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Surface Morphological Studies of Solar Absorber Layer Cu_2ZnSnS_4 (CZTS) Thin Films by Non-vacuum Deposition Methods

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The consumption of fossil fuel globally has been enormous and has reached an alarming rate resulting in fast depletion of the available resources and at the same time polluting the environment. Hence there is a growing need to take cognizance of abundant amount of inexpensive energy available in the nature especially solar energy. Development and commercialization of Photovoltaics has been in focus due to its low cost, high absorption coefficient and suitable direct band gap for solar energy conversion applications. An attempt has been made in this work to synthesize the CZTS thin films by Electro deposition and Sol-gel method on Indium Tin Oxide (ITO) glass and Soda Lime Glass(SLG) substrates respectively. CZTS thin films have been prepared using a 3-stage electro chemical system wherein the precursors are deposited using platinum foil as a counter electrode and AgCl electrode as a reference electrode and Sol gel method. Surface morphology and optical properties have been studied using Atomic Force Microscopy, Scanning Electron Microscopy, X-ray Diffractometer and UV-Vis Spectroscopy

Keywords: CZTS, Thin film photovoltaics (PV's) electro deposition, Surface morphological studies.

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1. INTRODUCTION

The use of thin film Photo Voltaic (PV) devices for solar energy applications is rapidly increasing. The efficiencies obtained by employing different thin films like CIGS [$Cu(In,Ga)S_2$] and CIGSe [$Cu(In, Ga)Se_2$], CuInSe (CIS), CdTe have already reached their optimum levels [1]. Also they contain rare materials like indium and gallium which are expensive and toxic [2]. The CZTS is a kesterite quaternary semiconductor which contains elements that are not toxic and are abundantly available on earth. In addition, it has an appropriate optical band gap ~ 1.50 eV and absorption coefficient of 104 cm^{-1} for solar cell applications [3]. Due to this, $Cu_2ZnSnSe_4$ (CZTSe), Cu_2ZnSnS_4 (CZTS) solar absorbers have gained attention for their potential application in non silicon based Photovoltaic cells [4]. It has been mentioned in literature that the CZTS solar absorbers which were synthesized using different methods such as thermal evaporation, sputtering technique and electrodepostion have found to have reached an efficiency of 5.4 %, 6.7 % and 7.2 % by evaporation, sputtering and electrodepostion respectively [5, 6, 7]. Even though electronic structure of the $Cu_2ZnSn(S, Se)_4$ material system has been investigated theoretically, there is still enough scope to improve the structure by carrying out experimental investigation [7]. An attempt has been made in this study to improve the surface morphology of CZTS thin films. Among all the above mentioned preparation techniques, sol-gel and electrodepostion possess advantages like low cost and uniform coatings. These methods are very simple and without requiring any vacuum system. The main objective of this work has been to show the possibility of sol-gel and electrodeposition of Cu–Zn–Sn alloy followed by Sulphur as precursor layers and their subsequent annealing in N_2 atmosphere. These films have been analyzed using Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM), X-Ray Diffractometer and UV-Visible Spectroscopy.

2. EXPERIMENTAL SECTION

While carrying out this work the following materials viz., Copper (II) Sulfate Pentahydrate ($CuSO_4 \cdot 5H_2O$), Zinc Sulfate Hepthahydrate ($ZnSO_4 \cdot 7H_2O$), Tin Sulfate ($SnSO_4$) and Sodium Thiosulfate ($Na_2S_2O_3$), Tri-sodium Citrate ($C_6H_5Na_3O_7$) which are of analytical grade have been considered. The materials pertaining to this study have been procured from Sigma Aldrich and Rankem Chemicals. An attempt has been made in the study to electro deposit a thin film of CZTS on ITO coated glass substrates using a cyclic voltammetry (CV) of CH instruments USA make.

The cyclic voltametry having a three electrode configuration has been employed in experiments to obtain an optimum potential for the deposition of CZTS thin film with potentiostatic. The electrochemical cell contains a saturated Ag / AgCl electrode as reference electrode, platinum (Pt) electrode as inert counter electrode and ITO-coated glass substrate with a deposition area of 2 × 2 square cm was used as working electrode. The CZTS thin films have been prepared from aqueous electrolytic bath containing copper (II) sulfate pentahydrate, zinc sulfate hepthahydrate, tin sulfate have been used. Tri-sodium citrate has been used for the complexing agent to dissolve the solvents completely at room temperature. After obtaining clear solution filtered using whatman filter paper (2 μm size) to remove the impurities. The deposition time

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is 15 minutes The Cyclic voltametry (CV) Curve as shown figure 1. The sulfurization has been carried out separately by mixing of Sodium Thiosulfate (0.02 M) in aqueous solution after deposition of CZT for 10 minutes and Hydro Choric acid (HCl) has been used as pH control solution to get a pH concentration of 5. The applied potential of CZT and sulfarization is 0 to – 1.5 V [8].

