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Effect of Annealing Temperatures on Zinc Thioindate Thin Films

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ABSTRACT: Ternary $ZnIn_2S_4$ (ZIS) films were deposited on a glass substrate using Spray pyrolysis method. The properties of as-deposited $ZnIn_2S_4$ film and annealed films were characterized using the XRD, UV-Vis-NIR spectroscopy and Raman spectrum, FESEM, EDAX and Photoluminance. The XRD result shows the hexagonal structure. Optical study shows the maximum transparency of nearly 88% for 550°C annealed film (ZIS-T5).Absorption edge for as-deposited (ZIS) , annealed films (ZIS-T1 -350°C, ZIS-T2 - 450°C and ZIS-T3 - 550°C) values found to be 536 nm and 525 nm, 498nm and 441nm.Band gap(E_g) values of the as-deposited, annealed film (350°C, 450°C, 550°C) values were estimated at 2.79 eV,2.89 eV, 2.94 eV and 3.3eV respectively. Morphology of as-deposited $ZnIn_2S_4$ film shows the rulles dollops rather than a microsphere, EDAX spectrum showed the Composition of the film closed to the stoichiometric compound. From the Pl spectrum strong emission band at ~470 nm was observed for as-deposited (ZIS) and annealed films (ZIS-T1, ZIS-T2).

KEYWORDS: Text detection, $ZnIn_2S_4$, annealing effect, nebulized spray pyrolysis.

I. INTRODUCTION

Image $A^{II}B_2^{III}C_4^{VI}$ ternary semiconducting materials are widely studied because of their excellent potential applications such as electro-optic, optoelectronic, and nonlinear optical devices. Most of these compounds have defect chalcopyrite space group (S24) or defect stannite space group (D112d) structure [1]. $ZnIn_2S_4$ (ZIS) compound comes from the thiospinel family (MIn_2S_4, M=Cd, Fe, Ni, Mn) [2].The $ZnIn_2S_4$ (ZIS) material properties similar to CdS properties, it is n-type semiconductor material [3]. $ZnIn_2S_4$ is found as a strong candidate photovoltaic material for a novel type of thin-film solar cell fabricated by sputtering process [4]. In particular, in the layered structure of $ZnIn_2S_4$ two kinds of intrinsic defects appear relevant: (i) random stacking faults in the layer structure; (ii) Zn ions in the In sub lattice, In ions in the Zn sub lattice and vacant sites in both Zn and In sub lattices. These defects characterize the electronic properties of the material because they give rise to charged centres acting as donors or acceptors [5]. $ZnIn_2S_4$ have different polymorphs and used for many applications, hexagonal $ZnIn_2S_4$ exhibit the photoluminescence and photoconductivity, cubic $ZnIn_2S_4$ exhibit thermoelectricity [6]. The $ZnIn_2S_4$ (ZIS)thin film prepared by various methods such as Successive ionic layer adsorption and reaction (SILAR) [7], solvothermal method [8,9], facile solvothermal method[10], hydrothermal method [11-13] electro deposition [14], microwave-assisted synthesis equipment[15], CBD method[16], thermal sulfidation of the oxidation precursor[17], spin coating method [18], magnetron sputtering [19], MOCVD [20], spray pyrolysis [21,22], Atomic layer deposition [23,24]. $ZnIn_2S_4$ thin film have different morphologies such as nanoribbons and nano wires [25], microspheres [26].Compared to other methods spray pyrolysis is basically a chemical process that involves spraying aqueous solution onto a substrate held at high temperature. In the present work, $ZnIn_2S_4$ (ZIS) thin films are prepared by the novel technique in a liquid phase (Nebulized Spray pyrolysis) and Characterized for structural, optical and Photoluminance properties. Post deposition heat treatment was carried out to see the effect of annealing temperature on its properties.

