

ONE STEP ELECTROCHEMICAL DEPOSITION OF CZTS FOR SOLAR CELL APPLICATIONS

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Single step electrodeposition of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) on indium tin oxide (ITO) substrate at different pH was studied. The deposition potentials were found to move in the anodic direction with increase in pH of the electrolyte. X-ray diffraction analysis of the samples showed that the films formed at pH 1.55 were of decreased crystallinity whereas pH 2.5 and 5 showed the presence of crystalline kesterite phase particles. The size of the particles forming the film was found to increase with pH. UV-vis spectroscopy results revealed that the particles had a band gap energy in the range of 1.5- 1.7 eV. Scanning electron microscopy analysis of the deposits showed that the deposits formed at pH 2.5 consist of uniformly sized particles. The elemental composition by energy dispersive analysis of X-rays showed that the deposits formed at pH 2.5 are closer to the required stoichiometry of 2:1:1:4. The IV characterization studies showed that the resistance of the deposits increases with increase in pH.

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1. Introduction

With the gradual increase in the global energy demand and the shortage of the available conventional energy sources, focus on the use of other renewable energy sources such as solar energy and wind energy have increased [1]. A solar cell uses photovoltaic effect to convert the light energy to electrical energy. Majority of the solar cells in use today are single crystal silicon type which offers a conversion efficiency of 15 to 20%. The main drawbacks of the single crystal silicon type of photovoltaic (PV) cells are that they are expensive and tend to break easily. Use of polycrystalline silicon for photovoltaics is cost effective and also gives stronger cells but the conversion efficiency is about 10 to 14% [1]. Thin film solar cells have gained attention in recent years because extremely thin films can be obtained by this method at much less fabrication cost. However, they suffer from the disadvantage of low conversion efficiency [2, 3]. Among the thin films studied for use in photovoltaic cells, amorphous silicon, cadmium telluride (CdTe) and copper indium diselenide (CuInSe_2) are important [2,3]. However, Cd is toxic and the production of CuInSe_2 involves the liberation of extremely toxic hydrogen selenide. As a solution to these problems the study on the use of copper, zinc, tin and sulphur (CZTS) thin films for photovoltaic application has gained popularity. Copper zinc tin sulfide commonly known as CZTS is one of the ideal alternatives with a band gap of 1.4-1.5eV and absorption co-efficient 10^4 cm^{-1} [4]. The fabrication of CZTS thin films does not involve the liberation of any toxic gas and the raw materials involved are abundant on earth [4].

Generally one of the two methods, viz. vacuum and non vacuum techniques, is used for CZTS deposition. The vacuum techniques include sputtering and evaporation deposition. The non vacuum techniques are spray pyrolysis, spin coating of precursor solution and electrochemical deposition [5]. Electrochemical methods are preferred when compared to other techniques because they can be conducted at room temperature and pressure and also has the advantage of better material utilization [5]. Sequential electrodeposition of CZT followed by sulfurization has been reported which claims a device efficiency of 3.2% [6]. Single step electrodeposition of CZT followed by sulfurization to form CZTS layer has been reported which on its application to fabricate the device resulted in an efficiency of 3.4% [7].

Electrochemical deposition of CZT using ionic liquids and subsequent sulfurization has been reported which resulted in a CZTS layer of 10^4 cm^{-1} absorption coefficient [4]. Most of the works on electrodeposition of CZTS use sulfurization at high or moderate temperatures in the range of 350 °C to 450 °C to incorporate sulfur which resulted in volumetric expansion during annealing. Thus incorporating sulfur during electrodeposition is preferred to overcome these issues [8]. One of the major issues in single step electrodeposition of CZTS is the significant difference in the reduction potentials of the elements Cu, Zn, Sn and S. Single step electrodeposition thus involves use of suitable complexing agent which have the ability to bring the reduction potentials closer by their binding activity [9]. Single step electrodeposition of CZTS has gained interest which enables deposition of CZTS in a single step using tartaric acid and trisodium citrate as complexing agents [8]. Further single step electrodeposition of CZTS at -1.05 V accompanied by high temperature annealing in sulfur environment has been reported to yield copper rich and sulfur deficient compositions [10]. Pulsed

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electrodeposition of CZTS has been reported to yield a good quality deposit of 1.5 eV band gap energy [11]. Co-electrodeposition of CZTS using eutectic solvent Reline as green electrolyte has also been reported [12]. This work reports single step electrodeposition of CZTS using sodium thiocyanate based electrolyte at three different pH. The CZTS deposit thus obtained was analyzed using UV-vis spectroscopy for optical properties, X-ray diffraction for crystalline nature characterization. The morphology and atomic ratio of the deposits were studied using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The samples were also characterized using Fourier transform Raman spectroscopy. The electrical characteristics were studied using IV characterization technique.