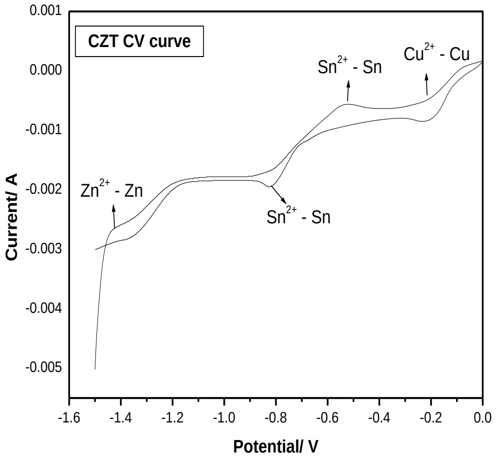


Fig. 1 – CV curve of CZTS solar absorber

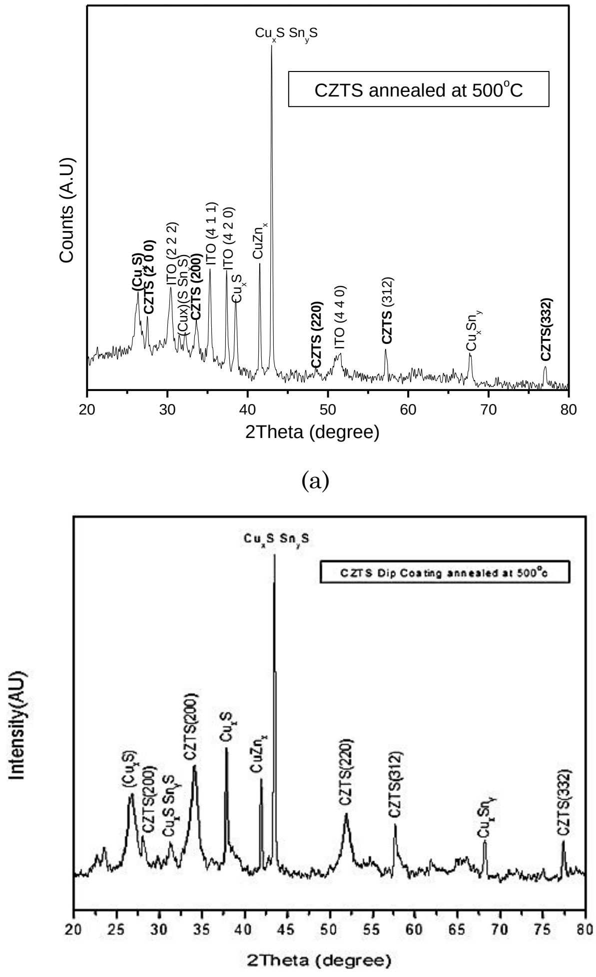
Sol-gel coating was performed at room temperature using Dip coating technique. Soda lime glass (SLG) substrates were used as a substrate base for CZTS growth. The stoichiometry of sol solution was optimized by variation of individual metallic species concentrations. The Dip coating was carried out using a sol solution of copper (II) acetate monohydrate, zinc (II) acetate dihydrate, and tin (II) chloride dihydrate which are of analytical grade have been considered. Monoethanolamine (≈ 5 ml) is used as stabilizer [9]. The materials pertaining to this study have been procured from Sigma Aldrich and Rankem Chemicals. The precursors were dissolved in 25 ml of 2-methoxyethanol. For Dip coating the SLG substrate was dipped in the sol solution and taken out at uniform speed and dried at 200 °C. The coating process was repeated four times to obtain the desired thickness of film. It was observed that the film coated more than four layers were peeled off after annealing. This is because the adhesive strength between substrate and film decreases with increase in thickness. The annealing of Sol gel coated dried films were carried out at a temperature of 500 °C for 1 hour.

