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Photo conversion efficiency of CZTS solar cells fabricated using ZnO as a buffer layer

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Abstract : Quaternary Cu_2ZnSnS_4 (CZTS), a P-type semiconducting material with a direct band gap of 1.4 to 1.5 eV and high absorption coefficient (10^4 cm^{-1}) in the visible range has been considered as an alternative absorber layer in the fabrication of solar cells.ZnO is a wide-gap n-typematerial, consisting of abundant and nontoxic elements, andis thus expected to be a good substitute for CdS buffer layer in solar cells.In this paper, we report the study of CZTS and ZnOnanoparticles synthesized by solvothermal method.The structural, optical and electrical properties of prepared nanoparticles were studied using X-ray powder diffraction (XRD), Raman analysis, scanning electron microscopy (SEM), UV-vis absorption and J-V Characteristic studies.The device fabrication and conversionefficiency of CZTS/ZnOsolar cellsare also discussed.

Introduction

Cu_2ZnSnS_4 (CZTS) has attracted much attention recentlyowing to its excellent photovoltaic properties such asoptimal direct-band gap energy of 1.5 eV for solar cells andhigh absorption coefficient in the visible region (>10^4cm^{-1}).Moreover, CZTS consists of nontoxic and inexpensive elements[1-7]. Much research effort has recently beenmade on CZTS-based solar cells, and a CZTS/CdSheteroj unction solar cell with an efficiency of 8.4% has been reported[8]. However, since Cd is a highly toxic element, an alternativematerial is desired for the buffer layer to realize a moreenvironmentally friendly device[9]. ZnOa wide-gap (3.37 eV) n-typematerial, consisting of abundant and nontoxic elements, is found to be an excellent substitute for CdS[10-12]. The conversion efficiencies of CZTS/ZnO cells have exceeded 5% but are still lower than those of the best CZTS/CdS cells[9]. In order to realize this,we investigated the structural, optical and electrical properties of CZTS, ZnO nanoparticles synthesized by solvothermal method.

Experimental

All chemicals used in the present work are analytical grade reagents and used without any further purification. In a typical procedure, 0.50mmol of copper acetate ($Cu(CH_3COO)_2$), 0.25 mmol of zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), 0.25 mmol of tin chloride pentahydrate ($SnCl_4.5H_2O$), and 1mmol of thiourea (CH_4N_2S) solutions are prepared in ethylene glycol. The solution was stirred continuously until a clear solution is obtained. The solution is then transferred to a Teflon lined autoclave and it was maintained at 180°C for about 6 hours and then air cooled at room temperature. The precipitates were filtered out, washed with distilled water and absolute ethanol. The final products were dried in vacuum at 60°C for three hours.

In a typical procedure, 0.5mmol of zinc acetate [$Zn(CH_3COO)_2$] and 1mmol of sodium hydroxide [NaOH] were taken in a beaker and dissolved in ethylene glycol. Then the mixture was stirred continuously to obtain a clear solution. After that, the solution was transferred into a Teflon lined autoclave and it was maintained at 160°C for about 5 hours and then air cooled at room temperature. The precipitate was filtered out, washed with deionized water and absolute ethanol. The white product was dried at 60°C for about 3 hours.

The synthesized CZTS and ZnO powders were characterized by X-ray diffraction (XRD) method using Schimadzu XRD-6000 X-ray diffractometer with a CuKα radiation (λ=1.5406 Å). Raman scattering measurements were performed using Horiba JobinYvon HR800 spectrometer. The morphological and compositional analysis of the nanoparticles were carried out using JEOL mode JSM 6390 SEM with EDX and optical studies of the samples were done using Cary 500 UV-Vis Diffuse Reflectance Spectrophotometer.

