



An electrochemical constructed p-Cu₂O/n-ZnO heterojunction for solar cell



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ABSTRACT

This article demonstrates a facile method to fabricate a solar cell based on p-Cu₂O/n-ZnO heterostructure, which was constructed through n-ZnO layer deposition by radio frequency magnetron sputtering and subsequent p-Cu₂O film cover by electrochemical deposition with two electrodes. The applied potential and deposition time of the Cu₂O were investigated and it was found to be critical to the morphologies, microstructure, and optical properties of the heterojunction solar cells. The current density–voltage (*J*–*V*) characteristics of p-Cu₂O/n-ZnO heterojunction solar cells were measured and show well-defined rectifying behavior. The results indicate that the crystal orientation and morphologies of the Cu₂O play key roles in photovoltaic conversion efficiency of the p-Cu₂O/n-ZnO heterojunction solar cell.

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1. Introduction

Due to the environmental pollution and ecological destruction resulted from a large amount of fossil energy consumption of the world, there is an urgent need to develop a versatile strategy to make use of the renewable clean energy. As a universal, huge reserves and pollution-free energy, solar power has attracted great attention as a potential alternative energy. Solar cells show great potential in effectively converting the sunlight to electrical power, and thus they are considered to be the most promising next-generation clean energy devices. Among the materials applied for solar cells, ZnO has a wide band-gap of 3.2 eV and a high excitation binding energy (60 meV), which lead it to be desirable for the applications in optoelectronics [1]. Nowadays, researches on ZnO nanomaterials demonstrate n-type characteristics and high quality p-type ZnO is very difficult to be obtained due to strong Fermi level pinning effects [2]. Therefore, the formation of p-ZnO/n-ZnO homojunctions faces constrained conditions [3,4]. Instead, the heterojunctions based on n-ZnO may provide another choice and relevant studies has been carried out recently [5–7]. As a p-type semiconductor material, Cu₂O exhibits properties such as nontoxicity, low cost, abundantly available, and high absorption coefficient in the visible region, which make it as a

promising material in fabricating heterojunctions [8–10]. Theoretically, the p-Cu₂O/n-ZnO photovoltaic devices offer a high energy conversion efficiency around 18% under AM 1.5 solar illumination [11]. Therefore, an enormous amount of research efforts have been devoted to the solar cells based on p-Cu₂O/n-ZnO heterojunctions [12].

At present, various methods have been used for the synthesis of Cu₂O. Among them, the electrochemical deposition (ECD) is a widely used approach for its relatively low cost and uncomplicated procedure [13]. Nowadays, the electrochemical deposition method with three electrodes is usually adopted for the preparation of p-Cu₂O/n-ZnO heterojunctions [14,15]. However, the construction of p-Cu₂O/n-ZnO heterojunctions employing two electrodes ECD is few reported. For instance, Jeong et al. [16] reported the potentiostatic electrodeposition of Cu₂O on ZnO with two electrodes, but the performance of the product as a solar cell material was not evaluated. In addition, the performance of the solar cell constructed above is not very ideal.

Here in this report, we report the construction of a solar cell based on p-Cu₂O/n-ZnO heterojunction with n-ZnO deposited by radio frequency magnetron sputtering and the following deposition of p-Cu₂O by ECD with two electrodes. The morphologies, microstructure, optical and electronic properties was found to be highly dependent on the applied potential and deposition time to form the heterojunction solar cell. The performance of the p-Cu₂O/n-ZnO heterojunction solar cells is investigated systematically.