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$ZnCl_2$, SC $(NH_2)_2$ obtained in Merck, Indium Chloride ($InCl_3$) (Himedia), used as a precursor. Molar solution of the precursors are prepared by dissolving appropriate amount of materials in deionized water .Chemically cleaned 2.5 cm X 2.5 cm glass slides are used as deposit substrate. A simple glass nozzle was fabricated to give a fine and very small droplets of precursor solution which is driven by cool air from the compressor. The pressure of the carrier gas (air) was kept constant at 1 bar. The Sprayed ZIS thin films were obtained from an aqueous solution containing Zinc chloride (0.3180 M), Indium chloride (1.4868 M) and thiourea (0.0682M) respectively. Equal volume of these three solutions mixed together 5 to 10 mins and then added 10 drops of ethanol to form smooth solutions. The substrates were mounted on an aluminium base attached to a heating hot plate. The substrate temperature maintained at 350°C. This substrate temperature was precisely maintained within ± 5°C of the desired value. The temperature was controlled by digital micro controller and the substrate temperature was measured by attaching a thermocouple near the substrate. Nozzle to substrate distance was kept constant at 50mm. Spraying was consummate using novel glass nebulizer. The possible chemical reaction that takes place on the heated glass substrate produces a well adherent uniform yellow $ZnIn_2S_4$ (ZIS) film. The as-deposited samples are annealed at various temperatures 350°C, 450°C, 550°C to study the influence of annealing and the samples labelled as ZIS, ZIS-T1, ZIS-T2 and ZIS-T3 for convenient depiction.

The X-ray diffraction (XRD) patterns, obtained on a XPERT-PRO analytical, X-ray diffractometer using Cu-Kα radiation (1.5406Å) at the applied current 30 mA and accelerating voltage 45 kV respectively. UV–Visible diffuse reflectance spectra were recorded on (UV–Vis-NIR) spectro- photometer (ModelJASCO-V-670). The information related to morphology and elemental composition of the samples are recorded by Field emission scanning electron microscopy (FESEM) attached to an energy dispersive X-ray spectroscopy (EDS) by OXFORD X-act tescan instrument. Raman spectra of the film were taken by HORIBA-LABRAM HR-800 equipment. Photoluminance of the film is characterized by Horiba JobinYvon Fluoromax-4 spectrofluorometer.

II. EXPERIMENTAL RESULTS

(A) Structural Characterization

X-ray Diffraction studies

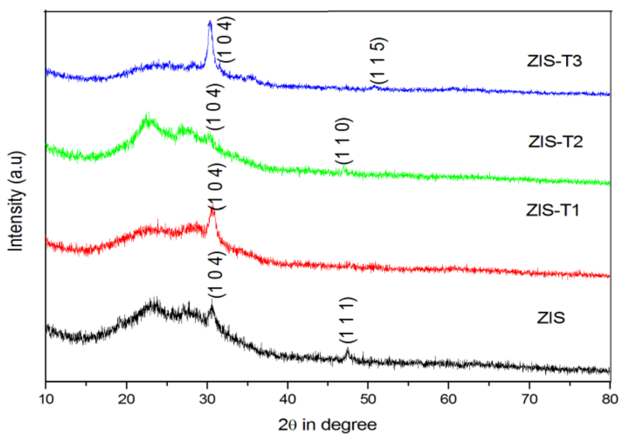

Fig. 1. Structural characterization of the as-deposited and annealed ZIS film

XRD diffraction technique confirmed the $ZnIn_2S_4$ film crystallinity and phase composition of the material. The XRD patterns of the ZIS as-deposited and annealed films are shown in Fig1. Well defined diffraction peaks observed in the XRD pattern of $ZnIn_2S_4$ thin films (104), (111), (110) and (115) well indexed to be hexagonal phase of $ZnIn_2S_4$ thin films (JCPDS-65-2023).No peaks attribute to other phase are observed and indicate the formation of pure hexagonal $ZnIn_2S_4$. The peak intensities are not too high. As the annealing temperature increases to 350°C peak intensity

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increases, for (104) plane, then decrease at 450°C,then increases at 550°C at the same time additional (110) plane peak observed at 450°C and (115) plane peaks at550°C . When the annealing temperature increases to 550°C the yellow colour $ZnIn_2S_4$ film fully changed in to white colour [15].The grain size of the films calculated using Debye Scherrer formula ,

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where,
K = shape factor (0.9 is the constant value),
λ - X-ray wavelength of Cu-Kα radiation at a wavelength (1.5406Å),
θ - Bragg's angle and
β - Full width at half maximum of the peak.