Device Fabrication

A typical solar cell configuration of SLG/Mo/CZTS/ZnO/Al:ZnO/Al structure was used in this study.A molybdenum (Mo) back contact with a thickness of 1 μm was deposited on soda-lime glass (SLG) substrate by DC magnetron sputtering.CZTS absorber layer deposited on Mo-coated soda lime glass substrates by doctor-blade technique using the CZTS paste.The ZnO nanoparticles were dispersed thoroughly in toluene and then coated onto SLG/Mo/CZTS substrate by drop casting method.The Al-doped ZnO (Al:ZnO) transparent conducting window layer was formed on top of the n-type ZnO buffer layerby RF sputtering. Aluminum (Al) metal grid of 1 μm thick layer was deposited by thermal evaporation onto the ZnO:Al window layer with a designed shadow mask. The fabricated device had a total area of approximately 0.45 cm^2 defined by mechanical scribing. J-V characteristics of solar cell device were recorded with a Keithley 6517B Electrometer. The photocurrent was measured by illuminating the samples with white light of intensity 100 mW/cm^2.

Results and discussion

XRDanalysis

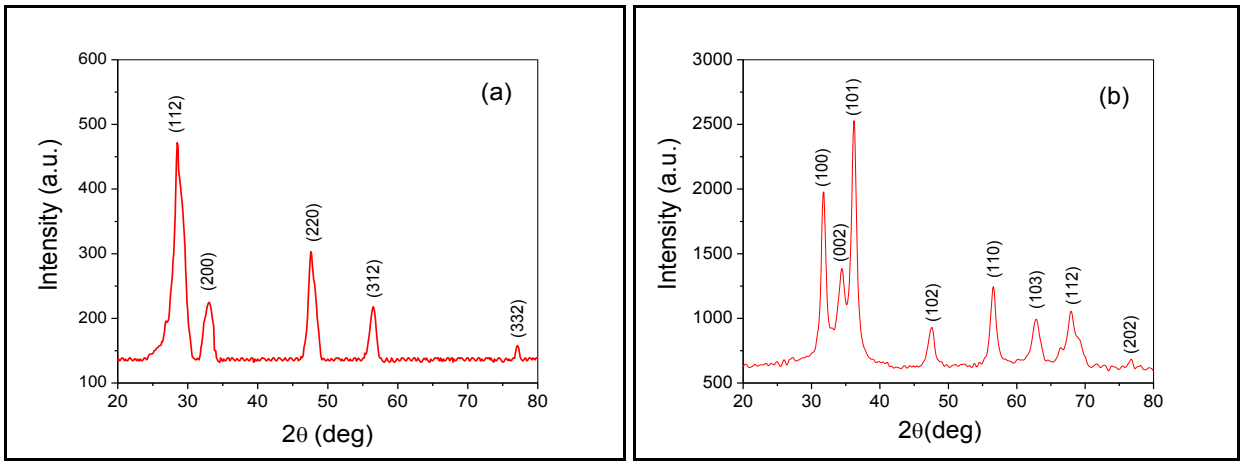

Fig. 1. XRD spectra of (a) CZTS and (b) ZnO nanoparticles

Fig.1(a) and 1(b) shows the XRD pattern of CZTS and ZnO nanoparticles. CZTS samples exhibit diffraction peaks corresponding to the (112), (200), (220), (312) and (332) reflection planes of kesterite structure, which is confirmed using standard JCPDS data (Card No. 26-0575). The broadening of the XRD peaks indicates the nanocrystalline nature of the samples. The mean crystallite size D is determined according to the Scherer equation $D = 0.9\lambda / \beta\cos\theta$, where λ is the X-ray wavelength (for Cukα radiation λ = 1.5406 Å), β is the full width half maximum (FWHM) and θ is the diffraction angle. The calculated mean crystallite size is 7 nm for CZTS nanoparticles. It is worth mentioning that the calculated lattice constant of CZTS nanoparticles (a = 0.5405 nm and c = 1.0871 nm), are the same as the value from the standard card (a = 0.5427 nm and c = 1.0848 nm).Similar results were reported by Mou Pal et al [13]with the crystallite sizes ranging from 7.5 nm to 10.2 nm by solvothermal method using ethylenediamine as a solvent.

