Efficient hybrid solar cell with P3HT:PCBM and Cu_2ZnSnS_4 nanocrystals

Se-Jeong Jang, Nhu Thuy Ho and Yong Soo Kim*

Department of Physics and Energy Harvest-Storage Research Center, University of Ulsan, Ulsan 44610, South Korea

*Email: yskim2@ulsan.ac.kr

Abstract. Recently, Cu_2ZnSnS_4 (CZTS) with band gap about 1.50 eV is predicted to become an ideal light absorption material due to the abundant component elements in the crust being nontoxic and environmentally friendly. In this study, we propose a hybrid solar configurations with solution-processed CZTS nanocrystals and P3HT:PCBM bulk heterojunction. The forming double heterojunction, as charge can be separated at both the P3HT:PCBM and CZTS:PCBM interface is attributed to enhance the light harvesting efficiency. As a result, organic solar cells with CZTS nanocrystals show the higher efficiency 3.32 % compare to 2.65 % of reference organic solar cells. Improvement of the power conversion efficiency of 25% is obtained by the increase of the short-circuit current and fill factor.

1. Introduction

Recently, the quaternary semiconductor Cu_2ZnSnS_4 (CZTS) has received considerable attention as a material capable of driving the development of low-cost and high performance photovoltaics [1]. Typically, CZTS is used as active material of CZTS/CdS based thin film solar cell (SC). Although the high-efficiency ($\eta \approx 10$ %) is obtained, the containing high toxic cadmium (Cd) and using vacuum deposition method leads to an increase in the prices of products [2,3]. Hence, many efforts have been made to develop new CZTS based SCs with non-toxic materials and cost competitive. Alternative processing strategies including electrochemical and chemical-solution synthesis and deposition have got some reasonable success.[4,5] A heterojunction with CZTS Nanostructures (NSs) and [6,6]-phenyl-C61-butyric-acid-methyl-ester (PCBM) of efficiency of 0.90 % has been reported by Saha *et. al* [2]. Even the η of SCs using CZTS NSs are lower than expectation, the CZTS NSs with controlled phase formation still reveals a great potential for devising low-cost and green SCs.

In this paper, the hybrid SC with CZTS NSs and the blend of poly(3-hexylthiophene) (P3HT) and PCBM is reported. CZTS NSs were synthesized by solution-processed and simply deposited on substrate by spin coating method. The interpenetrating networks where the CZTS nanocrystals (NCs) as an additional absorber within the blended P3HT:PCBM is expected to improve the light harvesting and thus enhance the efficiency of fabricated SCs.

2. Experiment

2.1. Synthesis of CZTS nanocrystals and Device Fabrication

The CZTS NCs were made by sol-gel method [4]. The precursors for CZTS including oleylamine (OLA), copper (II) acetylacetonate ($Cu(acac)_2$), zinc(II) acetate ($Zn(CH_3COO)_2$), tin(II) chloride dehydrate ($SnCl_2.2H_2O$), sulfur (S) were used as received from Sigma Aldrich. The CZTS NCs are dispersed in methanol (10 wt%). The ZnO sol-gel solution was prepared by dissolving zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] in 2-methoxyethanol (Sigma-Aldrich Co.) and ethanolamine. P3HT, PCBM (OSM company) were used as received. The inverted BHJ SCs were fabricated with a structure of ITO/ ZnO/ CZTS NCs/ P3HT:PCBM/ MoO_3/ Ag. The sol-gel solution of 0.75 M ZnO was spin coated on ITO surface. CZTS nanocrystals were deposited on ZnO layer by spin-coating method with different spin speed and annealed at 100°C for 10 min. Blended solutions of P3HT:PC61BM was then spin-coated. Finally, MoO_3 (5 nm) and Ag (100 nm) was thermally evaporated through shadow mask with defined area of 0.13 cm^2.

2.2. Characterization and measurement

The crystalline structure of CZTS NSs was analysed by the X-ray diffraction (XRD) technique. Atomic force microscopy (AFM) image was obtained using a Seiko E-Sweep atomic microscope in tapping mode. Keithley 2401 source meter was used to measure the current density-voltage (*J-V*) curves of the SCs under AM 1.5 simulated illumination. Impedance measurement was carried out at room temperature using impedance spectroscopy (IviumStat, Ivium Tech) in the frequency range from 1 MHz down to 1 Hz, and its results were fitted by the Z-view program. The external quantum efficiency (EQE) spectra of devices were obtained using a solar cell spectral response/QE/IPCE measurement system (Newport Co., Oriel IQE-200).