Grain sizes of the $ZnIn_2S_4$ films (ZIS, ZIS-T1, ZIS-T2 and ZIS-T3) were 15.54 nm, 9.26 nm, 10.21 nm and 31.6 nm respectively and the lattice constant are a=3.850Å ,c = 24.680Å.The annealing treatment affected the FWHM of the $ZnIn_2S_4$ films. The smaller FWHM means the larger grain size and the better crystal quality of the whole film. Decrease of the crystallite size, approves the weakening crystallinity of the films and increasing the crystallite size, indicating the improvement of the crystallinity of the films.

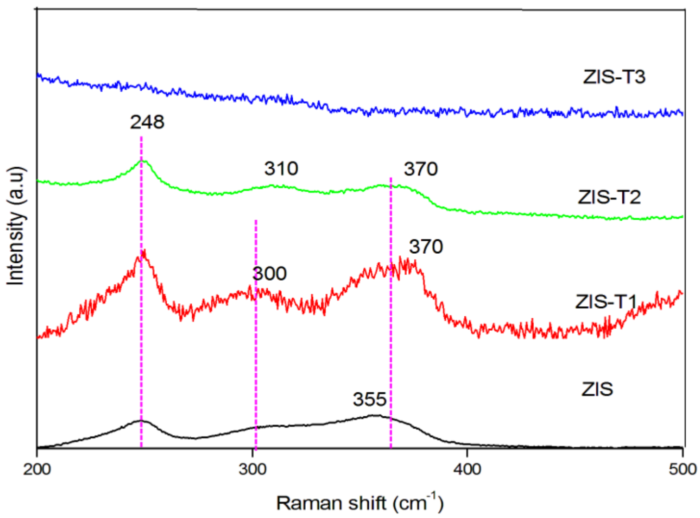

Fig. 2 Raman study of the as-deposited and annealed ZIS film

Raman scattering is an inelastic scattering which provides information on the vibrational states of a semiconductor. The crystalline samples present the sharp Raman peaks while the samples of poor crystallinity show very broad peaks. The Raman spectra provide qualitative information about the crystallinity of the films.

Fig. 2 shows the Raman spectra of the as-deposited and annealed $ZnIn_2S_4$ (ZIS) films (ZIS, ZIS-T1 -350°C, ZIS-T2 - 450°C and ZIS-T3 - 550°C). The peaks around 248 cm^{-1}, 301 cm^{-1} and 355 cm^{-1} in the spectra are typical molecular vibration of $ZnIn_2S_4$ which can be assigned to the longitudinal optical mode and (LO_1), transverse optical mode (TO_2) and longitudinal optical mode (LO_2) of $ZnIn_2S_4$ respectively [18]. As annealing temperature increases, blue shift occurred in ZIS-T1, ZIS-T2 film 355 cm^{-1} to 370 cm^{-1}, 300cm^{-1} to 310 cm^{-1}. The band at 370 cm^{-1} was assigned to A_1g mode [27, 28 and 29] of ZIS spectrum.

