Optimization of Annealing Process for Totally Printable High-current Superstrate CuInS$_2$ Thin-Film Solar Cells

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ABSTRACT- Planar superstrate CuInS$_2$ (CIS) solar cell devices are fabricated using totally solution-processed deposition methods. A titanium dioxide blocking layer and an In$_2$S$_3$ buffer layer are deposited by the spray pyrolysis method. A CIS$_2$ absorber layer is deposited by the spin coating method using CIS ink prepared by a 1-butylamine solvent-based solution at room temperature. To obtain optimum annealing temperature, these layers are first annealed at 150°C and then annealed at 210°C, 250°C and 350°C respectively. The optimum annealing temperature of the layer is found to be 250°C, where 23 mA current density and 505 mV open circuit voltage are measured for the best fabricated solar cell sample.

KEYWORDS: CuInS$_2$, Thin film solar cells, Superstrate structure, Solution-processed deposition method

I. INTRODUCTION

In recent years, Cu(In,Ga) Se$_2$ (CIGS) and CuInS$_2$ (CIS) chalcopyrite have been widely investigated in the field of environmentally friendly solar renewable energy using thin film photovoltaic cells [1,2]. Traditionally, CIGS absorbers have been produced by vacuum-based processes (i.e. co-evaporation and sputtering + selenization) with over 20% efficiency on both rigid and flexible solar cells [1]. Industrial-scale production of solar cells using these approaches will require solutions of several technical problems (e.g. wasted materials and non-scalability). A non-vacuum process for thin-film CIGS solar cell fabrication [2,3], employing either a colloidal nanoparticle solution precursor [4-7] (also called nano-ink, suspension) or a chemical solution precursor [8–16]), has been attracting a lot of attention as an alternative to the vacuum deposition techniques because of its cost effectiveness and scalability.

Despite the conceptual benefits of nanoparticle inks (e.g. removal of excess organics through pores between nanoparticles) compared to precursor inks, they have been widely investigated in recent years. In the precursor ink deposition method, during the deposition (while the films dries), thermal post treatments as well as selenization or sulfurization, formation of semiconducting absorber film take place [8–11]. Most solution-based researches have used standard cell configuration (glass/Mo/CIGS/Cds/ZnO/Al doped ZnO/Al contact) in CIGS thin-film solar cells [4-13]. Vacuum processing is still used for ZnO/Al doped ZnO/Al layers in this structure. To propose totally solution-processed CIGS solar cells, heterojunction superstrate structure solar cells (TCO/Blocking layer/ buffer layer/absorber layer/back contact) have recently been considered as a means of providing an easier and non-vacuum fabrication process [14-16].
However, since, in the superstrate structure, the buffer layer is deposited before the absorber layer, the absorber layer crystal growth is hardly possible and annealing process becomes a critical process [14].

During the annealing process in this configuration, which is necessary for removing the solvent and excess organics and loss of sulfur or selenium, residual carbon impurity remains in the final film. Another problem in this method is Cu diffusion. Diffusion of Cu in semiconducting materials has a strong influence on their electrical, optical and also photoelectrical properties. For example, Cu is one of the well-known fast diffusing impurities in crystalline silicon (c-Si) [17] leading to a strong reduction of the diffusion length of minority charge carriers in significant concentrations [18]. Cu was also found to diffuse from Cu(In,Ga)(S,Se)2 [19] or from CuSCN [20, 21] into the In2S3 during an annealing step in air at temperature of about 200°C, which is mandatory for optimal solar cell performance.

Reported heterojunction superstrate solution-based CIGS solar cells, fabricated by low-temperature annealing, produce much lower efficiency compared to vacuum-based solar cells [14-16, 22,23]. There are a few reports on annealing in air conditions for formation of CIS absorber layers [15]. They have used Au/CIS/CdS/ 3d ZnO/ ZnO (blocking layer)/ITO structures. In addition to low-current density (<11 mA/cm2), Au and ZnO blocking layers are deposited by radio-frequency magnetron sputtering and RF sputtering. They are also 3d ZnO structures used for solar cell fabrication, which is not practical for industrial purposes.

In this study, we carried out the annealing optimization process for totally printable high-current superstrate CIS solar cells, based on Carbon past/CIS/In2S3/flat blocking TiO2 layer/FTO/glass structures (Fig. 1). The objective of the investigation is to avoid costly vacuum-based deposition methods as well as chemical bath processes. The relationship between photovoltaic performance and annealing temperature were explored in an attempt to optimize the cell performance by investigating the evolution and devolution of crystal phases. The annealing temperature was also optimized to obtain the highest efficiency and a high-current density.