From the Fig. 1(b), the sharp peaks at scattering angle 2θ of 31.71˚, 34.36˚, 36.26˚, 47.38˚, 56.59˚, 62.83˚, 67.89˚ and 76.69˚ corresponds to the reflection from: (100), (002), (101), (102), (110), (103), (112) and (202) crystal planes, indicating crystalline ZnO with hexagonal wurzite structure, consistent with the standard JCPDS (Card No.89-0510). No characteristic peaks of impurities could be detected within the precision limit of XRD measurement, which confirms the highly pure and single phase nature of ZnO. The calculated mean crystallite size is 13 nm for ZnO nanoparticles. The calculated lattice constant of ZnOnanoparticles (a = 0.3252nm and c = 0.5190 nm), are almost same as the value from the standard card (a = 0.3248nm and c = 0.5205 nm). The lattice parameter 'c' was found to be slightly higher than the standard value for ZnO nanoparticles. This may be due to the internal stress in the crystals.Bao et al [14], have reported slightly higher 'c' values for ZnO thin films prepared on quartz substrates by a sol-gel method. Y. Zhang et al [15], have reported the difference in c-axis lattice parameter and it was attributed to the occurrence of stress in the thin films.

Raman Analysis

In order to find out the existence of the secondary phase, Raman spectroscopy was performed. Fig. 2(a) and 2(b) shows the Raman Spectra of CZTS and ZnO nanoparticles.Fig. 2(a) shows the Raman spectra of CZTS nanoparticles at the excitation wavelength of 512 nm. It indicates the presence of the two major peaks at 338 cm^{-1} and 289 cm^{-1} and is similar to that reported by earlier researchers [16,17]. Both these peaks correspond to the CZTS phase. The stronger peaks at 338 cm^{-1} is due to the A_1 symmetry and it is related with the vibration of the S atoms in CZTS [18,19]. Peaks at 289 cm^{-1} attributes to the vibration of the Zn atoms and S atoms with some contribution from the Cu atoms in CZTS lattice[20]. Moreover, it is obvious that there are no extra peaks related to the presence of other compounds such as SnS_2 (314 cm^{-1}), Cu_2SnS_3 (352 cm^{-1} and 374 cm^{-1}), cubic ZnS (352 and 275 cm^{-1}) and orthorhombic Cu_2SnS_3 (318 cm^{-1}).

The Raman spectrum of the ZnO nanoparticles at the range of 200–800 cm^{-1} is shown in Fig. 2(b).The dominant feature at 437cm^{-1} is the result of ZnO nonpolaroptical phonons E_2 (high) mode. The E_2 (high) mode corresponds tocharacteristic band of hexagonal wurtzite phase. The peak locatedat 332 cm^{-1} may be attributed to amultiphonon scattering process(E_{2H}–E_{2L}) [21]. In addition,the E_1 (LO) peak can also be observed at 581cm^{-1}. The appearanceof the E_1 (LO) peak is associated with the formation of defects suchas oxygen vacancy, zinc interstitial, or their complexes [22].