3. CHARACTERIZATION OF CZTS SOLAR ABSORBER

The obtained films were characterized by D2 Phaser X-ray Diffracotmeter from Bruker Axs, Germany for Phase transitions, Desktop Scanning Electron Micrsocope from Phenom, Netherlands and Atomic Force Microscope from park Systems, South Korea for Surface Morphological studies. The Preliminary results are in well agreement with the established reports

3.1 Structural Characterization

The CZTS thin films prepared by Electrodeposition and Sol-gel method are annealed at 500 °C for one hour in vacuum furnace to get Crystallinity Sturcuture. Figure 2a show X-rd peaks CZTS thin film prepared by Electrodepostion. It can be observed that crystallanity has been formed after annealing. The structural property of CZTS thin films have been analyzed using XRD measurement with 2 theta scanning from 20° to 80°. It is observed that all the XRD patterns consist of (112), (200), (220), (311) and (332) diffraction peaks corresponding to different crystallographic planes of Cu_2ZnSnS_4 suggesting that the films are polycrystalline with kesterite crystal structure. The diffraction peaks of (411), (420), (440) corresponding to crystallographic planes of ITO. These results are in agreement with reported literature [4, 9, and 10]. Furthermore, some metal sulfide and other secondary phases, such as Cu_xS, SnS_x and Cu_xSn_y, have also been detected. These secondary phases are often observed in CZTS thin films are copper-rich chalcopyrite structure [11-13]. Fig. 2b shows X-rd peaks of CZTS by Sol gel dip coating. It can be observed that crystallinity has been formed after annealing. The structural property of CZTS thin films have been analysed using XRD measurement with 2 theta scanning from 20° to 80°. It is observed that all the XRD patterns consist of (200), (220), (311) and (332) diffraction peaks correspond-



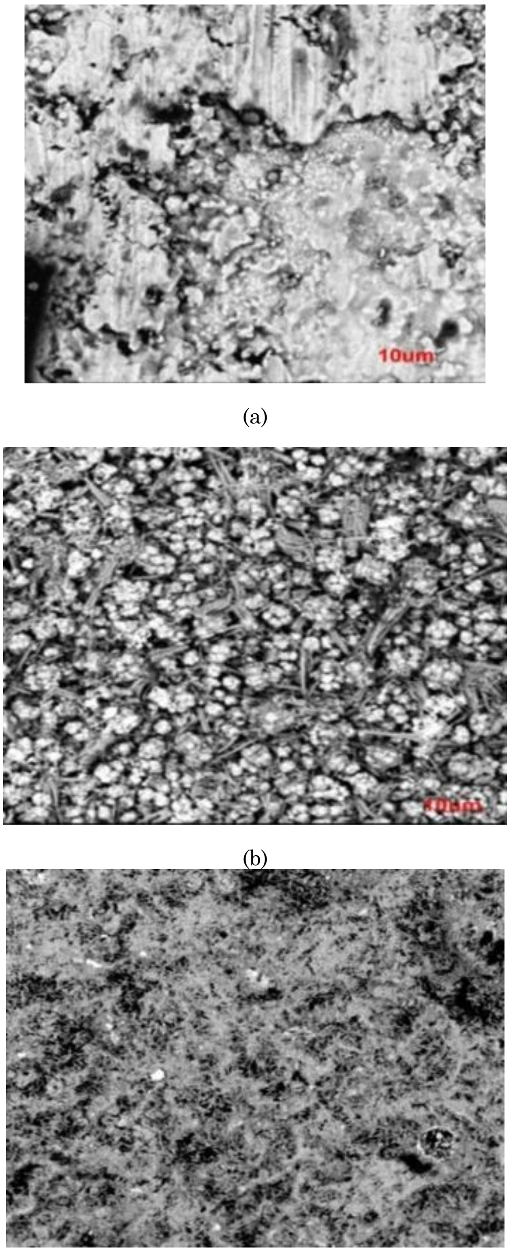
(a)

(b)

Fig 2 – X-rd patterns of CZTS thin film by electrodepositon (a) and Sol gel synthesi (b) ing to different crystallographic planes of Cu_2ZnSnS_4 suggesting that the films are polycrystalline with kesterite crystal structure. These results are in agreement with reported literature [11-13]. Furthermore, some metal sulfide and other secondary phases, such as Cu_xS, SnS_x and Cu_xSn_y, have also been detected. These secondary phases are often observed in CZTS thin films are copper-rich chalcopyrite structure.