2. Experimental

CZTS thin film were electrodeposited using an electrolytic solution containing copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), tin chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and sodium thiosulphate pentahydrate ($\text{Na}_2\text{S}_3\text{O}_8 \cdot 5\text{H}_2\text{O}$) as precursors of Cu, Zn, Sn and S respectively. Sodium thiocyanate (NaSCN) was used as complexing agent. All the chemicals used were of analytical grade (supplied by Merck & Lobachem). Deionized water was used for preparing the solutions. The electrolyte was prepared from 20 mM of CuSO_4 , ZnSO_4 , SnCl_2 and $\text{Na}_2\text{S}_3\text{O}_8$ each. Sodium thiocyanate of 2.5M concentration was used as the complexing agent. The deposition experiments were conducted in CHI 6091E (CH instruments, USA). A three electrode cell was used with Ag/AgCl reference electrode and a platinum wire counter electrode. Working electrode was indium tin oxide (ITO) coated glass slide (Sigma Aldrich, India). Before the experiment, ITO coated slides were washed with deionized water, acetone and isopropanol and dried. The pH of the electrolyte was adjusted using 1M KOH solution or dilute HNO_3 solution. To fix the deposition potential, initially cyclic voltammetry runs were performed. Cyclic voltammetry (CV) were run for individual precursors with and without complexing agent to study their deposition potential. The CV runs were run from 1 to -1.2 V vs. Ag/AgCl. The scan was started at 1V, reversed at -1.2 V and completed at 1 V. A scan rate of 0.05 V s^{-1} was used. Once the deposition potential was found out from the CV the deposition was carried out by performing bulk electrolysis with coulometry at constant potential for 15 min. The deposit thus obtained was washed with deionized water and dried. The dried samples were annealed at 300°C for 30 min.

The morphology and chemical composition of the samples deposited at different pH conditions were analyzed using scanning electron microscopy (ZEISS EVO Series- Model EVO 18) and energy dispersive X-rays (INCA 250 EDS WITH X-MAX 20 mm detector) respectively. The crystalline nature of the samples was analyzed using PANalytical 3 kW X'pert X-ray diffraction unit. Raman spectroscopy was performed in Bruker RFS 27: Stand alone FT-Raman Spectrometer. UV-vis spectroscopy studies were conducted using Shimadzu, UV-1800 spectrophotometer. The IV characterization studies were performed using CHI 6091E (CH instrument U.S.A.) electrochemical work station.

3. Results and discussion

3.1 Cyclic voltammetry

Figs. 1a and b show the CV plots of the individual precursors with 2.5M NaSCN at pH 2.5. Fig.1a also shows the CV for the electrolyte containing all four CZTS precursors along with NaSCN at pH 2.5. It is seen from Fig.1a and b that the cathodic peak potentials for Cu^{2+} , Zn^{2+} , Sn^{2+} and S^{2-} ions reduction were observed at -0.95 V, -1.35 V, -0.99 V and -1.11 V respectively. The difference in the deposition potential of the individual ions range from 57 to 368 mV. From Fig 1a, the cathodic peak potential for the combined precursor solution at the same pH was found to be at -0.989 V. Fig 2 shows the CV for the electrolyte with all precursors in 2.5M NaSCN at pH 1.55, 2.5 and 5 respectively. The peak positions are -0.99 V, -0.915 V and -0.892 V respectively. The deposition potentials were found to move towards right with increase in pH.

