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3-D architecture between indium tin oxide nano-rods and a solution processed $CuInGaS_2$ absorber layer for thin film solar cells

Van Ben Chu [a,b], Chan Sik Kim [c], Gi Soon Park [a,d], Young Ki Lee [c], Yun Jeong Hwang [a], Young Rag Do [c,*], Byoung Koun Min [a,d,**]

[a] Clean Energy Research Center, Korea Institute of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea
[b] Department of Chemical and Biochemical Engineering, Dongguk University, 30 Pildong-ro, Jung-gu, Seoul 04620, Republic of Korea
[c] Department of Chemistry, Kookmin University, 77 Jeongneung-ro, Seongbuk-gu, Seoul 02707, Republic of Korea
[d] Green School, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

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The performance of thin film solar cells can be significantly enhanced by efficient light management. In this study, we integrated one-dimensional indium tin oxide (ITO) nanorods into $CuInGaS_2$ (CIGS) films to fabricate 3-D nanostructured thin film solar cells. 400, 600, and 1000 nm ITO nanorod substrates were used as back contact electrodes. Precursor solutions of Cu, In, and Ga with and without binder materials were prepared to fill the gaps between the ITO nanorods and increase the thickness of the CIGS films, respectively. Heat treatments both in air and in H_2S were applied to form polycrystalline CIGS films while minimizing carbon impurities. 3-D nanostructured solar cell devices with Al,Ni/AZO/i-ZnO/CdS/CIGS/ITO nanorods/Glass structures were fabricated and characterized. Under standard irradiation conditions, the 600 nm ITO nanorod solar device was found to have the maximum power conversion efficiency of 6%. This superior efficiency may be attributed to enhanced light absorption and complete gap filling.

1. Introduction

Thin film photovoltaic technology has become of significant importance recently because of its potential to reduce material costs when manufacturing solar cells. Of the thin film solar cell material candidates, chalcopyrite material (e.g. $CuInGaS_2$ (CIGS)) has attracted the most interest due to its preeminent optical and electrical properties for thin film solar cell applications [1–3] and it achieved a milestone by obtaining the highest efficiency of any thin film solar cell, 22.6% [4]. Most high efficiency chalcopyrite thin films were deposited by vacuum based methods, particularly co-evaporation [5,6] and sputtering [7], which produce high quality CIGS with large crystal grains. However, these methods are considered expensive and raise the fabrication costs of CIGS thin film solar cells. Many groups are finding ways to reduce the fabrication costs of CIGS thin film solar cells by applying solution based processes. This approach allows the creation of high quality CIGS films with large grains, but its use of highly toxic and explosive solvents, such as hydrazine [8], has limited its industrial application. Meanwhile, the use of low toxicity solvents, such as alcohol [9], has generally produced low quality CIGS films featuring small grains, which result in high recombination rates and reduce solar cell performance. To improve the efficiency of solution based CIGS thin films one can either enlarge the diffusion length of photo-generated charge carriers or reduce film thickness while improving the light absorption of the absorber film [10,11].

Nanostructures show great promise for enhancing light harvesting in photovoltaic applications. They improve thin film solar cell performance not only by increasing light absorption via particular photon management configurations [12,13] but also by enhancing charge carrier collection [14]. Thus, integrating nanostructures into solution based CIGS thin films would result in highly efficient and cost-effective solar cell devices. Three dimensional (3-D) nanostructured thin film solar cells [15] formed between a nanostructure electrode and a photoactive layer have been applied to bulk heterojunction polymer and dye-sensitized solar cells [16–19]. 3D solar cells are unique because their charge carriers can travel in all three dimensions before collection, due to the intercalation of the absorber and the 2D nanostructure substrate array. These solar cells have an improved photo current because of the ability of nanostructures to enhance light absorption. 3-D nanostructured thin film solar cells may also feature enhanced open circuit voltage by decreasing bulk recombination and hence dark current [20]. Previously, our lab has also demonstrated 3-D nanostructured CIGS thin film solar

* Corresponding author.
** Corresponding author at: Clean Energy Research Center, Korea Institute of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea.
E-mail addresses: yrdo@kookmin.ac.kr (Y.R. Do), bkmin@kist.re.kr (B.K. Min).

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cells using an ITO nanorod back contact electrode. Superstrate-type 3-D nanostructured CIGS thin film solar cells featuring ITO nanorod spatial regions firstly coated by a CdS buffer layer and then filled with $CuInS_2$ nanoparticles were found to show a bulk heterojunction structure [21] and achieve a 1% solar cell efficiency. Moreover, a much higher efficiency (6.3%) was attained using a substrate-type device according to the general configuration of CIGS thin film solar cells. The gap filling of CIGS material into the ITO nanorods was achieved first and then a CdS buffer layer was deposited by a chemical bath deposition method [22]. The main reason for the increase in efficiency was considered to be the enhanced optical properties associated with the 3-D configuration between the CIGS absorber layer and the ITO electrode [23–25].

Herein, we extended our study to the fabrication of 3-D nanostructured CIGS thin film solar cells by using ITO nanorod back contact electrodes of different lengths. Fig. 1 shows a schematic of the solar cell device with 400 nm, 600 nm and 1000 nm long ITO nanorod substrates. Two precursor solutions of different viscosities were used to fill the gaps between the ITO nanorods and increase the thickness of the absorber layers. The polycrystalline CIGS absorber films were formed after several spin-coating cycles and heat treatment processes. The ITO nanorods film and particularly the filling of its gaps by the precursors were investigated by scanning electron microscopy. The crystallinity and optical properties of the absorber films were investigated by x-ray diffraction and UV–Vis spectroscopy. 3-D nanostructured CIGS solar cell devices (Al-Ni/AZO/i-ZnO/CdS/CIGS/ITO NRs or planar/Glass) of various ITO nanorod lengths were fabricated and characterized, revealing a maximum power conversion efficiency of 6.03%, which was obtained with the solar cell comprised of 600 nm ITO nanorods.