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2. Experiment

2.1. Samples preparation

The scheme of p-Cu₂O/n-ZnO heterojunction solar cell was shown in Fig. 1. The AZO film was deposited on BK-7 glass substrate by radio frequency magnetron sputtering (a commercial ZnO and Al₂O₃ mixture (97:3 wt.%) of ≥99.99% purity as target) as our previous report [17]. And then the ZnO film was deposited on the AZO film by radio frequency magnetron sputtering. The thickness of AZO and ZnO are 500 nm and 200 nm characterized by SEM from the cross-section, respectively. Then the p-Cu₂O was deposited on ZnO using ECD method with two-electrode, where the graphite worked as counter electrode and the AZO/ZnO film on glass did as working electrode. In a typical procedure, the electrolytic solution was composed of 0.083 mol/L cupric acetate and 0.22 mol/L lactic acid which was used to stabilize the existence of Cu²⁺ in alkaline solution. The pH value (Sentek pH probe) was adjusted to 12.0 using NaOH solution with the solution stirring all the time. The electrodeposition on the ZnO/AZO glass substrate was potentiostatically carried out at 1.00 V for 90 min. Finally, 100 nm Ag film was deposited on p-Cu₂O as electrodes using thermally evaporating. The applied potential and time in depositing Cu₂O was varied as necessary.

2.2. Samples characterizations

The scanning electron microscope (SEM, JSM-7500LV), X-ray diffraction (XRD, MiniFlex II), and the double-beam spectrophotometer (Perkin Elmer Lambda 950, 0.8 nm in spectral resolution) were used to characterization. The current density–voltage (*J*–*V*) were measured by Keithley 2400 meter at room temperature under the white light at 100 mW/cm².

3. Results and discussion

3.1. The effect of applied potential in electrochemical deposition Cu₂O

To gain Cu₂O layers with high quality, we varied the applied potential in electrochemical deposition and systematically investigated the effect of potential. Fig. 2 shows the SEM images which clearly displays the morphologies of the Cu₂O layers. It can be seen that the morphologies of the Cu₂O layers is fairly different with the potential ranging from 0.95 V to 1.05 V. When the applied potential kept at 0.95 V, Cu₂O film was made of irregular grains in the size of about 2 μm (Fig. 2(a)). While the potential increased to 1.00 V, the Cu₂O film became relatively compacted and some small particles with triangle cone structure were presented on the surface (Fig. 2(b)). With applied potential further increasing to 1.05 V (Fig. 2(c)), the sharpness of grains decreased rapidly and its surface was covered by tiny particles.

To further investigate the crystallinity of Cu₂O layers deposited with different applied potential, the X-ray diffraction was performed and the corresponding XRD pattern of the three samples was shown in Fig. 3. All samples show highly-crystalline with preferential orientation toward Cu₂O (111) as well as Cu₂O (200)

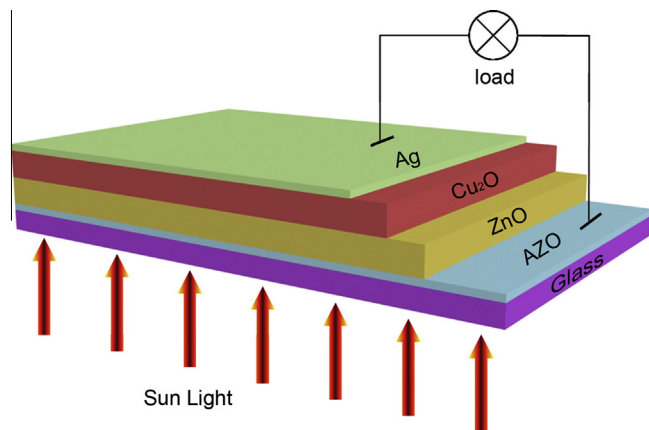


Fig. 1. The schematic diagram of the p-Cu₂O/n-ZnO heterojunction solar cell.

directions. An important point should be noted that the degree of the (111) preferred orientation of the Cu₂O layers is highly dependent on the electrodeposition potential. The intensity of the Cu₂O (111) peak reaches a highest value with deposition voltage at 1.00 V. Either increasing or decreasing the applied potential will lead to a decay of the (111) preferential orientation of the crystalline structure, and instead, tend to bring about the increase of the relative intensity of the peaks (200), (220), (311) and (110). As was discussed above, the applied potential of 1.00 V is a critical prerequisite to obtain Cu₂O layer with high performance.

