The 6th International Conference on Applied Energy – ICAE2014

Cu(In,Ga)Se₂ thin film solar cells with solution processed metal nanowire based transparent conductor

Xiao-Hui Tan*, Gang Liu, and Ye-Xiang Liu

School of Energy Science and Engineering, Central South University, Changsha, 410083, China

Abstract

Since the traditional sputtered metal oxide thin films are not suited for using as transparent electrodes of flexible thin film solar cells and their increasing prices limit development of solar cells industry, high performance, low cost and flexible transparent conductor technology has aroused researchers’ great interests. In this paper, we successfully apply a solution processed silver nanowire composite film as the transparent electrode for Cu(In,Ga)Se₂ thin film solar cells with ZnS buffer layers. Compared with traditional sputtered window layer, the solution processed transparent electrode causes no physical damage to the adjacent device layers and junction region, which can greatly decrease the required thickness of the ZnS buffer layer. Properties of the silver nanowire composite transparent conductor and its effects on performance of Cu(In,Ga)Se₂/ZnS thin film solar cells are studied.

Keywords: CIGS thin film solar cells, metal nanowire, transparent electrodes

1. Introduction

Copper-Indium-Selenium and its alloys with Gallium (CIGS) are promising absorber materials for thin film solar cells due to high efficiency and low cost. In Solar Frontier, the CIGS manufacturing capacity is even over 1GW. Using low-cost flexible substrates enable roll-to-roll processing and can further lower the prices of CIGS solar cell products. However, the traditional sputtered electrodes are not compatible with flexible devices due to brittleness of sputtered metal oxides thin films.

Typically the CIGS thin film solar cells are fabricated with CdS buffer layers. However, the use of Cd is undesirable from viewpoint of environmental safety. During the past decade, ZnS thin films synthesized by chemical bath deposition (CBD) as buffer layers for CIGS solar cells have attracted increasing interest due to non-toxicity and wide band gap. However, the growth of ZnS thin film is complicated, and the ZnS film has defects such as film cracks and poor step coverage on the CIGS absorber, which may causes shunt paths to easily form during subsequent TCO sputter deposition [1].

* Corresponding author. Tel.: +86-18692238259.
E-mail address: tan-xh@csu.edu.cn.
Hence the performance of CIGS thin film solar cells with ZnS buffer layers is highly sensitive to the transparent conductor deposition process. In order to reduce sputtering damage to the junction region, researchers in the Nakada’s group increased buffer layer thickness to over 100nm by repeating the CBD process 2-3 times [1]. Solar Frontier uses ZnO:B grown by expensive metal-organic chemical vapor deposition (MOCVD) as the window layer for CIGS/ZnS solar cells and a relatively damage-free interface between buffer layer and absorber surface layer was obtained [2].

Here we successfully apply a solution processed silver nanowire-ITO nanoparticle (AgNW-ITONP) composite film as the transparent conducting layer for CIGS thin film solar cells with ZnS buffer layers. The optical and electrical properties of AgNW-ITONP films were studied. Significant differences in device performance between CIGS/ZnS solar cells with AgNW-ITONP electrode and conventional sputtered ITO conducting layer were also discussed.

2. Results and discussion

2.1. SEM results

Fig. 1 shows the cell structure of hydrazine solution processed CIGS solar cells with ZnS buffer layers and AgNW-ITONP transparent electrodes. The ZnS buffer layer is around 105nm thick and covers the surface of CIGS absorber. The AgNW-ITONP film is about 300nm thick and is continuous across the ZnS layer. The AgNW-ITONP film is composed of large numbers of ITO nanoparticles each with a diameter of roughly 50 nm. The AgNWs in the AgNW-ITONP film are generally tens of microns long and around 100nm in diameter. As can be seen Fig. 1, some AgNWs are not firmly attached to the surface of the ZnS layer, but the post deposited ITONPs can fully fill in and below the AgNW networks, forming a composite thin film of AgNW networks buried in ITONPs. Compared with a bare AgNW film, AgNW-ITONP composite films exhibit excellent adhesion to the underlying layer. Frequently, the conductivity of ITONP films without high temperature annealing is low due to poor electrical contact between ITO nanoparticles or agglomerates. In AgNW-ITONP composite electrodes, the AgNWs networks offer long-range conductive pathways for transporting electrons, which greatly enhance the conductivity of the ITONP thin film. In addition, since ITONPs can enter the gaps of AgNW network and attach to the surface of substrates, the charges of the adjacent layer even with large surface roughness could also be efficiently collected. Therefore the performance of AgNW-ITONP composite electrodes is not sensitive to the morphology of substrates surface.