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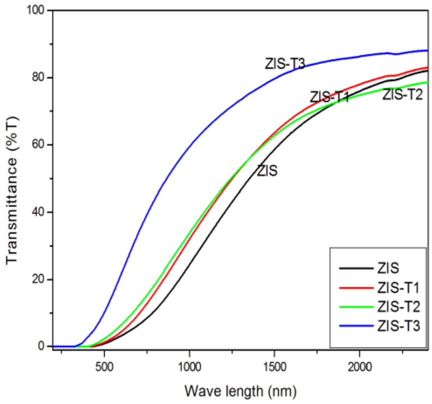
(B) **OPTICAL PROPERTIES**



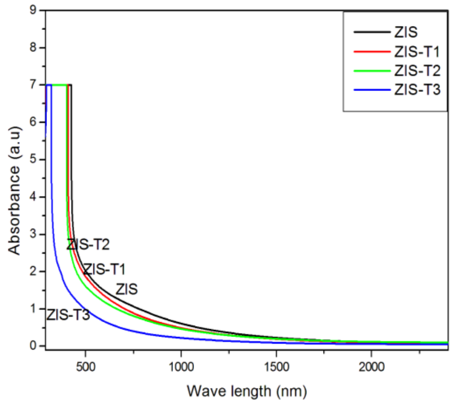
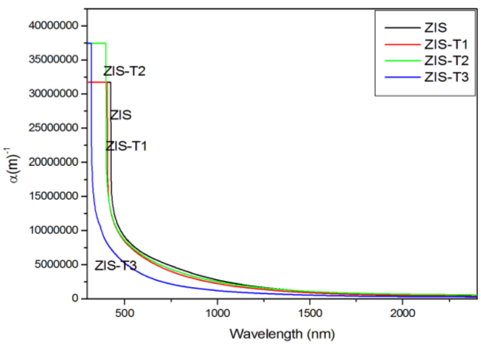


Fig.3 Transmittance of the the as-deposited and annealed ZIS film **Fig.4** Absorption of the as-deposited and annealed ZIS film

Fig.3 shows the transmittance spectra of samples in the light wavelength range (λ) of 200 nm- 2400 nm. The average transparency of the as-deposited (ZIS) and annealed films such as ZIS-T1,ZIS-T2 and ZIS-T3 around 82 %.The higher transmittance indicates fairly smooth surface and relatively good homogeneity of the film. The transmittance spectra of samples exhibit a maximum transparency of 88% in the near infra-red region for ZIS –T3 film. The optical absorption intensity of ZIS-T3 is lower in the visible region as shown in the Fig 4. Aabsorption edge decreases with increasing the annealing temperature and found to be 536 nm and 525 nm, 498nm and 441nm for ZIS, ZIS-T1, ZIS-T2 and ZIS-T3 respectively.



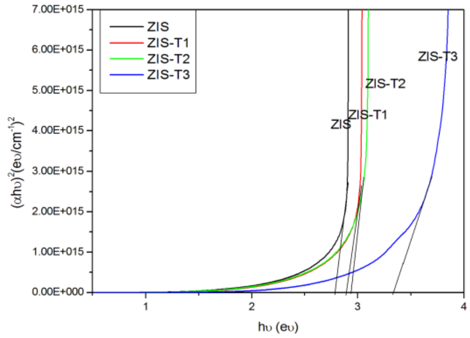


Fig.5 Absorption coefficient of the as-deposited and annealed ZIS film **Fig.6** Direct band gap of the as-deposited and annealed ZIS film

The absorption co efficient follows the formula $(\alpha h\nu)^2 = A(h\nu - Eg)$ for a direct band gap material. The plots of $(\alpha h\nu)^2$ versus photon energy (hν) of $ZnIn_2S_4$ were obtained and are shown in Fig 5. Fig 6 shows the variation of absorption co efficient (α) of various samples with the wavelength. The direct band gap energy of ZIS films were estimated to be 2.79 eV, 2.89eV, 2.94 eV and 3.3eV for ZIS,ZIS-T1,ZIS-T2 and ZIS-T3 respectively.