II. EXPERIMENTAL PROCEDURE

A. Cell fabrication

CIS solar cells were fabricated in a superstrate structure based on Fluorine-doped tin oxide glass (FTO) substrates which were cleaned prior to film deposition by ultra-sonication for 15 min in acetone and then ethanol solvent, followed by heat cleaning at 450°C. A TiO2 dense film (~100 nm) was deposited by the spray pyrolysis method at 450°C from a solution containing ethanol (Merck), acetyl acetone (Merck) and titanium tetraisopropoxide (Merck) as previously reported [16, 24]. For deposition of β-In2S3 crystalline layer (~60-100 nm), an aqueous solution of InCl3 (0.025 M) and thiourea (0.15 M) was prepared. This solution was sprayed on the FTO/TiO2 substrate at 350°C. During the spray deposition, the rate of spray and the distance between the substrate and the nozzle were maintained constant and were equal to 2.5 ml/min and 20 cm respectively.

The CIS ink, prepared by modifying the method reported by Li et al. [23], in molar ratio of Cu/In/S: 1.05/1/4, was spin-coated onto the substrate at 2000 rpm for 20 seconds. The process was repeated for 2 or 3 times. The
films were then placed on a 150°C hot plate for 10 min in order to eliminate the volatile solvent. Then, the films were moved to a preheated hot plate for post-annealing, where they were maintained for 10 minutes. During the annealing, the film changed from colorless to yellow and then red and was finally stabilized as a shiny black. After the heat treatment, the samples were allowed to cool to room temperature in the air. To complete the solar cell devices, a graphite paste (Sharif Solar) was deposited by Dr Blade method and then dried at 120°C for 20 minutes. This coating method was repeated for 2 or 3 times. The total active area of the fabricated samples was 0.2 cm².

B. Characterization method

The morphology and composition of the films were recorded using scanning electron microscopy (SEM Philips, XL30) equipped with an EDS analyzer. The crystal structure of the layers was analyzed by X-ray diffraction patterns (XRD, X’Pert Pro MPD, PANalytical). UV-visible absorption measurement was carried out using a Perkin Elmer (Lambda 25) spectrophotometer. The performance of the solar cells was measured under simulated solar light (Sharif Solar) using a source meter (Keithely 2400). The power of the simulated light was calibrated to AM 1.5 (100 mW/cm²) using a calibrated photodiode.

III. RESULTS AND DISCUSSION

Due to their high-band gap and liability to non-vacuum deposition methods, TiO₂ blocking layers have been used wildly in superstrate depleted heterojunction structure solar cells. Usually the thickness of the TiO₂ blocking layers in the flat two dimensional superstrate CIS₂ solar cell are about 100-150 nm [16, 25]. The layers thicknesses were obtained by using conventional method from UV-Vis transmission spectrum [26]. The evolution of the crystal-phase structure of TiO₂ thin blocking layer was investigated by XRD analyses. After deposition of about 100 nm of a TiO₂ blocking layer, as shown in Fig. 2, typical XRD peaks for anatase TiO₂ such as (101), (200) and (211) were observed at 25.20, 47.80 and 54.80 degrees respectively (JCPDS 71168). Spray pyrolysis was used for buffer layer deposition because this deposition technique provides a scheme for high deposition rate of non-toxic buffer layers in industry. After deposition of 4 mL of an aqueous solution containing InCl₃ and thiourea, an In₂S₃ thin layer of less than 80 nm thick was obtained. Thickness of buffer layers is critical for CIGS solar cells and should be chosen less than 100 nm. Fig. 2(b) shows the XRD pattern of this buffer layer. The peaks show the formation of a tetragonal (220) oriented In₂S₃ film (JCPDS 731366).

The optimum thickness of buffer layer should be about 50 nm [25] measured by optical methods [26].