![Fig. 1. Cross sectional scanning electron microscopy (SEM) image of CIGS solar cells with ZnS buffer layer and AgNW-ITONP transparent conductive layer.](image-url)
2.2. Optical and electrical properties of transparent conductor

Fig. 2 shows the optical transmission spectra of the AgNW-ITONP composite film (~350nm thick) and a typical sputtered ITO thin film (~120nm thick). From the transmission spectra, it can be seen that both films show transmittance of about 80%-90% in visible range. Although the AgNW-ITONP film is much thicker than sputtering ITO film, the transmittance of AgNW-ITONP film is still slightly higher than that of sputtered ITO thin film. This is probably because the sub-bandgap absorption of highly crystalline ITONPs is less than that of the amorphous sputtered film, and AgNWs exhibit minimal absorption, instead producing a small percentage of reflection in the visible and near-infrared range. On the other hand, the AgNW-ITONP electrode shows a sheet resistance of 34Ω/sq, while the sheet resistance of sputtered ITO film is 26Ω/sq, indicating comparable electrical conductivity between the two electrodes.

Fig. 2. Light transmittance spectrum of the AgNW-ITO composite film and sputtered ITO thin film.

2.3. Device performance and analysis

Table. 1 shows the dependence of device parameters on the thickness of the ZnS buffer layer. The photovoltaic performance of CIGS/ZnS solar cells with sputtered ITO improved markedly as the thickness of ZnS buffer layer was increased to 105nm-140nm. This improvement of cell performance is attributed to reduction of possible shunt paths as ZnS buffer layer thickness increases [1]. The device performance deteriorated at around a 175nm thick ZnS layer since the thick ZnS layer leads to high series resistance. For the CIGS/ZnS solar cells with AgNW-ITONP electrodes, it is interesting to note that the device reaches its best performance at thickness of ZnS layer of 35nm. The device parameters, especially $J_{sc}$ and $FF$, decrease rapidly as the thickness of ZnS layer increases. The significant differences in dependence of device performance on the thickness of the ZnS layer between cells with sputtered ITO and AgNW-ITONP electrode are mainly caused by the ZnS thin film morphological properties. The thick ZnS buffer layers always present cracks. The sputtered ITO can go into the ZnS film along the cracks, forming weak conducting paths or even forming shunting paths. However, the ITO nanoparticles can not lower the resistance of ZnS layer as sputtered ITO does due to solution process and comparatively large diameter of ITO nanoparticles. Thus thick ZnS buffer layers would only increase the series resistance of AgNW-ITONP cells. Because solution processed AgNW-ITONP film has no physical damage to the ZnS buffer layer and junction region, the optimal thickness of the ZnS buffer layer for CISS thin film solar cells is greatly decreased, which would significantly reduce industrial manufacturing cost.
Table 1. Device parameters of CIGS/AgNW-ITONP solar cells and CIGS/ITO solar cells with different thickness of ZnS buffer layers.

<table>
<thead>
<tr>
<th>Thickness of ZnS layer (nm)</th>
<th>CIGS/ZnS/sputtered ITO solar cells</th>
<th>CIGS/ZnS/AgNW-ITONP solar cells</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_{sc}$ (mA/cm²)</td>
<td>$V_{oc}$ (V)</td>
</tr>
<tr>
<td>35</td>
<td>18.7</td>
<td>0.264</td>
</tr>
<tr>
<td>70</td>
<td>26.8</td>
<td>0.402</td>
</tr>
<tr>
<td>105</td>
<td>27.2</td>
<td>0.535</td>
</tr>
<tr>
<td>140</td>
<td>26.8</td>
<td>0.528</td>
</tr>
<tr>
<td>175</td>
<td>21.4</td>
<td>0.403</td>
</tr>
</tbody>
</table>

3. Conclusions

In this study, a solution processed Ag nanowire composite film was successfully applied as transparent conducting layer for CIGS/ZnS thin film solar cells. The AgNW composite electrodes do not need high-temperature annealing post treatment and exhibit good adhesion to the underlying device layers due to introducing ITONPs. Sheet resistance and transmittance in the visible range of the AgNW-ITONP film are comparable to those of the sputtered ITO thin films. Most importantly, since the AgNW-ITONP electrodes deposition causes no physical damage to the adjacent junction materials, the optimal thickness of the ZnS buffer layers for CIGS solar cells could be greatly decreased. Although the Ag as a noble metal limits mass industrial application of AgNW film, the low-cost solution processing makes AgNW electrode still highly competitive. As the low-cost metal nanowire based technique develops (such as Ni shell/Cu core nanowire), we believe that the metal nanowire based transparent conductor would be a promising alternative for solar cells and other optoelectronic devices.

Acknowledgements

This publication was partly supported by the post doctor fund program of Central South University.

References


Biography

Xiao-Hui Tan received his Ph.D. in Optics Engineering from Zhejiang University in 2011. Now he served as research staff and post doctor in Central South University, mainly working on photovoltaic materials, devices and PV system.