3. Discussion

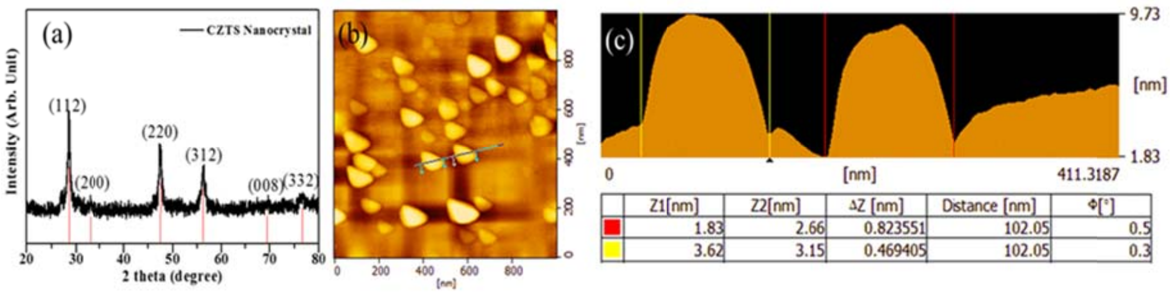

Figure 1. (a) X-ray diffraction, (b) AFM image of CZTS NPs (scan area: 1 μm × 1 μm), and (c) height profile along the white line in the AFM image.

Fig. 1(a) showed an XRD spectrum of the as-synthesized CZTS NCs. The diffraction peaks presented kesterite-type tetragonal phase (JCPDS No. 26–0575) [2, 4]. It reveals that all the CZTS has good crystallinity. AFM image of CZTS NCs on Si wafer in Fig. 1(b) show that those were fully diluted in methanol and retained its monodisperse morphology during the mixing and spin coating process. The density of NCs on substrate could be easily controlled by spin speed during the deposition process. The cross-section AFM image verified the flake-like structure of CZTS NCs that have diameter of 100 nm and thickness of 10 nm (Fig. 1 (c)).

Fig. 2(a) and (c) present schematic and band alignment of the reported device. The flake-like CZTS NCs were first spin coated on the electron transport layer (ZnO). Then the blended of P3HT:PCBM solution was following dropped and spin coated on the top of it to form an interpenetrating network. Therefore, the active layer composed of a CZTS NCs and bulk-heterojunction polymer that filled the vacancy or pores among the CZTS NCs. This structure was attributed to form double heterojunction, as charge can be separated at both the P3HT:PCBM and CZTS:PCBM interface. A similar structure of ZnO/CZTS/P3HT:PCBM was fabricated on SiO_2 substrate for FE-SEM measurement. Fig. 2(b) shows the cross-section image of reported device with the presents of CZTS NCs in the active layer. The P3HT:PCBM polymer covered on the top and filled vacancies among CZTS NCs.

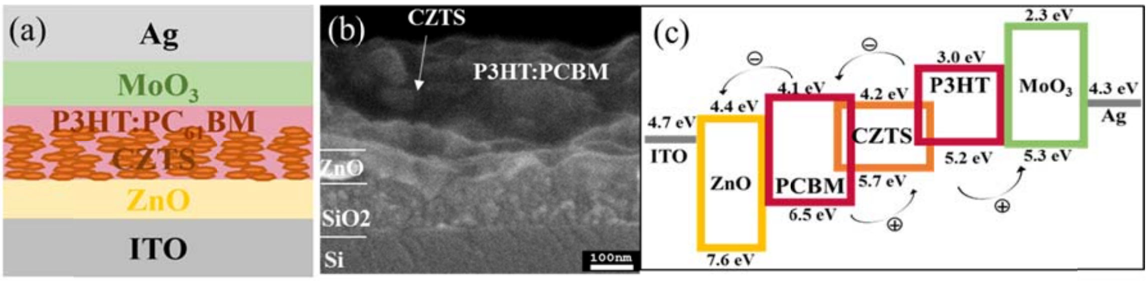

Figure 2. (a) Configuration of hybrid solar cell, (b) cross section FE-SEM image of device, and (c) systematical energy level diagram.

The *J–V* characterizations of the devices with and without CZTS NCs were shown in Fig. 3(a). The density of the CZTS NCs in the devices was varied by speed of spin coating process. The parameters of reported solar cells were shown in Table 1. Without using CZTS NCs, the reference sample exhibited the current density (J_{sc}) of 7.21 mA/cm^2, open-circuit voltage (V_{oc}) of 0.59 V, fill factor (*FF*) of 0.62 and the efficiency (η) of 2.64 %. With the present of the CZTS NCs at the spin speed of 400 rpm, the η of device was decreased. Poor homogeneous packing of CZT NCs with high density could restrict the polymer covering. When the spin speed of 800 rpm was applied, the J_{sc} of sample is dramatically increased leading to improvement in efficiency.

Table 1. Hybrid SC performance parameters according to CZTS NCs spin coating speed

CZTS Spin speed	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF* (%)	η (%)	R_s (Ω)	R_{sh} (Ω)
Reference	7.21	0.59	62	2.64	8.32	4.37
400 rpm	6.52	0.59	64	2.46	7.19	5.11
600 rpm	7.62	0.59	65	2.92	7.87	5.97
800 rpm	8.28	0.59	68	3.32	7.36	7.49
1000 rpm	8.06	0.59	61	2.90	8.32	5.77
1200 rpm	7.61	0.59	61	2.73	8.24	3.97

The best performance was archived with J_{sc} of 8.28 mA/cm^2, V_{oc} of 0.59 V, *FF* of 0.68 and η of 3.32 %. The increase of J_{sc} and *FF* boost the efficiency rising nearly 25 % in compare to that of reference sample. While the J_{sc} was based on the generation and collection of light-generated carriers, deviations of *FF* could be explained by the parasitic loss mechanisms of series (R_s) and shunt resistance (R_{sh}) in Table 1. Then the device performance became worse when the spin coating speed was increased over 800 rpm. It is notable that EQE spectra shown in Fig. 3 (b) was improved in long wavelength (>500 nm) region. This was attributed to the enhancement of light absorption by CZTS NCs (E_g of 1.5 eV) and generation of electron-hole pairs at CZTS:PCBM junction.