3.2. The effect of growth time in electrochemical deposition Cu₂O

3.2.1. Surface morphology

Furthermore, to improve the quality of Cu₂O layer, the different deposition time in electrochemical deposition were carried out with the applied potential of 1.00 V for constant. Fig. 4(a)–(d) shows the surface morphologies of the Cu₂O with different deposition time characterized by SEM. The edges and corners were clearly observed on all samples. However, the overall morphologies depended on the deposition time. The surface was relatively smooth and the main grains were small with a triangle cone, when the growth time was short. As the growth time increased, the grain size increased and the sharp triangle cone became cube. On the other hand, the electric field intensity will rise as a result of the increasing thickness of the film due to the extension of deposition time. So Cu²⁺ will obtain more energy to corrode the surface, and the small nanoparticles will be etched. Therefore, the size of the Cu₂O nanoparticles increase as the deposition time prolong [18].

3.2.2. Structural characterization

The crystal structures of samples obtained with different deposition time were characterized by X-ray diffraction (XRD), and the corresponding X-ray diffraction pattern of the Cu₂O and ZnO was shown in Fig. 5. The diffraction peak located at 36.6° can be identified as the (002) plane of ZnO. While the rest of the diffraction peak represent the standard cubic structure of the Cu₂O [19]. The Cu₂O film is polycrystalline phase with a preferential orientation along the (111) plane. As previous reports, Cu₂O microcrystallines with (111) plane would have better photocatalytic activity [20,21]. The atomic arrangement of the ZnO (002) plane is similar to that of the Cu₂O (111) plane, and their lattice mismatch is merely 7.1%, which is much smaller than that of 31.4% between the ZnO (002) plane and the Cu₂O (200) plane [22]. In addition, the intensity of the Cu₂O (111) peak enhances with the growth time increase from 60 to 120 min and then decreases while the growth time continues to 150 min, suggesting that the Cu₂O has best crystallinity when the deposited time was 120 min. It clearly shows the degree of the (111) preferred orientation of the Cu₂O layers depend on the electrodeposition time. The emergence of ZnO (002) plane with growth time of 150 min is due to the reduction of the Cu₂O (111) peak intensity.

The mean grain size (*d_g*) can be calculated by the Scherrer formula [23]:

$$d_g = \frac{0.89\lambda}{\beta_{1/2} \cos \theta}$$

In the formula, λ , θ , and $\beta_{1/2}$ represents X-ray wavelength, Bragg diffraction angle, and full width at half maximum of diffraction peak, respectively. Therefore, the grain size of the Cu₂O can be calculated, to be approximately 28.1 nm, 33.3 nm, 24.5 nm, and 23.0 nm with deposited time at 60 min, 90 min, 120 min, and 150 min respectively. It was reported that the different grain size contains different dislocation defects, which have a great effect on the electronic property of heterojunction [24].

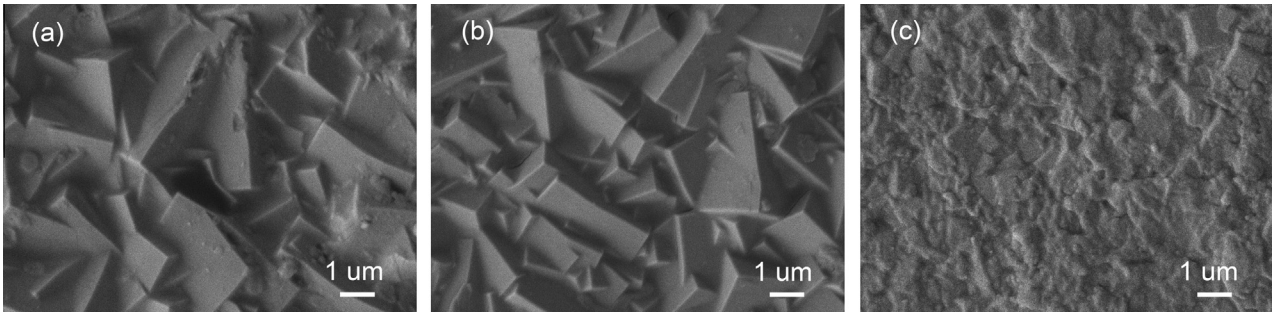


Fig. 2. SEM image of Cu₂O layers after 2 h deposition at different applied potential (a) 0.95 V, (b) 1.00 V, (c) 1.05 V.