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(C) SURFACE MORPHOLOGY

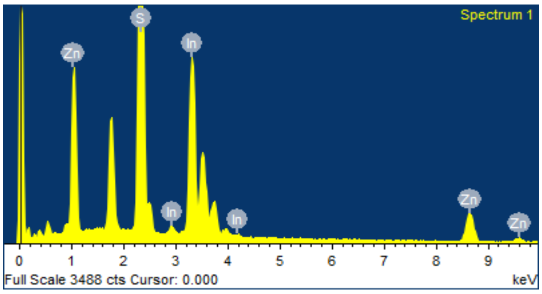

Fig.7 EDAX Spectrum of the as-deposited $ZnIn_2S_4$ (ZIS) thin film

Fig.7. show the typical EDAX pattern of a synthesied $ZnIn_2S_4$. It indicates that the sample is composed of Zn,In and S elements .The EDAX analyses also illustrates that the atom content ratio of Zn,In and S of the as-deposited $ZnIn_2S_4$ is 1:2:4 which is close to the stoicheometric composition of $ZnIn_2S_4$.

Table 1:Elemental composition of the $ZnIn_2S_4$ thin film

Elements	Wt%	At %
Zn	17.86	15.74
In	48.88	24.52
S	33.26	59.74

Table 1 shows the as-deposited $ZnIn_2S_4$ film composition at Wt% and At %.Surface morphology of as-deposited was studied from FESEM images.

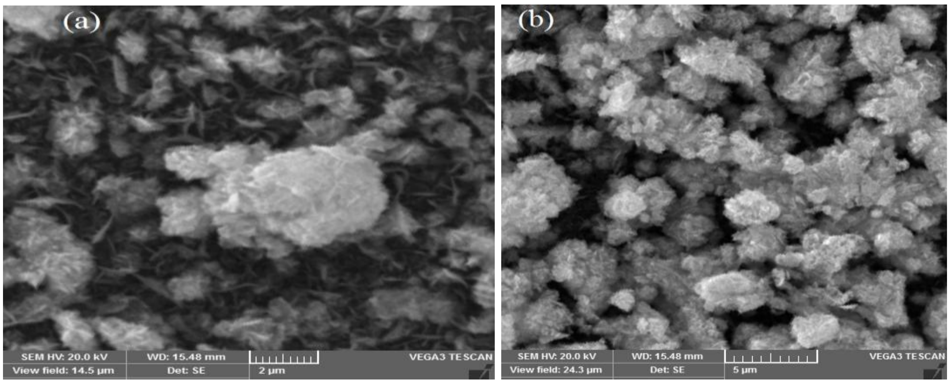

Fig.8 FESEM as-deposited $ZnIn_2S_4$ (ZIS) thin film with diffenet magnification such as (a)2µm,(b)5µm.

Fig 8 (a and b) shows the FESEM images of as deposited ZIS thin films at different magnifications. The as-deposited ZIS thin film without cracks or pinholes and well covers in the glass substrate. $ZnIn_2S_4$ as deposited film shows the rulles dollops morphlogy which agree with Zhixin Chen et al [30].