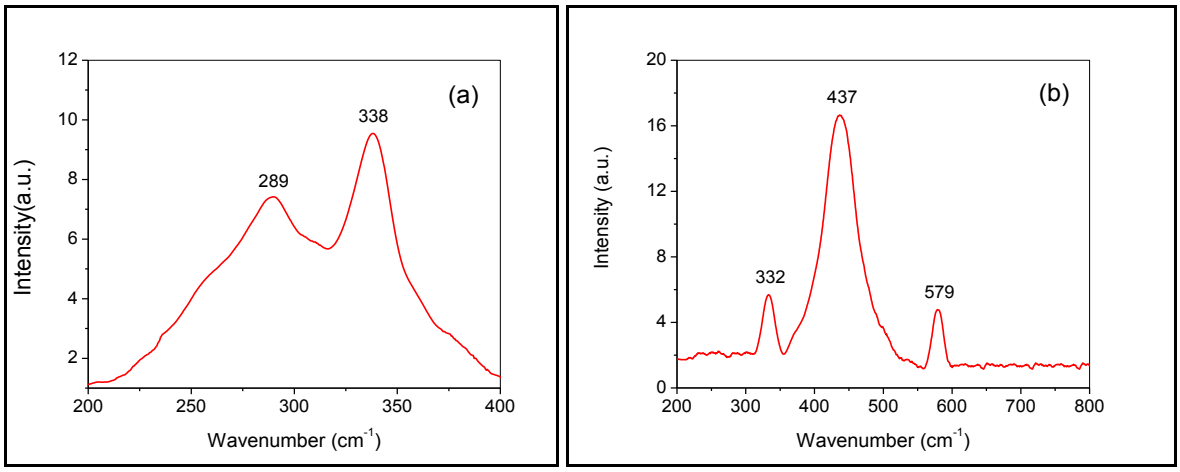

Fig. 2. Raman spectra of (a) CZTS and (b) ZnO nanoparticles

SEM analysis

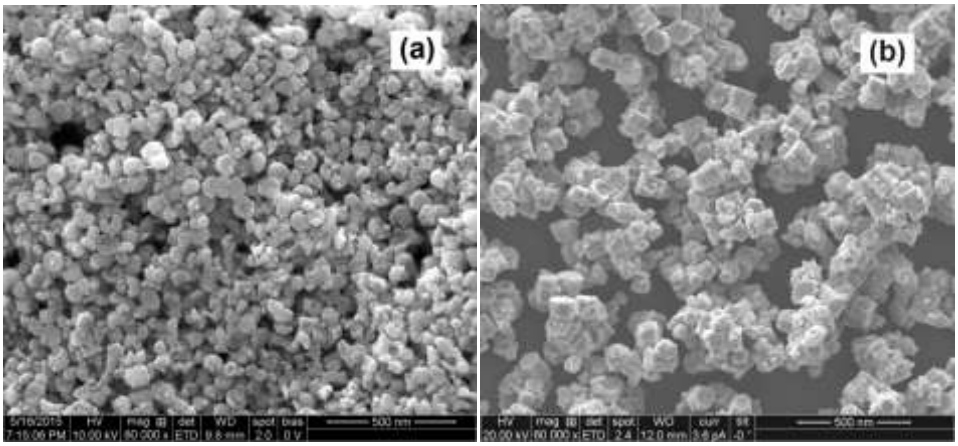

Fig. 3. SEM Micrographs of (a) CZTS and (b) ZnO nanoparticles

Fig. 3(a) shows the SEM images of CZTS nanoparticles. The images confirm that the particles are in the nanometer size range. Figure shows that the CZTS samples have nearly uniform monodisperse particles. The scanning electron micrographs of the ZnO nanopowder are shown in Fig.3(b). The ZnO particles were observed to be of uniform size with hexagonal shape.