Nyquist plots of impedance data and simulated spectra are shown in Fig. 3(c). Impedance responses of SCs were modelled by an equivalent circuit consisting of a series resistance R_c accounted for connection resistances, *R* elements account for the junction resistance and *C* presents for cell capacitance. From the impedance spectra, it clearly depicts that the semicircle's diameter for reference device is much larger than that of the CZTS device. In sample without CZTS, the simulated spectra showed R_c of 20 Ω, R of 613.6 Ω, C of 13.1 nF. When device was fabricated with CZTS nanocrystals, the simulated data of device showed R_c of 15 Ω, R of 64.9 Ω, and C of 15.1 nF. It is interesting to find that with the CZTS NCs the junction R of device in complex impedance plane is apparently decreased than that of reference sample [6]. Furthermore, the excessed electrons and holes in conduction and valance bands separation might cause slightly increased capacitance [7]. In other words, the CZTS NC not only enhance the light harvesting but also serve as extra charge transport path for photo-generated carriers, thus leading to improve the charge transfer and decreased energy loss.

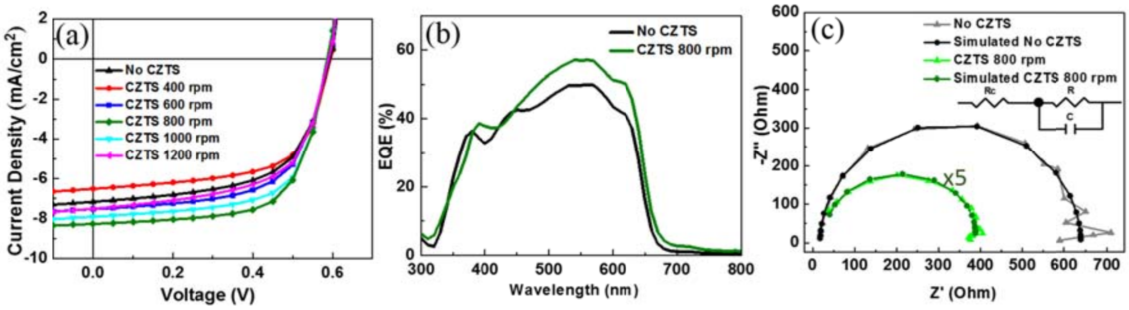

Figure 3. (a) *J-V* characteristics of reported devices, (b) external quantum efficiency spectra of solar cells, and (c) Nyquist presentation of impedance data and equivalent circuit for curve simulation.

4. Conclusion

In this report, we demonstrated a novel hybrid solar cell model using the earth-abundant, non-toxic materials and solution-processed CZTS/P3HT:PCBM. The optical and electrical effect of CZTS nanocrystals on performance of devices have been carefully demonstrate through *J-V*, EQE and impedance measurement. The present of CZTS nanocrystals was attributed to serve as an additional absorber and form extra charge transport path within the photoactive layer. Consequently, optimum device shows η of 3.32 %, 25 % higher than efficiency of reference device without CZTS nanocrystals. To the best of our knowledge, this is one of the highest efficiency of hybrid solar cells based on CZTS material

Acknowledgements

This research was supported by the "Leaders INdustry-university Cooperation" Project, supported by the Ministry of Education (MOE).

References

[1] Lai Y, Liu F and Su Z 2013 *Int. Photonics and Optoelectronics Meetings* (Wuhan: China) p ASu3A.2
[2] Saha S K, Guchhait A and Pal A J 2012 *Phys. Chem. Chem. Phy.* **14** 8090
[3] Barkhouse D A R, Gunawan O, Gokmen T, Todorov T K and Mitzi D B 2012 *Prog. Photovoltaics* **20** 6
[4] Steinhagen C, Panthani M G, Akhavan V, Goodfellow B, Koo B and Korgel B A 2009 *J.Am. Chem. Soc.* **131** 12554
[5] Wang Y, Li C, Yin X, Wang H and Gong H 2013 *ECS J. Sol. State Sc.* **2** Q95
[6] Li Z, Li S, Zhang Z, Zhang X, Li J, Liu C, Shen L, Guo W and Ruan S 2016 *Phys. Chem. Chem. Phy.* **18** 11435
[7] Suman C K, Seunguk N, Seohee K, Sin-Doo L, Changhee L, Donggu L and Jeongho P 2008 *J. Korean Phys. Soc.* **53** 3278