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(D) PHOTOLUMINANCE STUDY

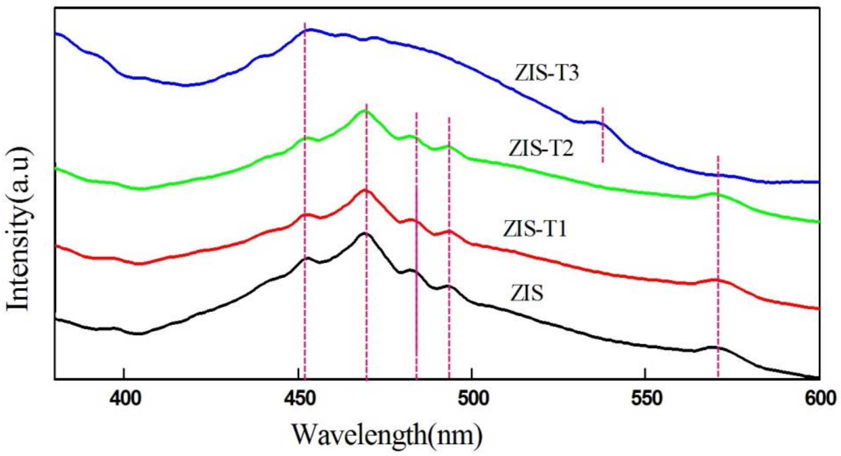

Fig.9 PL Spectrum of the of the as-deposited and annealed ZIS film

The emission spectrum was engaged to study the surface structure and excited states. Fig.9 shows the Photoluminescence spectra of $ZnIn_2S_4$ thin film as-deposited and annealed samples (ZIS, ZIS-T1, ZIS-T2 and ZIS-T3). For the as-deposited and annealed film (ZIS-T1, ZIS-T2) pl spectrum consists of five emission bands appeared at 452 nm, 484 nm, 493 nm, 537 nm and 570 nm respectively. The PL spectrum of as-deposited (ZIS) and annealed film (ZIS-T1, ZIS-T2) consists of strong emission band at ~470 nm. The peak intensity was gradually decreases with increasing in the annealing temperature. Disappearance of the peak was observed for (ZIS-T3) spectrum annealed at 550°C. The emission peak intensity at 570 nm was blue shifted to 537 nm.

III. CONCLUSION

ZIS as-deposited and annealed films deposited using nebulized spray pyrolysis method. The XRD shows all ZIS as-deposited and annealed film exhibited hexagonal phase. UV-Vis -NIR spectrum shows the maximum transparency of which is nearly 88% for annealed film (ZIS-T5).Absorption edge was found to be 536 nm and 525 nm, 498nm and 441nm for ZIS ,ZIS-T1, ZIS-T2 and ZIS-T3 films. Band gap (Eg) values for ZIS, ZIS-T1, ZIS-T2, ZIS-T3 thin films value estimated to be 2.79 eV, 2.89 eV, 2.94 eV and 3.3eV respectively. Using FESEM image shows the as-deposited ZIS ($ZnIn_2S_4$) film shows the rulles dollops. Composition of the film closed to the stoichiometric value. In PL studies strong emission peak was observed at ~470 nm was observed for as-deposited (ZIS) and annealed films (ZIS-T1, ZIS-T2).

REFERENCES

[1] Shunji Ozaki and Sadao Adachi, Optical properties and electronic band structure of $ZnIn_2Te_4$, Physical Review B, 64, 085208-1-085208-7, 2001.

[2] Biao Xu, Peilei He, Huiling Liu, Pengpeng Wang, Gang Zhou, and Xun Wang, Angew. A 1D/2D Helical CdS/ZnIn2S4 Nano-Heterostructure, Chem. Int. Ed. 53, 1–6, 2014.

[3] O. Vigil, O. Calzadilla, D. Seuret, J. Vidal , $Znln_2S_4$ As a Window In Heterojunction Solar Cells, Solar Energy Materials, 10, 139-143, 1984.

[4] Hiroshi Deguchi, Hiroshi Miura, Kazuaki Tsuji, and Hajime Yuzurihara, ZnInS Thin Film Solar Cell Fabricated by Sputtering Process , Japanese Journal of Applied Physics , 51 , 10 NC37-1-10 NC37-4, 2012.

[5] A Serpi, Trap distribution in $ZnIn_2S_4$ from photoconductivity analysis, J. Phys. D: Appl. Phys., 9, 1881-1892, 1976.

[6] 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., 40, 2607-2613, 2011.

[7] Jianbo Yin, Junhong Jia,Gewen Yi and Liqiang Wang, Preparation of $ZnIn_2S_4$ Film Electrodes by the SILAR Technique, J. Chin. Chem. Soc. *59*, 1365-1368, 2012.

[8]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. 128, 7222-7229, 2006.

[9] YUAN Wen-Hui, LIU Xiao-Chen,LI Li, Improving Photocatalytic Performance for Hydrogen Generation over Co-Doped $ZnIn_2S_4$ under Visible Light, Acta Phys. - Chim. Sin. 29 (1), 151-156, 2013.