The performance of the CIS solar cell is affected by the quality of the absorber layer ink. For preparation of the CIS ink mol fraction of the Cu, In and S are fixed at 1.05, 1 and 4 mM respectively. The quality of the CIS films is examined by different methods. The CIS films were deposited using spin coating of the inks on FTO/TiO₂/In₂S₃ substrates, subsequent drying at 150°C, and annealing and crystallization at a higher temperature. The optical properties of our CIS samples were
valuated based on UV-visible spectroscopic analyses. Figure 3 shows the absorption spectra of the CIS films annealed at different temperatures for particular time intervals. The onset of the absorption spectra shows a red shift with an increase of the annealing time and temperature. The graphs demonstrate that 150°C is not sufficient for the calcination of the ink and formation of a large-grained CIS phase.

For annealing temperatures of above 200°C and particularly 250°C, the absorption edge shifts to the right position, indicating that a CIS phase is formed and the size of crystallites is more than the quantum confinement range. For temperatures higher than 250°C, nanocrystal absorption becomes more considerable with a sharp band edge. Due to loss of sulfur element, annealing at 350°C takes place in sulfur atmosphere under Ar flow as a buffer gas. The observed shoulder is attributed to excitonic absorption of the nanocrystals [23]. XRD measurements were used to investigate the mechanism of CIS crystal growth at various temperatures. The film crystallinity strongly depends on the annealing temperature and is improved at higher temperatures, as the peaks are sharpened (see Fig. 4). Since the crystallinity and absorbance spectra of the CIS layer at 350°C (Figs. 3 and 4) show better results, we expect that this temperature is the optimum annealing temperature. However, as it will be shown, this will not happen at this temperature.

As depicted in Fig. 4(a), at low temperatures (150°C - 210°C) from broad peak at 25° to 33°, it seems that the ink contains a mixture of CIS₂, In₂S₃ and CuS (JCPDS 782121) nanocrystals. At 180°C, XRD peaks from CIS₂ (112) and (204) can be observed clearly. When temperature increases to 210°C, CIS₂ XRD peaks such as (112), (200), (204/220) and (116/312) appear at 27.9°, 32.36°, 46.4 and 54.8°. After that, at 250°C, CuS phase peaks disappear and CIS₂ phases completely dominate. For better cell performance, the

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**Fig. 3. UV-Vis Optical absorption spectra for CIS films annealed at different temperatures and different time intervals**

**Fig. 4. XRD pattern of CIS layer at different temperatures. a) Below 250 in air condition and b) above 250 and in air and sulfur and argon atmosphere**
crystalline phase purity is needed, but only a slight CuS (JCPDS 782121) impurity phase is here observed at 250°C. At 300°C and in air condition, as depicted in Fig. 4(b), indium oxide impurity is observed. This is related to the oxidation of indium at a high temperature in air. To avoid this impurity phase at a higher temperature, annealing process must take place in inert atmosphere in sulfur presence. In this condition, high-quality pure Chalcopyrite crystal can be obtained.

The atomic concentrations of Cu, In, and S were measured using energy dispersive spectroscopy (EDS). One of the issues in using ink deposition methods for solar cell fabrication is that the organic impurity in the absorber layer can influence the cell performance. Besides, it should be checked whether or not the film converts to the right stoichiometry after drying and calcinations. It is very important because, typically, the best CIS crystal is obtained at higher temperatures. Figure 5 shows the EDS spectra of the film annealed at 150°C and 250°C, each for 10 minutes.

Table 1 shows the atomic concentrations of CIS elements. All these films are originally made from Cu rich ink. From the data in Table 1, it can be seen that high temperature annealing of the films in presence of sulfur significantly reduces chlorine impurity without losing the sulfur content, but carbon impurity is still high. Therefore, solar cell performance at this temperature decreases as will be shown later. For a complete removal of carbon impurity, an intermediate annealing temperature (250°C) is needed.

Figure 6 shows the cross-sectional view of TiO2/In2S3/CIS layers that are deposited on the FTO substrate and annealed at different temperatures. The final step for fabrication of the solar cell device was completed by carbon past deposition. Improvement in crystallinity at higher temperatures can be seen in Fig. 6. At low temperature (210°C) two layers spin-
coated from ink were completely distinguishable as depicted in Fig. 6.