Compositional analysis

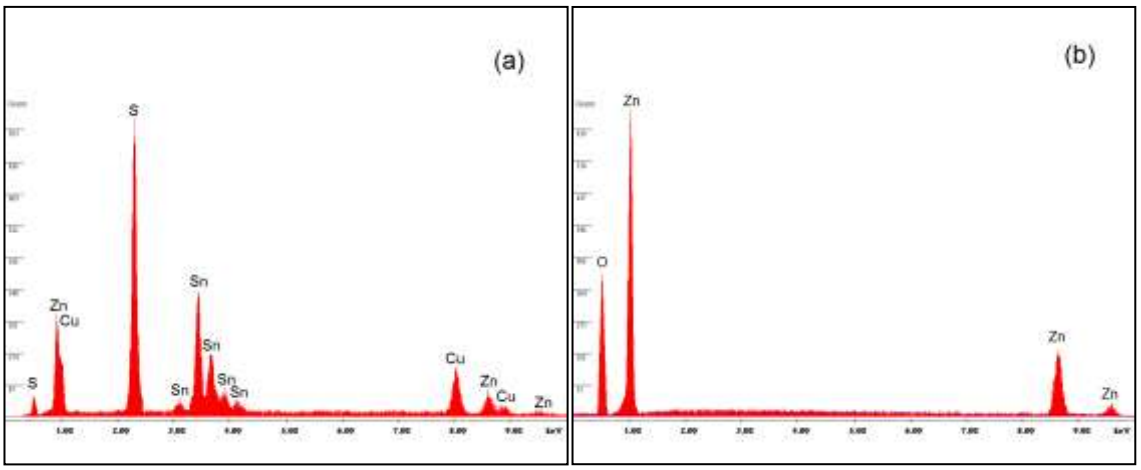

Fig. 4. EDX spectra of (a) CZTS and (b) ZnO nanoparticles

The elemental analysis of CZTS and ZnO nanoparticles were carried out by energy dispersive X-ray analysis (EDX) technique. The respective EDX spectra are shown in Fig. 4(a) and 4(b). Fig. 4(a) indicates the presence of copper, zinc, tin and sulfur for the CZTS sample. The stoichiometric ratio of Cu, Zn, Sn and S were computed by integrating the area under each Cu, Zn, Sn and S peak. The EDX spectra of nanoparticles exhibits nearly the stoichiometric composition with atomic percentage of Cu, Zn, Sn and S ratio in the range 24.85 : 12.37 : 12.72 : 50.06 and theoretically expected stoichiometric composition of CZTS (in terms of at %) is Cu : Zn : Sn : S equal to 25.00 : 12.50 : 12.50 : 50.00. Fig. 4(b) indicates the presence of Zinc and Oxygen for the ZnO sample. The average atomic ratio of Zn/O was calculated from the quantification of peaks. Theoretically expected stoichiometry composition of ZnO (in terms of At %) was Zn:O equal to 50.00 : 50.00. The EDX spectra of nanoparticles exhibits nearly the stoichiometric composition with atomic percentage of Zn and O ratio in the range 51.23 : 48.77. EDAX spectrum also reveals that the prepared samples are free from impurities.

Optical absorption and band gap

The room temperature UV–vis absorption spectra of CZTS and ZnO samples are shown in Fig. 5(a) and 5(b). The UV–vis absorption spectra of the samples were recorded in diffuse reflectance mode using $BaSO_4$ as reference. The reflectance values were converted to absorbance by application of the Kubelka-Munk function [23]. The Kubelka-Munk formula can be expressed by the relation $F(R) = (1-R)^2/2R$, where F(R) is the Kubelka-Munk function which corresponds to the absorbance and R is the reflectance (%).