2. Experimental

2.1. Preparation of the ITO nanorod films

ITO nanorod films of various lengths (400 ± 20 nm, 600 ± 30 nm and 1000 ± 50 nm) were grown on glass substrates (2.5 cm $\times$ 2.5 cm) using radio frequency magnetron sputtering. The fabrication of the ITO nanorod films and their properties were described in detail in our previous report [26]. Briefly, sputter deposition was performed in an Ar atmosphere under the following conditions: a background pressure of 2×10^{-6} Torr, a working pressure of 7.8×10^{-3} Torr, a radio frequency power of 40 W, and a substrate temperature of 500 °C. Three small In metal disks (d ~ 3 mm) were placed on an ITO target and used as the catalyst for the growth of the ITO nanorods. The Sn/(In + Sn) atomic ratio of the target pellet was fixed at 10%. The length of the ITO nanorods was controlled by varying the deposition time. Note that longer deposition times led to increased ITO nanorod density and lengths due to a vapor-liquid-solid mechanism in which droplet shaped metal-rich particle seeds form first and then ITO nanorods grow from those seeds [27]. After deposition, the sputtering chamber was allowed to cool to room temperature under vacuum.

2.2. Preparation of the precursor solutions and CIGS films

To deposit CIGS films on various heights and distributions of ITO nanorod substrates, a moderately low viscosity solution was used to infiltrate the gaps between the ITO nanorods yet still adhere to the substrate after spinning by spin-coater. In addition, a high viscosity binder-based solution was used to increase CIGS film thickness. Thus, two precursor solutions with different viscosities were prepared. Solution 1 with low viscosity was prepared by dissolving $Cu(NO_3)_2 \cdot xH_2O$ (99.999%, Alfa Aesar), $In(NO_3)_3 \cdot xH_2O$ (99.99%, Alfa Aesar) and $Ga(NO_3)_3 \cdot xH_2O$ (99.999%, Alfa Aesar) in a mixture of alcohol solvents (ethanol:1,2-propanediol = 4:1, 10 mL). The molar ratio of Cu/In/Ga was 1.0:0.8:0.4 and the total concentration of the solution was 0.9 M. Solution 2 had the same metal molar ratio but a higher viscosity and a total solution concentration of 1.4 M, obtained by dissolving the precursors in methanol (10 mL) and then mixing with polyvinyl acetate (PVA, Sigma-Aldrich) binder solution (PVA 1 g/methanol 7 mL). After vigorous stirring using a magnetic bar, the solutions became transparent with a bluish color. They were then purified using a 0.2 μm syringe filter and stirred again for 5 min before deposition.

2.3. Fabrication of the solar cell devices

To fabricate the 3-D nanostructured CIGS thin film solar cell devices, we developed two precursor solution recipes to fill the ITO nanorod gaps and increase the thickness of the CIGS absorber. The fabrication processes followed our previous recipe [22,28] with slight modification due to the usage of longer ITO nanorod substrates to effectively fill the gaps. Firstly, the low viscosity precursor solution of Cu, In, and Ga ions in alcohol solvents was drop-cast on an ITO nanorod film and ultrasonically vibrated so that it would infiltrate the gaps between the nanorods. After all the ITO nanorods were immersed in precursor solution, the substrates were rotated at

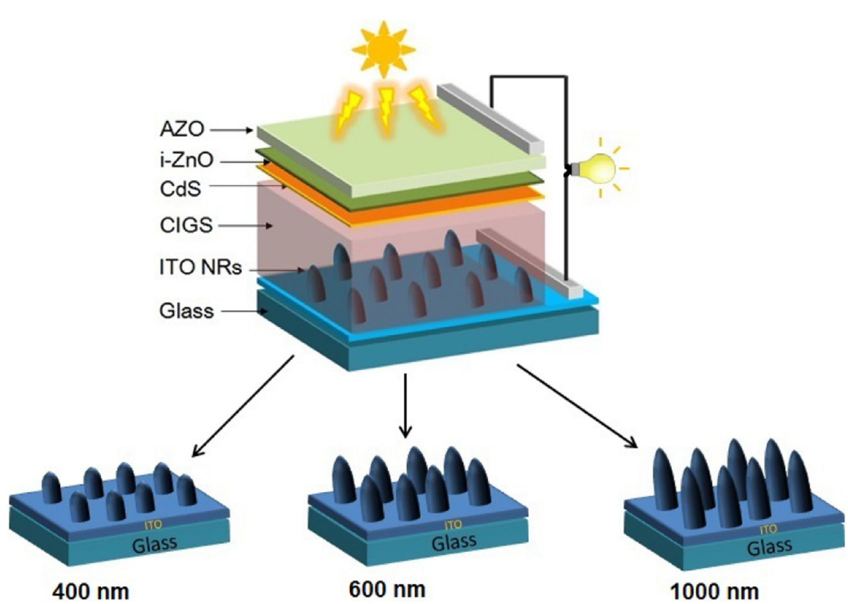

Fig. 1. Schematic of 3-D nanostructured CIGS thin film solar cells using ITO nanorod back contact electrodes of different lengths.