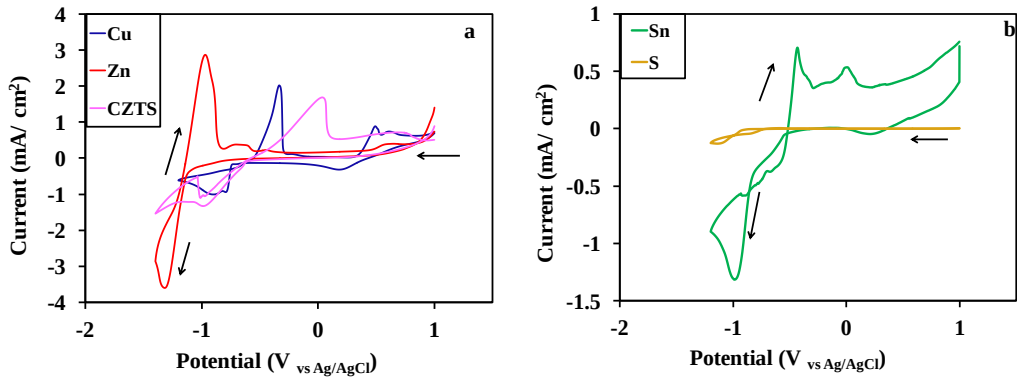


Fig. 1. Cyclic voltammetry plots at pH 2.5 for a) 20mM Cu precursor in 2.5M NaSCN, 20 mM Zn precursor in 2.5M NaSCN and combined CZTS precursors in 2.5M NaSCN b) 20mM Sn precursor in 2.5M NaSCN, 20 mM S precursor in 2.5M NaSCN

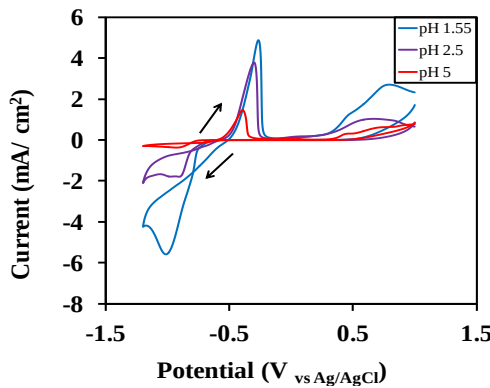


Fig. 2 Cyclic voltammetry plots for CZTS precursors at different pH

3.2 UV- vis spectroscopy

Fig. 3 shows the Tauc plots for the CZTS deposits prepared at pH 1.55, 2.5 and 5 respectively. The Tauc plots were obtained from analysis of the optical absorption spectra of the samples from 200 nm to 1100 nm. The band gap of the deposits was calculated using the relation in equation 1[6]

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (1)$$

where α is absorption coefficient, E_g is the band gap energy in eV, $h\nu$ is photon energy (E) and n is constant which takes the value 2, 3, 1/2 and 3/2 indirect allowed, indirect forbidden, direct allowed and direct forbidden respectively [6]. If the plot of $(\alpha E)^2$ vs. photon energy (E) is linear then it is directly allowed transition [6]. In Fig. 3, the straight line portions of the Tauc plots are extrapolated to zero absorption coefficient which gives the intercepts or bandgap values. The band gap values for the deposits prepared at pH 1.55, 2.5 and 5 are 1.75, 1.5 and 1.7 eV respectively. It is observed that the band gap values match well with the reported values [12-16].

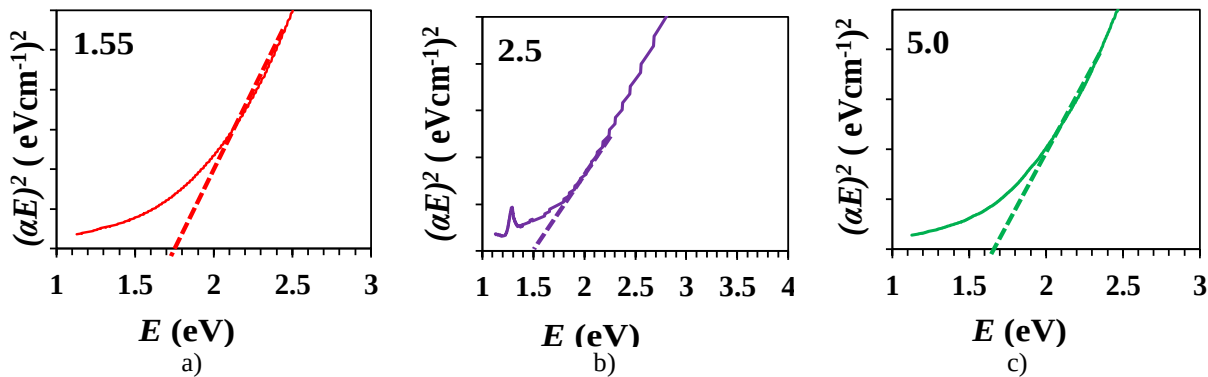


Fig. 3. Tauc plots for the CZTS deposits prepared at different pH
a) pH=1.55, b)pH=2.5, c)pH=5.0

