaneously decreases compared to the $ZnIn_2S_4$ film. From the Pl study emission peaks were observed 474 nm, 495 nm and 560 nm.

References

1. Yongjuan Chen, Shunwei Hu, Wenjun Liu, Xueyuan Chen, Ling Wu, Xuxu Wang, Ping Liu and Zhaohui Li.,Controlled syntheses of cubic and hexagonal $ZnIn_2S_4$ nanostructures with different visible-light photocatalytic performance, Dalton Trans., 2011, 40, 2607-2613.
2. Radautsan S. I, Donika F. G, Kyosse G. A. , Mustya I. G., Polytypism of Ternary Phases in the System Zn-In-S, phys. stat. sol. 1970,37(2), K123-K127.
3. Wang T X, Xu S H and Yang F X , $ZnIn_2S_4$ nanopowder as an efficient visible light-driven photocatalyst in the reduction of aqueous Cr(VI), Mater. Lett, 2012, 83, 46-48.
4. Chen Z, Li D, Xiao G, He Y and Xu Y J, Microwave-assisted hydrothermal synthesis of marigold-like ZnIn< sub> 2</sub> S< sub> 4</sub> microspheres and their visible light photocatalytic activity, J. Solid State Chem. 2012,186, 247-254.
5. Fang F, Chen L, Chen Y B and Wu L M, Synthesis and Photocatalysis of ZnIn2S4 Nano/Micropeony, J. Phys.Chem. C, 2010,114, 2393—2397.
6. Zhibin Lei, Wansheng You, Meiying Liu, Guohua Zhou, Tuyoshi Takata, Michikazu Hara,Kazunari Domenand Can Li, Photocatalytic water reduction under visible light on a novel ZnIn2S4 catalyst synthesized by Hydrothermal Method, CHEM. COMMUN., 2003, 2142–2143.
7. Seo W S, Otsuka R, Okuno H, Ohta M and Koumoto K, Thermoelectric properties of sintered polycrystalline $ZnIn_2S_{4,}$ J. Mater. Res., 1999, 14, 4176-4184.
8. Xianluo Hu, Jimmy C. Yu, Jingming Gong and Quan Li, Rapid Mass Production of Hierarchically Porous $ZnIn_2S_4$ Submicrospheres via a Microwave-Solvothermal Process Crystal Growth and Design 7(12),2007,2444-2448.
9. Romeo N, Dallaturca A, Braglia R and Sberveglieri G Charge storage in $ZnIn_2S_4$ single crystals Appl. Phys. Lett.,1973, 22, 21.
10. Wen Cai, Yinsheng Zhao, Jie Hu, Jiasong Zhong and Weidong Xiang, Solvothermal Synthesis and Characterization of Zinc Indium Sulfide Microspheres , J. Mater. Sci. Technol., 2011, 27(6), 559-562.
11. Shaohua Shen, Xiaobo Chen, Feng Ren, Coleman X Kronawitter, Samuel S Mao and Liejin Guo, Solar light-driven photocatalytic hydrogen evolution over $ZnIn_2S_4$ loaded with transition-metal sulfides, Nanoscale Research Letters, 2011, 6:290.
12. Hongtao Yu, Xie Quan, Yaobin Zhang, Ning Ma, Shuo Chen, and Huimin Zhao, Electrochemically Assisted Photocatalytic Inactivation of Escherichia coli under Visible Light Using a $ZnIn_2S_4$ Film Electrode,Langmuir 2008, 24, , 7599-7604.
13. Pascal Genevee, Frederique Donsanti,Nathanaelle Schneider, and Daniel Linco, Atomic layer deposition of zinc indium sulfide films: Mechanistic studies and evidence of surface exchange reactions and diffusion processes , J. Vac. Sci. Technol. A, 2013, 31(1), 01A131-1 - 01A131-6.
14. Yian Xie,Yufeng Liu,Houlei Cui,Wei Zhao,Chongyin Yang,Fuqiang Huang, Facile solution-based fabrication of $ZnIn_2S_4$ nanocrystalline thin films and their photoelectrochemical properties, Journal of Power Sources 265, 2014, 62-66.
15. Zhixin Chen, DanzhenLi , GuangcanXiao , YunhuiHe , Yi-JunXu, Microwave- assisted hydrothermal synthesis of marigold-like $ZnIn_2S_4$ microspheres and their visible light photocatalytic activity,Journal of Solid State Chemistry., 2012, 186, 247-254.
16. Ryoaki Nomura, Haruo Matsuda, Takashi Miyai, Akio Baba, Growth of spinel zinc thioindionate thin film by single-source MOCVD,Thin Solid Films.,1999, 342, 108-112.
17. Huimin Jia,Weiwei He, Yan Lei, Xuewu Chen, Yong Xiang, Shu Zhang, Woon Ming Lau and Zhi Zheng, Controllable fabrication of ternary $ZnIn_2S_4$ nanosheet array film for bulk heterojunction solar cells, RSC Advances, 2013, 3,8909-8914.
18. Kong-Wei Cheng, Chia-JuiLiang, Preparation of Zn–In–S film electrodes using chemical bath deposition for photoelectrochemical applications, Solar Energy Materials & Solar Cells .,2010,94, 1137-1145.
19. Yuexiang Li , Kai Zhanga, Shaoqin Penga, Gongxun Lub, Shuben Li, Photocatalytic hydrogen generation in the presence of ethanolamines over Pt/ $ZnIn_2S_4$ under visible light irradiation, Journal of Molecular Catalysis A: Chemical, 2012,363– 364, 354-361.