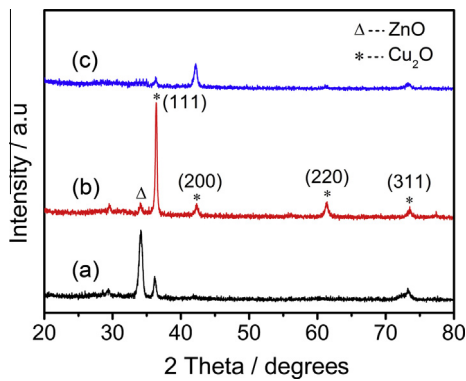


Fig. 3. X-ray diffraction spectra for ZnO on AZO substrate after stacking Cu₂O layers at (a) 0.95 V; (b) 1.00 V; (c) 1.05 V, respectively.

3.2.3. Optical property

Fig. 6(a) shows the absorbance spectra of the ZnO/AZO substrate and p-Cu₂O/n-ZnO heterostructures with the Cu₂O deposited with different time. It can be seen that the optical absorption of

ZnO/AZO substrate is high at the wavelength below 380 nm, which correspond to the bandgap energy of ZnO thin film [25]. After depositing Cu₂O on ZnO/AZO substrate, the absorption spectra significantly change, and the absorption range red-shifts to the visible light, which was probably ascribed to the variation of crystallinity and crystalline size of the Cu₂O [26]. Hence, the band gap (E_g) of the Cu₂O deposited at different time can be estimated by extrapolating the linear $(\alpha h\nu)^2$ versus $h\nu$ plots to the photon energy axis intercept. The E_g are about 2.08 eV, 2.05 eV, 2.11 eV, and 2.19 eV respectively when the deposition time increased from 60 min, 90 min, 120 min to 150 min, as shown in Fig. 6(b), which are consistent with previous reports (1.87–2.21 eV) [27,28]. The crystallinity, growth orientation, crystal size will affect the band gap of the Cu₂O film. And a suitable band gap is necessary to obtain high photovoltaic conversion efficiency.

3.2.4. J–V characteristics of p-Cu₂O/n-ZnO heterojunctions

In order to visualize the performance of the p-Cu₂O/n-ZnO heterojunction solar cells, we conducted the current density–voltage (J–V) characterization of heterojunction solar cells using Keithley 2400 at room temperature under the sun light at