3.2 Morphological Characterization

The morphology of electrodeposited metal layer and sol-gel approach is crucial for producing smooth dense CZTS films. Figures 3a and b show SEM micrographs of CZTS before and after annealing respectively. At higher magnification of the image, two distinct gain structures viz., spherical and fiber are observed. The average grain size is found to be 0.8 μm ± 0.4 μm for spherical grains and 2.5 ± 0.5 μm × 0.2 ± 0.1 μm for fiber grains which is in agreement with the reported literature [14]. Fig. 3c shows SEM micrographs of CZTS after annealing by sol-gel. However, the film appears to be quite dense with few voids and a highly interconnected network of grains. It is necessary to produce such dense films with good interconnection between grains for high performance photovoltaic devices [15].

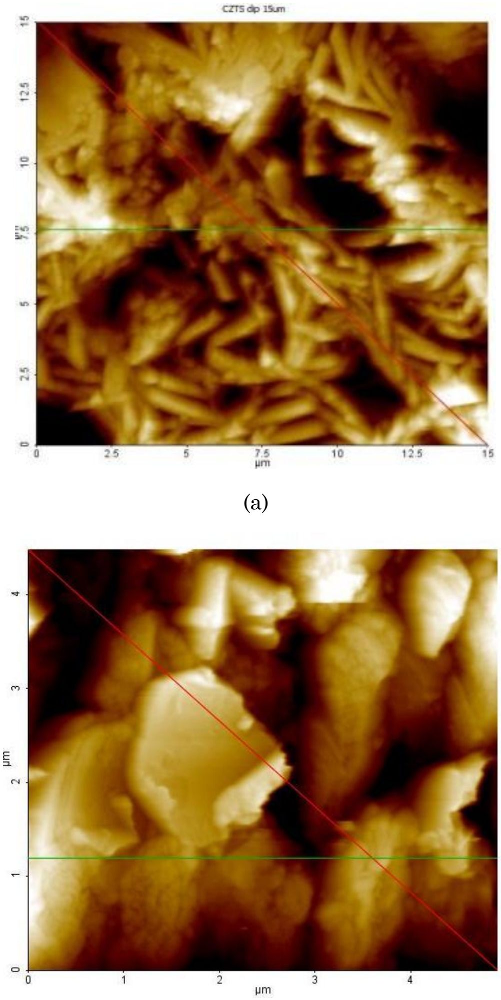


(a)

(b)

(c)

Fig. 3 – a – before annealing; b – after annealing by Electro deposition; c – after annealing by sol-gel



(a)

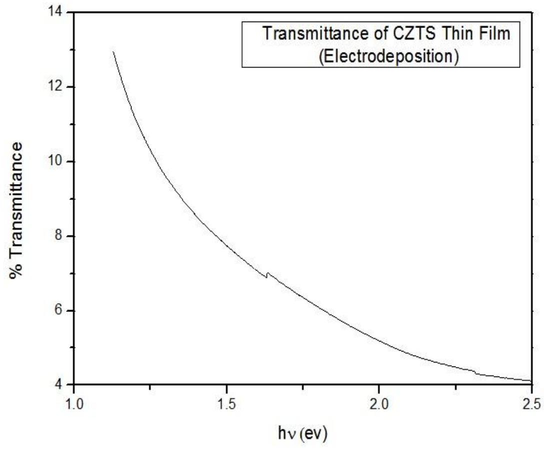
(b)

Fig. 4 – AFM Images of Surface Morphology CZTS thin films by Electrodepostion (a) and sol-gel process (b)

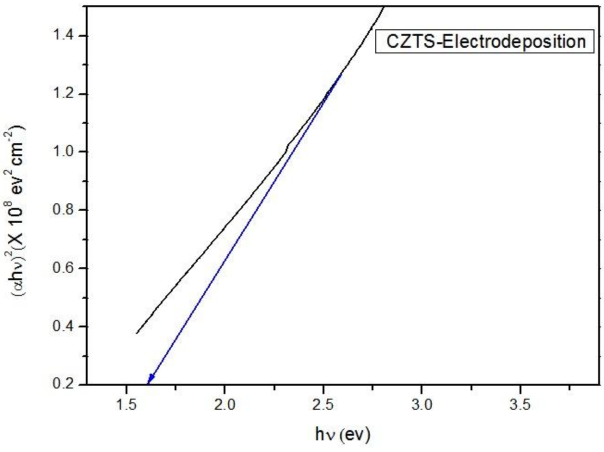
2D AFM images taken over a 5 μm^2 and 15 μm^2 area of an annealed CZTS film is shown in Figure 4a and 4b by Electrodepostion and sol-gel technique respectively. From figure 4a, the average surface roughness and root mean squared roughness of the film in vertical and horizontal directions is found to be around 86.9 and 51.6 nm respectively. Also, it can be observed that the root mean squared roughness of the film in vertical and horizontal directions is around 101.6 and 67.2 nm respectively. The average particle size from 2D AFM images is observed to be 0.6 μm ± 0.4 μm. The Point average roughness of the film in vertical and horizontal directions is approximately equal to 319.1 and 198.7 nm. It can be seen from Figure 4b that the average film thickness is around 100 nm. From Figure 4b, the length of the particle is 1.5 μm ± 1 μm. The average particle size from 2D AFM images is observed to be 150 nm ± 2 nm. The average film thickness is around 100 nm.