20. Mingtao Li, Jinzhan Su, Liejin Guo, Preparation and characterization of $ZnIn_2S_4$ thin films deposited by spray pyrolysis for hydrogen production, International journal of hydrogen energy., 2008, 33, 2891-2896.
21. F. Rahmana, J. Poddera, and M. Ichimura, Studies on Structural and Optical Characterization of In-Zn-S Ternary Thin Films Prepared by Spray Pyrolysis, International journal of optics and photonics., 2011,5(2)79-86.
22. Jianbo Yin, Junhong Jia,Gewen Yi and Liqiang Wang, Preparation of $ZnIn_2S_4$ Film Electrodes by the SILAR Technique, J. Chin. Chem. Soc. 2012, *59*, 1365-1368.
23. Xinglong Gou, Fangyi Cheng, Yunhui Shi, Li Zhang, Shengjie Peng, Jun Chen, and Panwen Shen, Shape-Controlled Synthesis of Ternary Chalcogenide $ZnIn_2S_4$ and $CuIn(S,Se)_2$ Nano-/Microstructures via Facile Solution Route, J. AM. CHEM. SOC. 2006, 128, 7222-7229.
24. U. Rau, D. Abou-Ras, and T. Kirchartz, Advanced Characterization Techniques for Thin Film Solar Cells (Wiley-VCH, 2011).
25. Perez Rodriguez, L. Calvo-Barrio, J. Alvarez-Garcia, J. R. Morante, V. Bermudez, O. Ramdani, J. Kurdi, P.P. Grand, L. Parissi, and O. Kerrec, "Raman scattering microcrystalline assessment and device quality control of electrodeposited CuIn(S,Se)(2) based solar cells," Thin Solid Films,2008,516(20), 7021–7025.
26. Shaohua Shen, Penghui Guo, Liang Zhao, Yuan chang Du, Liejin Guo, Insights into photoluminescence property and photocatalytic activity of cubic and rhombohedral $ZnIn_2S_4$, Journal of Solid State Chemistry., 2011,184, 2250–2256.
27. Zhixin Chen, Low-Temperature and Template-Free Synthesis of $ZnIn_2S_4$ Microspheres, Inorg. Chem. 2008, 47, 9766-9772.
28. Shaohua Shen, Jie Chen, Xixi Wang, Liang Zhao, Liejin Guo, Microwave-assisted hydrothermal synthesis of transition-metal doped $ZnIn_2S_4$and its photocatalytic activity for hydrogen evolution under visible light, Journal of Power Sources 196 (2011) 10112-10119.

*****