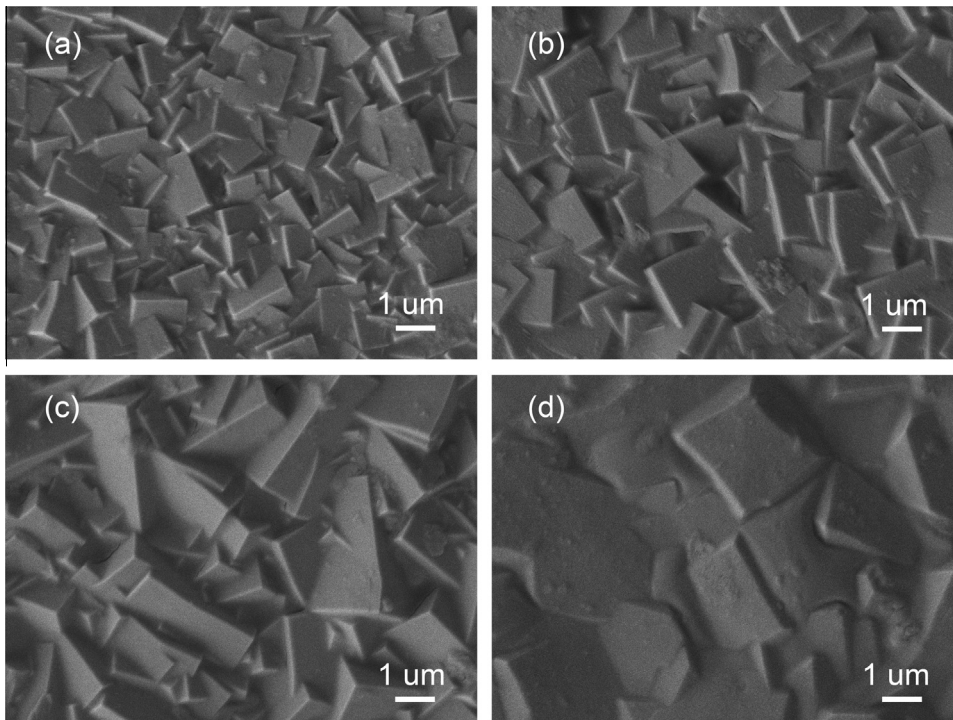


Fig. 4. SEM images of p-Cu₂O/n-ZnO heterostructures with the Cu₂O deposited by different time: (a) 60 min, (b) 90 min, (c) 120 min, (d) 150 min.

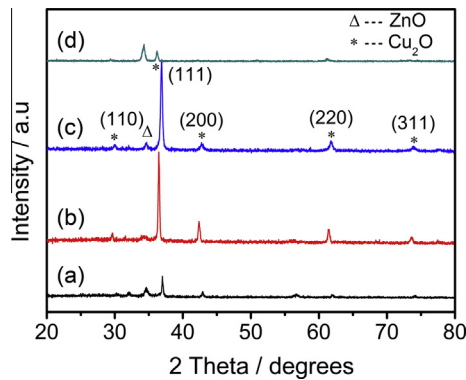


Fig. 5. X-ray diffraction of the p-Cu₂O/n-ZnO heterostructures with the Cu₂O deposited by different time: (a) 60 min, (b) 90 min, (c) 120 min, (d) 150 min.

100 mW/cm² (500 W mercury lamp as light source) or in the dark. The corresponding current density–voltage curves are shown in Fig. 7. The solar cells exhibit significant rectification properties as shown in Fig. 7(a) in the dark, indicating that a p–n junction are formed. Fig. 7(b) shows the current density–voltage curves of the p-Cu₂O/n-ZnO heterojunction solar cells under the sun light at 100 mW/cm², it can be seen that the short-circuit current are about 2–5 mA/cm², while the open circuit voltage are in a range of 0.2–0.3 V. The detail parameters of p-Cu₂O/n-ZnO heterojunction solar cells are calculated and the details can be found in Table 1.

As can be seen from Table 1, the performance of the p-Cu₂O/n-ZnO heterojunctions solar cell is dependent on the

deposition time of Cu₂O. The short-circuit current density (J_{SC}) increase from 2.18 mA/cm² to 4.85 mA/cm², when the deposition time of the Cu₂O increase from 60 min to 120 min, and then decrease to 2.46 mA/cm² when the deposition time of the Cu₂O prolong to 150 min. Meanwhile, the open-circuit voltage (V_{OC}) and the fill factor (FF) have the same variation trends. The best performance of the heterojunction solar cell shown photovoltaic conversion efficiency (PCE) is about 0.520%, with J_{SC} , V_{OC} , and FF being 4.85 mA/cm², 277 mV, and 38.78%, respectively, when the Cu₂O deposited with the applied potential of 1.00 V for 120 min. It was worthy to be noted that when the Cu₂O deposited with the applied potential of 1.00 V for 120 min, the Cu₂O has the highest intensity of the preferential orientation along the (111) plane with large grain size and the sharp triangle cone as shown in XRD (Fig. 4) and SEM images (Fig. 5). Therefore, it is proposed that the crystal orientation and morphology of Cu₂O played a significant role in photovoltaic conversion efficiency. To further enhance the performance, a suitable preparation conditions of the Cu₂O is necessary to be explored. To our best knowledge, Wei et al. [29] have constructed p-Cu₂O/n-ZnO heterojunction solar cells in the same way. They obtained solar cells constructed with p-Cu₂O

Table 1

The detail parameters of p-Cu₂O/n-ZnO heterojunction solar cells.