**Table 1.** EDS elemental composition values of CIS films at different annealing temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Cu/In in ink</th>
<th>Cu/In in film</th>
<th>S/In in film</th>
<th>C in film</th>
<th>Cl in film</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>1.05</td>
<td>1.2</td>
<td>2.1</td>
<td>28.0</td>
<td>0.62</td>
</tr>
<tr>
<td>250</td>
<td>1.05</td>
<td>1.06</td>
<td>1.9</td>
<td>10.0</td>
<td>8.50</td>
</tr>
<tr>
<td>210</td>
<td>1.05</td>
<td>1.18</td>
<td>2.1</td>
<td>47.0</td>
<td>10.5</td>
</tr>
</tbody>
</table>

To complete the planar superstrate CIS solar cell (FTO/TiO2/In2S3/CIS/Carbon), all these layers were applied by the solution-processed method. TiO2 and a buffer layer were deposited by spray pyrolysis. The CIS absorber layer was deposited by the spin-coated method from CIS nanocrystal ink and then dried and annealed at 210°C, 250°C and 350°C respectively. Finally, carbon paste was applied by the doctor blade method. The performance of the solar cells was monitored by J-V characterization curve in simulated AM 1.5 light.

Figure 7 shows the photovoltaic performance of the fabricated samples at different annealing temperatures in simulated AM 1.5 light. It seems that, at a low temperature (210°C) and a low crystal quality (Figs. 4a and 6) and a high carbon impurity (Table 1), the current density and open-circuit voltage of the fabricated samples decrease.

For intermediate temperatures (e.g. 250°C), the best results were obtained. Therefore, it seems that 250°C is the optimum annealing temperature. Table 2 tabulated all parameters of our solar cell presented in the Fig 7. In comparison to the other work [15, 22, 23] the current density improved significantly. Open circuit voltage reduced while fill factors are worsened. The improved current density related to use of Indium chloride instead of conventional Indium acetate [27]. The big difference in the solar cell structures and use of Indium sulfide as buffer layer in compared with conventional CdS, may be affected on fill factor.

At higher temperatures, current density and open-circuit voltage decrease significantly. This may be results in from more Cu diffusion to other In2S3 layers in higher temperature compared to lower temperature.

With regard to the dark current (Fig. 7(b)), Cu diffusion to other layers causes to reduce shunt resistance and increase series resistance.

**Table 2.** Solar Cell parameters that obtained from I-V characteristic from Fig 7

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Voc (mV)</th>
<th>Jsc (mA/Cm2)</th>
<th>FF(%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>295</td>
<td>4.0</td>
<td>28.0</td>
<td>0.36</td>
</tr>
<tr>
<td>250</td>
<td>505</td>
<td>23</td>
<td>35.0</td>
<td>4.05</td>
</tr>
<tr>
<td>210</td>
<td>408</td>
<td>15</td>
<td>31.0</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Fig. 7. (a) J–V curves under simulated AM1.5 light for CIS solar cells prepared from inks with a Cu/In ratio of 1.05 annealed at 210°C, 250°C and 350°C. (b) J-V curves of the sample devices in dark.

Cu diffusion to another semiconductor layer is very well-known and starts from 200 °C [19-
CuIn₅S₈ is a metastable impurity phase that exists in CIS chalcopyrite with very low carrier density. Cu atoms can occupy vacancies on the tetrahedral sites and substitute for Indium on the octahedral sites in the spinal like β-In₂S₃ lattice. Cu is, therefore, believed to diffuse by vacancy mechanisms in crystalline β-In₂S₃ structures [21]. Also, CuS impurity leads to low shunt and series resistance at low temperatures (Figs. 7(b) and 4(a)) because CuS is a semi-metal.

IV. CONCLUSION

Two dimensional thin-film CIS solar cells were fabricated at low temperatures. A dense TiO₂ film and an In₂S₃ buffer layer were deposited by the spray pyrolysis method. Alkyl amine precursor ink was used for CIS deposition. By an annealing process, the formation of crystal structure of a CIS absorber layer was monitored by UV-VIS spectroscopy and X-ray diffraction measurement of CIS nanocrystals. This formation took place at a relatively low temperature (150-350°C). CIS thin films were also monitored by SEM technique measurement. An optimized annealing temperature was obtained for the highest efficiency and a high current density. An efficiency of 4.0% and a current density of 23.0 mA/cm² were measured in these conditions.

REFERENCES


Mehdi Dehghani earned his M.Sc. in 2006 and his Ph.D. in Atomic and molecular physics at Yazd University, Photonics Research Group, in 2015. During his Ph.D. he joined Dr. Taghavinia’s group at the Sharif University of Technology, he developed solution processed CIGS nanostructured solar cell. Currently he works on printable solar cells.
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