3.3 Band Gap Measurement

Band gap measurements of CZTS thin films have been carried out using transmittance data obtained from Shimadzu spectrophotometer equipped with UV Probe spectrum, software version 2.30. Fig 5a shows the optical transmittance of Electrodeposited CZTS thin film annealed at 500 °C. The percentage transmittance is found to be 13 % i.e. there is more absorption of photons in CZTS film. For Cu_2ZnSnS_4 film, the curve of absorption coefficient $(\alpha h\nu)^2$ vs Energy $(h\nu)$ has been plotted, as shown in Fig. 5b. The band gap of the Cu_2ZnSnS_4 film was found to be 1.6 eV.



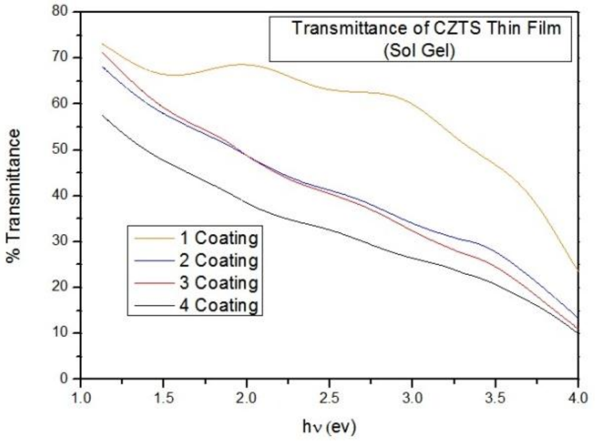
(a)



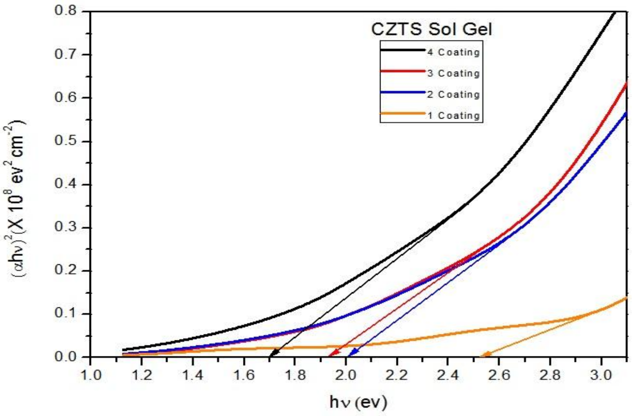
(b)

Fig. 5 – Transmittance of Spectra Band gap calculation of CZTS thin films by Electrodeposition

Fig. 6a shows the optical transmittance of sol-gel prepared CZTS thin film annealed at 500 °C of various thicknesses. The percentage of transmittance is decreasing with increase in thickness of the film. For the annealed dip coated CZTS film at 500 °C, plotted the graph between Absorption coefficient $(\alpha h\nu)^2$ vs. Energy $(h\nu)$ has been shown in Fig. 6b. The band gap of CZTS film for first coating was found to be 2.5 eV and further it decreases to 1.7 eV while increasing the thickness of film which is the desired band gap of CZTS thin film. The optical band gap is in agreement with the literature [14]. The obtained optical band gap by Electro deposition and Sol-Gel suggests that CZTS is suitable for solar cells.