Deposition time	60 min	90 min	120 min	150 min
J_{SC} (mA/cm ²)	2.18	4.22	4.85	2.46
V_{OC} (mV)	260	261	277	235
FF (%)	31.51	28.38	38.78	43.22
PCE (%)	0.179	0.313	0.520	0.250

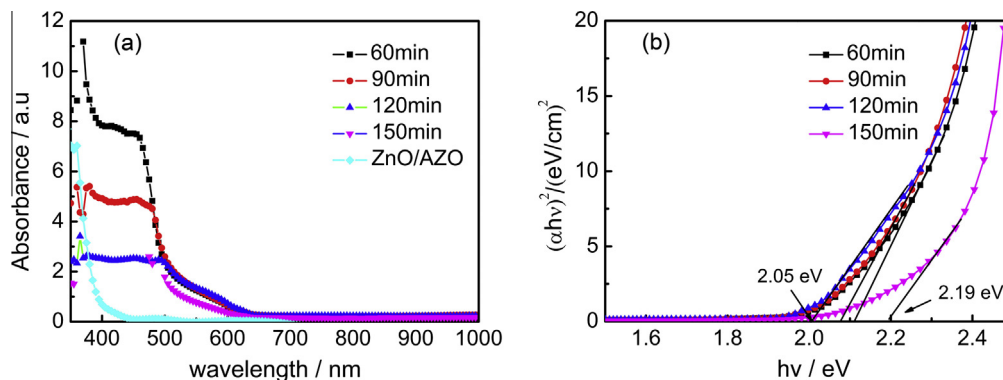


Fig. 6. (a) Absorbance spectra of ZnO/AZO substrate and p-Cu₂O/n-ZnO heterostructures with the Cu₂O deposited by different time and (b) Optical absorption spectra of Cu₂O drawn as plots of α^2 versus photon energy $h\nu$.

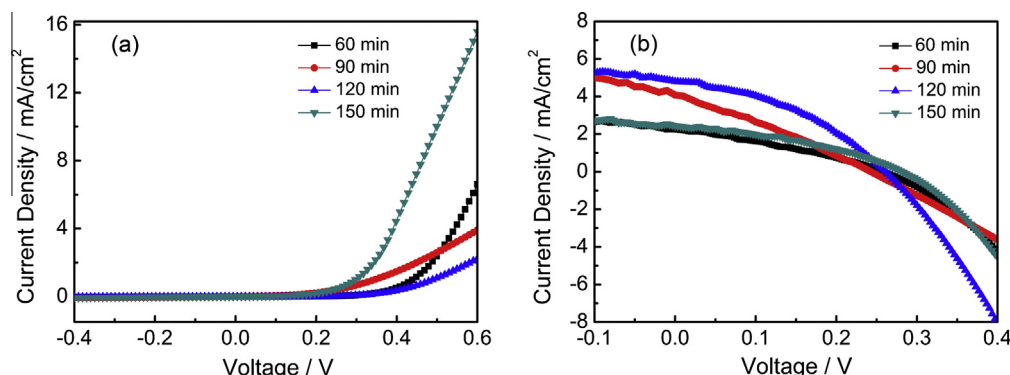


Fig. 7. Current density–voltage curves of p-Cu₂O/n-ZnO heterostructures with the Cu₂O deposited by different time in the dark (a) and under AM 1.5 illumination (b).

film/n-ZnO film, p-Cu₂O film/n-ZnO nanorod and p-Cu₂O film/n-ZnO nanotubes, and the photovoltaic conversion efficiency are 0.02%, 0.13% and 0.11% respectively.

4. Conclusions

The p-Cu₂O/n-ZnO heterojunction solar cell were designed and fabricated. The applied potential and deposition time of the Cu₂O layer with electrochemical deposition method were investigated systematically. The Cu₂O film is polycrystalline phase with a best preferential orientation along the (111) plane in the applied potential of 1.00 V and 120 min to deposit the Cu₂O. The current density–voltage (*J*–*V*) characteristics of p-Cu₂O/n-ZnO heterojunction solar cells were investigated and all show well-defined rectifying behavior. The best photovoltaic conversion efficiency is 0.52% in p-Cu₂O/n-ZnO heterojunction solar cell which contained the highest intensity of the preferential orientation along the (111) plane with large grain size and the sharp triangle cone.

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