3.3 X-Ray diffraction and FT-Raman spectroscopy studies

Fig. 4 shows the XRD spectra of the CZTS thin films deposited at pH 1.55, 2.5 and 5 respectively. It is clearly seen that the films synthesized at different pH differ significantly. The nature of the film synthesized at pH 1.55 was found to be less crystalline when compared to other samples.

The peaks at 2θ values 23.15° , 28.5° , 29.6° , 32.9° , 47.3° and 56.1° are attributed to the kesterite phase CZTS [17, 18]. The increased peak intensities of the samples deposited at pH 2.5 and 5 indicate the presence of more crystalline particles in the deposits [19]. The mean crystallite size (d) of the deposits was calculated from Scherrer's formula given in equation 2 [20].

$$d = \frac{0.9\lambda}{\beta_{1/2} \cos \theta} \tag{2}$$

where λ is the wavelength of Cu-K α radiation ($1.540 \text{ \AA}$), $\beta_{1/2}$ is the line width at half of the maximum peak intensity on a 2θ scale and θ is the position of peak maximum [21]. The crystallite size of the CZTS deposits formed at pH 2.5 and 5 were calculated to be 69 nm and 70 nm respectively. The results of XRD analysis were further confirmed with the FT Raman spectroscopy results. Fig.5 shows the Raman spectroscopy results of the deposit synthesized at pH 2.5. The peaks at 257 cm^{-1} , 288 cm^{-1} and 333 cm^{-1} correspond to CZTS which confirm the results obtained from XRD studies [22].

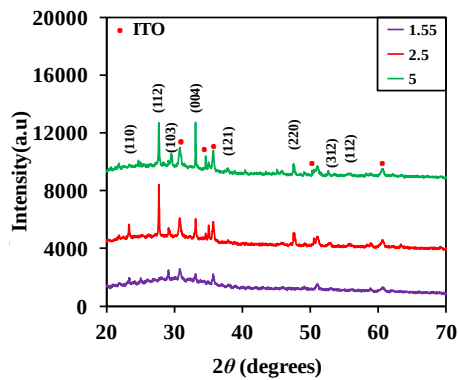


Fig. 4. X-ray diffraction pattern of the CZTS deposits prepared at different pH

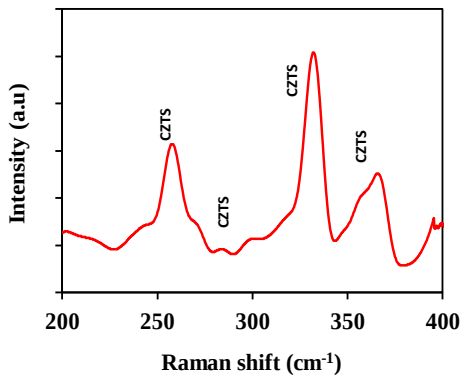


Fig. 5. FT Raman spectroscopy studies of the CZTS deposit electrodeposited at pH 2.5

3.4 Scanning electron microscopy (SEM)
Fig. 6 shows the SEM images of the CZTS deposits prepared at different pH conditions. It is clearly seen that the morphology of the deposits prepared at different pH conditions differ significantly. The deposit prepared at pH 2.5 consists of densely packed structure when compared to the deposits formed at other pH. Table 1 shows the elemental composition of the deposits from EDAX analysis. It is seen that the samples deposited at pH 2.5 are closer to stoichiometric composition. The other pH conditions resulted in sulfur rich deposits.