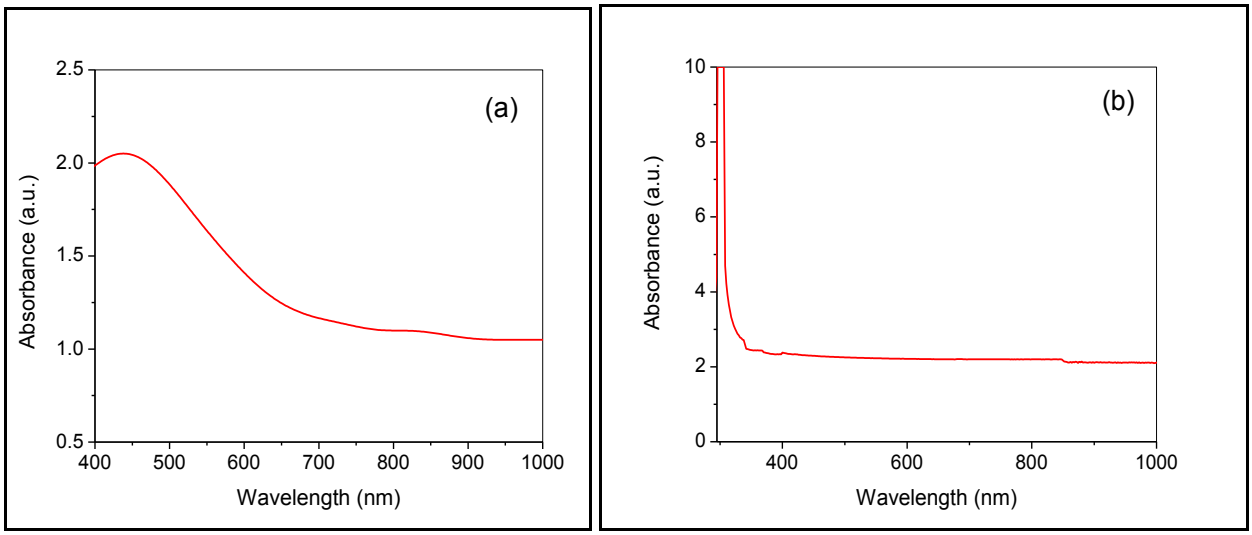

Fig. 5. UV-absorption spectra of (a) CZTS and (b) ZnO nanoparticles

Fig. 5(a) exhibited broad absorption in the visible region and the tails extending to longer wavelengths. The band gap energy of the samples are measured by the extrapolation of the linear portion of the graph between the modified Kubelka-Munk function $(F(R)h\nu)^2$ versus photon energy (hν), as shown in Fig. 6(a) and 6(b) for CZTS and ZnO respectively. It is found that the band gaps of the CZTS sample is 1.53 eV.For designing a highly efficient solar cell, the band gap of the material that maximizes absorption of incident light is highly desirable and should be in the order of 1.3-1.5 eV[24]. Conversion efficiency of 3.03% has been reported by Feng Jiang et al [25] for CZTS thin film with a band gap 1.5eV. It is also reported that the values of band gap for CZTS nanocrystals with diameter ranging from 11 nm to 3 nm are 1.48 eV to 1.89 eV respectively [26]. In the present work, band gap value 1.53 eV was observed for the particle size 7 nm. The spectrum Fig. 5(b) reveals a maximum absorption at 325 nm for the ZnOsample. It was found that the bandgap of ZnOsample was 3.42eV and is in agreement with that of the earlier reports[27, 28].The band gap values for ZnO and CZTS nanoparticles arequite close to the optimum band gaps required for buffer andabsorber layers, respectively in solar cells.