(a)



(b)

Fig. 6 – Transmittance of Spectra (a) and Band gap calculation (b) of CZTS thin films by sol-gel approach

4. CONCLUSIONS

The following conclusions are drawn from the results of structural and morphological characterization carried out. It is clear from the above discussions that the optimal deposition potential of CZTS thin films explored by cyclic voltammetry is found to have a reduction potentials of Zn, Cu, and Sn is – 1.4, – 0.8 and – 0.2 V respectively in aqueous solution. X-ray diffraction patterns indicate the absence of crystallinity formation before annealing. However, the formation of crystallinity is observed after annealing. X-ray diffraction patterns of CZTS thin films indicate a kesterite structure including secondary metal, metal sulfide phases and Copper rich chalcopyrite. From surface morphology studies carried out using Scanning Electron and Atomic Force Microscopes confirm that the average particle size of the spherical grians are 0.8 μm ± 0.4 μm and 0.6 μm ± 0.4 μm respectively. It is observed that the average dimensions of the fibered grains are approximately around 2.5 ± 0.5 μm × 0.2 ± 0.1 μm. In Case of Sol-Gel method, X-ray diffraction patterns indicate the absence of crystallinity formation before annealing. However, the formation of crystallinity is observed after annealing. X-ray diffraction patterns of CZTS thin films indicate a kesterite structure (Copper rich Zinc poor compounds) including secondary metal, metal sulfide phases and copper rich chalcopyrite. It is observed from AFM that the length of the particle is 1.5 μm ± 1 μm and the average particle size is 150 nm ± 2 nm. Film thickness is found to be 100 nm. The Thickness of the thin films of CZTS coated on glass substrates are varied. It is observed that the band gap decreases with increase in film thickness. Band gap is found to be 1.7 eV. From surface morphological studies, it can be concluded that the particles are quite dense and a highly interconnected network of grains, which is necessary for high performance of photovoltaic devices.

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REFERENCES

1. Minlin Jiang, *J. Photon. Energ.* **1**, 019501 (2011).
2. M. Gancheva, L. Kaupmeesa, J. Iliynaa, J. Raudojaa, O. Volobujevaa, H. Dikovb, M. Altosaara, E. Mellikova, T. Varemaa, *Energ. Procedia* **2**, 65 (2010).
3. M. Jeona, Y. Tanakab, T. Shimizub, S. Shingubarab, *Energ. Procedia* **10**, 255 (2011).
4. Minsung Jeon, Tomohiro Shimizu, Shoso Shingubara, *Mater. Lett.* **65**, 2364 (2011).
5. Ji Li, Tuteng Ma, Ming Wei, Weifeng Liu, Guoshun Jiang, Changfei Zhu, *Appl. Surf. Sci.* **258**, 6261 (2012).
6. J.K. Katagiri Hironori, S. Yamada, T. Kamimura, W.S. Maw, T. Fukano, T. Ito, T. Motohiro, *Appl. Phys. Express* **1**, 041201 (2008).
7. S. Ahmed, K.B. Reuter, O. Gunawan, L. Guo, L.T. Romankiw, H. Deligianni, *Adv. Energ. Mater.* **2**, 253 (2011).
8. Yanfeng Cui, Shaohua Zuo, Jinchun Jiang, Shengzhao Yuan, Junhao Chu, *Sol. Energ. Mater. Sol. C.* **95**, 2136 (2011).
9. Remigijus, Juskenasn, Stase Kanapeckait Violeta Karpavicien, Zenius Mockus, Vidas Pakstas, Ausra Selskiene, Raimondas Giraitis, Gediminas Niaura, *Sol. Energ. Mater. Sol. C.* **101**, 277 (2012).
10. B.S. Pawar, S.M. Pawar, S.W. Shin, D.S. Choi, C.J. Park, S.S. Kolekar, J.H. Kim, *Appl. Surf. Sci.* **257**, 1786 (2010).
11. A. Ghazali, Z. Zainal, M.Z. Hussein, A. Kassim, *Sol. Energ. Mater. Sol. C.* **55**, 237 (1998).
12. Y. Cui, S. Zuo, J. Jiang, S. Yuan, J. Chu, *Sol. Energ. Mater. Sol. C.* **95**, 2136 (2011).
13. P. Fernandes, P. Salome, A. Cunha, *Thin Solid Films* **517**, 2519 (2009).
14. R. Schurr, A. Hölzing, S. Jost, R. Hock, T. Vo, J. Schulze, A. Kirbs, A. Ennaou, M. Lux-Steiner, A. Weber, I. Kötschau, H.W. Schock, *Thin Solid Films* **517**, 2465 (2009).
15. N. Kamoun, H. Bouzouita, B. Rezig, *Thin Solid Films* **515**, 5949 (2007).