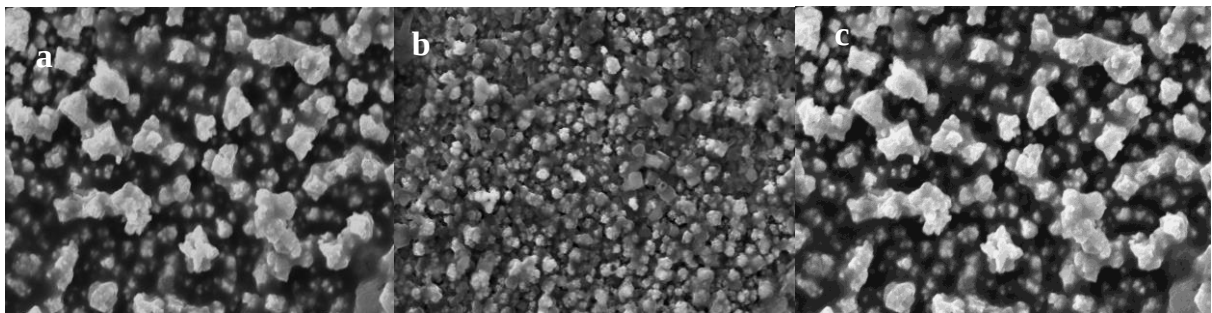


Fig. 6. Scanning electron microscopy images of the CZTS deposits prepared at a) pH=1.55 b) pH=2.5 c) pH=5

Table 1. Elemental composition of the deposits prepared at different pH of the electrolyte (in atomic %)

pH Element	1.55	2.5	5
S K	66.02	56.09	75.23
Cu K	11.07	28.36	13.04
Zn K	12.58	10.40	6.36
Sn L	10.33	5.15	5.37
Total	100.00	100.00	100.00

3.5 IV characterization

The IV characteristics of ITO/CZTS/ITO system in the presence and absence of 200 W incandescent light source using the CZTS deposits formed at different pH are shown in Fig. 7. The IV curves are linear which indicate the ohmic nature of the deposits with contacts [22,23]. The resistance of the deposits in the presence of light source presented significant decrease which indicates that the deposits are suitable for solar cell applications. The resistance of the deposits was found to be in the range of 40 Ω to 100 Ω in the presence of light source. The resistance of the samples was found to increase with increase in pH of the medium.

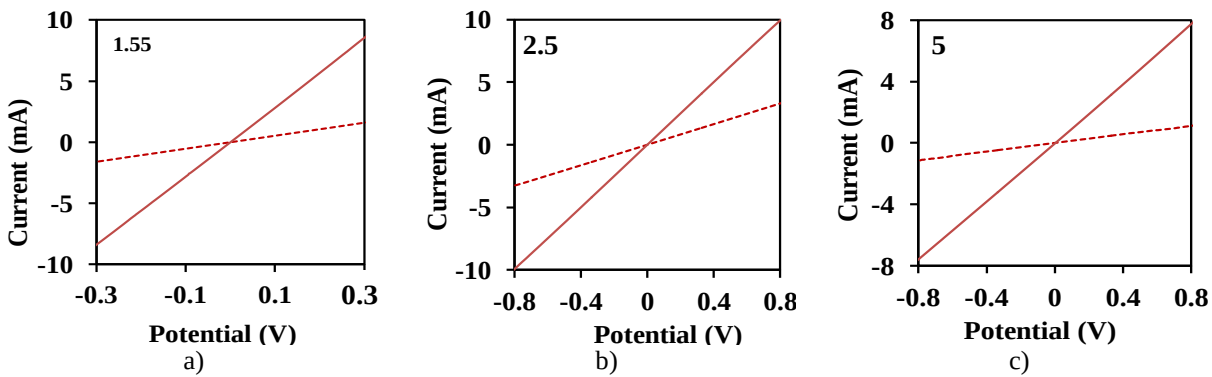


Fig. 7. IV characteristics of ITO/CZTS/ITO deposits prepared at different pH
a) pH=1.55, b)pH=2.5, c)pH=5

4. Conclusions

Single step electrodeposition of CZTS on ITO substrate using sodium thiocyanate as complexing agent for solar cell applications has been studied. The pH of the electrolyte was found to influence the properties of the deposits significantly.