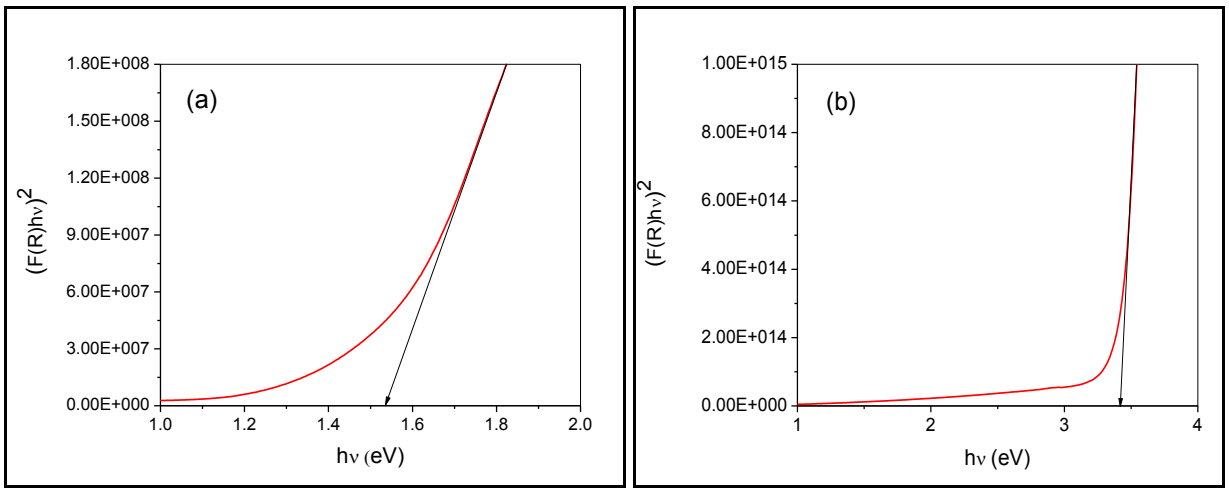

Fig. 6. Plot of $(F(R)h\nu)^2$versus (hν) of (a) CZTS and (b) ZnO nanoparticles

J-V Characteristics

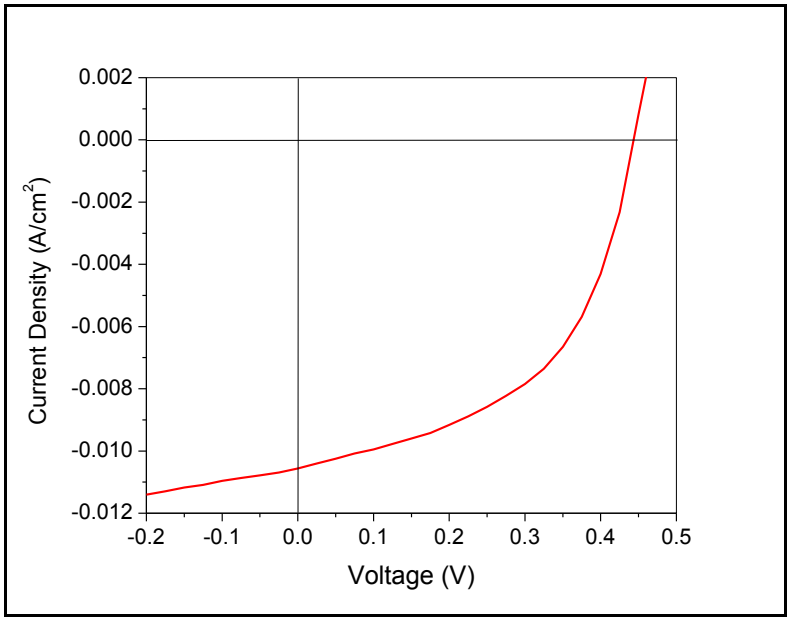

Fig. 7. J-V curve of CZTS/ZnO solar cell

The current density voltage (J-V) characteristics of SLG/CZTS/ZnO/Al:ZnO/Al solar cell is shown in Fig. 7 and this has beenmeasured under the light intensity of 100 mW cm^2 (AM1.5G). The solar cell exhibited the conversion efficiency (η) of 2.37 % with fill factor (FF) = 50.84 %, open circuit voltage (V_{oc}) = 0.44 V,short circuit current density (J_{sc}) = 10.54 mA/cm^2, series resistance (R_s) = 9.19 Ω cm^2 and shunt resistance (R_{sh}) = 154.14 Ω cm^2.Higher V_{oc} in theCZTS/ZnO cell could be considered as a benefit of utilizingwider band gap ZnO that might induce the formation of ahigher built-in potential. On the other hand, the lowerJ_{sc} could be related with the recombination of minoritycarriers that is enhanced by the defects at CZTS/ZnO interface[10].

Conclusion

CZTS and ZnO nanoparticles were synthesized by a simple solvothermal method. The XRD results reveal that the CZTS and ZnO nanoparticles are kesterite and hexagonal crystalline in nature with the particle size of 7 nm and 13 nm. Raman analysis confirms the formation of single phase CZTS and ZnO nanoparticles. The SEM micrograph shows that the CZTS particles are homogeneous in nature and ZnO sample possess uniform hexagonal structures. The CZTS/ZnO heterojunction solar cell exhibited the photovoltaic performance with η of 2.37 % and FF of 50.84 %. This result suggests that ZnO can be an attractive Cd-free buffercandidate for CZTS based solar cells.

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