[10] Yuexiang Li , Jianxia Wang, Shaoqin Peng , Gongxuan Lu , Shuben Li, Photocatalytic hydrogen generation in the presence of glucose over ZnS-coated $ZnIn_2S_4$ under visible light radiation, international journal of hydrogen energy , 35, 7116-7126, 2010.

[11] Lily Mandal, Nilima S. Chaudhari, and Satishchandra Ogale, Self-Powered UV-vis Photodetector Based on ZnIn2S4/Hydrogel Interface, ACS Appl. Mater. Interfaces, 5, 9141−9147, 2013.

[12] Wen-Juan Fan , Zheng-Fa Zhou , Wei-Bing Xu , Zhi-Feng Shi , Feng-Mei Ren ,Hai-Hong Ma, Shuang-Wu Huang, Preparation of $ZnIn_2S_4$/fluoropolymer fiber composites and its photocatalytic H_2 evolution from splitting of water using Xe lamp irradiation ,international journal of hydrogen energy , 35, 6525-6530, 2010.

[13] Zhibin Lei, Wansheng You, Meiying Liu, Guohua Zhou,Tuyoshi Takata, Michikazu Hara,Kazunari Domen and Can Li, Photocatalytic water reduction under visible light on a novel $ZnIn_2S_4$ catalyst synthesized by hydrothermal method , CHEM. COMMUN , 2142–2143, 2003.

[14] 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, 24, 7599-7604, 2008.

[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, 186,247–254, 2012.

[16] Kong-Wei Cheng, Chia-JuiLiang, Preparation of Zn–In–S film electrodes using chemical bath deposition for photoelectrochemical applications, Solar Energy Materials & Solar Cells 94, 1137–1145, 2010.

[17] 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, 184, 2250–2256, 2011.

[18] 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, 265 , 62-66,2014.

[19] 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, 3,8909-8914, 2013.

[20] Ryoaki Nomura, Haruo Matsuda, Takashi Miyai, Akio Baba, Growth of spinel zinc thioindionate thin film by single-source MOCVD, Thin Solid Films , 342, 108-112, 1999.

[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, Summer-Fall, 5(2), 79-86, 2011.

[22]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 33, 2891-2896, 2008.

[23] 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, 31(1), 01A131-1-01A131-6, 2013.

[24]Pascal Genevee, Frederique Donsanti, Gilles Renou, and Daniel Lincot, Study of Growth Mechanism and Properties of Zinc Indium Sulfide Thin Films Deposited by Atomic Layer Chemical Vapor Deposition over the Entire Range of composition, J. Phys. Chem. C, 115, 17197–17205, 2011.

[25] 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. 128, 7222-7229, 2006.

[26] Dengwei Jing, Maochang Liu, Liejin Guo , Enhanced Hydrogen Production from Water over Ni Doped $ZnIn_2S_4$ Microsphere Photocatalysts , Catal Lett, 140,167–171, 2010.

[27] Shaohua Shen, Liang Zhao, Liejin Guo, Morphology, structure and photocatalytic performance of $ZnIn_2S_4$ synthesized via a solvothermal/hydrothermal route in different solvents , Journal of Physics and Chemistry of Solids, 69, 2426– 2432, 2008.

[28] YianXie, Facile solution based fabrication of ZNIn2S4 nanocrystalline thin films and their photoelectrochemical properties, Journal of power science 265,62-66, 2014.

[29] S.A. Lopez-Rlvera, L. Martinez, B. Fontal, W. Giriat, F. Medina, Raman study of a ZnInS, layered compound, Semicond. Sci.Technol. 10, 645-652, 1995.

[30] Zhixin Chen, Low-Temperature and Template-Free Synthesis of $ZnIn_2S_4$ Microspheres, Inorg. Chem. 47, 9766-9772, 2008.