The CZTS deposit prepared at pH 2.5 was found to have the composition closer to the required stoichiometry of 2:1:1:4. The XRD studies showed that the deposits formed at pH 1.55 were of low crystalline nature when compared to other samples. The XRD studies also indicated the formation of kesterite phase CZTS in the deposits. The band gap of the samples was calculated to be in the range from 1.5 eV to 1.7 eV.

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References

[1] N. Asim, K. Sopian, S. Ahmadi, K.Saeedfar, A.A. Alghoul, O. Saadatian, S. Zaidi, Renew. Sust. Energ. Rev. **16**, 5834 (2012).
[2] B.R. Sankapal, R.S. Mane, C.D. Lokhande, Mater. Res. Bull. **35**, 177 (2000).
[3] N. Khare, J. Power Sources **24**, 121 (1988).
[4] K. Tanaka, N. Moritake, H. Uchiki, Sol. Energ. Mat. Sol. **C 91**, 1199 (2007).
[5] H. Wang, Int. J. Photoenergy **801292**, 1(2011).
[6] J.J. Scragg, P.J. Dale, L.M. Peter, Electrochem. Comm. **10**, 639 (2008).
[7] A. Ennaoui, M. Lux-Steiner, A. Weber, D. Abou-Ras, I. Kötschau, H.-W. Schock, R. Schurr, A. Hölzing, S. Jost, R. Hock, T. Vo, J. Schulze, A. Kirbs, Thin Solid Films **517**, 2511 (2009).
[8] S.M. Pawar, B.S. Pawar, A.V. Moholkar, D.S. Choi, J.H. Yun, J.H. Moon, S.S. Kolekar, J.H. Kim, Electrochim. Acta **55**, 4057 (2010).
[9] J.J.M. Jebaraj, D.H. Rasmussen, I.I. Suni, J. Electrochem. Soc. **158**, D54 (2011).

- [10] K.V. Gurav, J.H. Yun, S.M. Pawar, S.W. Shin, M.P. Suryawanshi, Y.K. Kim, G.L. Agawane, P.S. Patil, J.H. Kim, Mater. Lett. **108**, 316 (2013).
- [11] S.G. Lee, J. Kim, H.S. Woo, Y. Jo, A.I. Inamdar, S.M. Pawar, H.S. Kim, W. Jung, H.S. Im, Curr. Appl. Phys. **14**, 254 (2014).
- [12] H. Chen, Q. Ye, X. He, J. Ding, Y. Zhang, J. Han, J. Liu, C. Liao, J. Mei, W. Lau, Green Chem. **16**, 3841 (2014).
- [13] H. Deligianni, L. Guo, R. Vaidyanathan **US 2012/0048378 A1** (2012).
- [14] P.K. Sarswat, M. Snure, M.L. Free, A. Tiwari, Thin Solid Films **520**, 1694 (2012).
- [15] K. Holger, S. Jorg, V. Torsten **EP2032743 B1** (2010).
- [16] H. Katagiri, K. Jimbo, W.S. Maw, K. Oishi, M. Yamazaki, H. Araki, A. Takeuchi, Thin Solid Films **517**, 2455 (2009).
- [17] S.R. Kodigala, Thin film solar cells from earth abundant materials: Growth and earth abundant Materials, Elsevier, London (2014).
- [18] W. Wei, S.H. Lie, J. Jia-Le, L.J. Ze, M. Yue, Chin. Phys. B **24(5)**, 056805 (2015).
- [19] S. Chen, A. Xu, J. Tao, H. Tao, Y. Shen, L. Zhu, J. Jiang, T.Wang, L.Pan, ACS Sustainable Chem. Eng. **3(11)**, 2652 (2015).
- [20] X. Jin, J. Li, G. Chen, C. Xue, W. Liu, C. Zhu, Sol. Energ. Mater. Sol. Cells **146**, 16 (2016).
- [21] A. Singh, R. Manivannan, S.N. Victoria, Arabian J. Chem. DOI: 10.1016/j.arabjc.2015.03.013 (2015).
- [22] M. Jiang, Y. Li, R. Dhakal, P. Thapaliya, M. Mastro, J.D. Caldwell, F. Kub, X. Yan, J. Photon. Energy **1(1)**, 019501 (2011).
- [23] B. Ananthoju, A. Kushwaha, F.J. Sonia, M. Aslam, AIP Conf. Proc. **1512**, 706 (2013).