Fabrication and characterization of copper oxide-zinc oxide solar cells prepared by electrodeposition

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Abstract. Copper oxide-based heterojunction solar cells were fabricated by electrodeposition, and the electronic and optical properties were investigated. ZnO was used as an n-type semiconductor, and copper oxides were used as p-type semiconductors. A photovoltaic device based on an FTO/ZnO/Cu$_2$O heterojunction structure provided short-circuit current density of 2.7 mA cm$^{-2}$ and open circuit voltage of 0.28 V under an air mass 1.5 illumination. Microstructures of the solar cells were investigated by scanning electron microscope and X-ray diffraction, which indicated formation of copper oxides and ZnO. Energy levels of the solar cells were discussed.

1. Introduction

Copper oxide semiconductors are a promising alternative to silicon-based solar cells because Cu$_2$O possess high optical absorption and composed of low cost materials. Cu$_2$O is one of suitable materials for high efficiency solar cells because their band gap of ~1.5 and ~2.1 eV, respectively, are close to the ideal energy gap, and well matched with a solar spectrum. A maximum efficiency of ~3.8 % has been obtained for Cu$_2$O solar cells using high-temperature annealing and pulse laser deposition technique [1].

The purpose of the present work was to fabricate Cu$_2$O/ZnO and CuO/ZnO thin film solar cells by electrodeposition, and to investigate the effect of Cu$_2$O and ZnO layers on their electronic properties. ZnO has been used for a good electron acceptor and n-type semiconductor for Cu$_2$O/ZnO heterojunction solar cells [2-5]. The electrodeposition method has advantages of low cost and low temperature methods. Cu$_2$O and CuO thin films prepared by the electrodeposition method have also been reported previously [6-8]. Cu$_2$O or CuO/ZnO solar cells in the present study were investigated by measurements of optical absorption and photovoltaic activity.

2. Experimental

Cu$_2$O and CuO layers were prepared on pre-cleaned indium tin oxide (ITO) glass plate by electrodeposition using platinum counter electrode. Copper (II) sulfate (CuSO$_4$, 0.4 mol L$^{-1}$, Wako 97.5 %) and L-lactic acid (3 mol L$^{-1}$, Wako) were dissolved into distilled water. Electrolyte pH was adjusted to 12.5 by adding NaOH. The electrolyte temperature was kept at 65 °C during electrodeposition. Preparation of Cu$_2$O layers were carried out at current density at 1.5 mA cm$^{-2}$ and quantity of electric charge of 4.0 C cm$^{-2}$. ZnO layers were also galvanostatically prepared at current...
density at 5 and 10 mA cm\(^{-2}\) from 8 mM aqueous solution of Zn(NO\(_3\))\(_2\) on Cu\(_2\)O layers. Electric charge was adjusted 1.5 C cm\(^{-2}\). Gold (Au) metal contacts were vacuum deposited as top electrodes. Structure of heterojunction solar cells were shown in Figure 1 (a) and 1 (b), which were denoted as ITO or FTO/ZnO/CuO or Cu\(_2\)O/Au.

![Figure 1](image)

**Figure 1.** Structures of (a) ZnO/Cu\(_2\)O and (b) ZnO/CuO heterojunction solar cells.

Current density-voltage (J-V) characteristics (Hokuto Denko, HSV-110) of the solar cells were measured both in the dark and under illumination at 100 mW cm\(^{-2}\) by using an AM 1.5 solar simulator (San-ei Electric, XES-301S). The solar cells were illuminated through the side of the ITO substrates, and the illuminated area was 0.16 cm\(^2\). Optical absorption of the solar cells was investigated by means of UV visible spectroscopy (Jasco, V-670). The incident photon to current conversion efficiency (IPCE) of solar cells of investigated (Peccell technologies, PEC-S20). The microstructures of the copper oxides were investigated by X-ray diffractometer (XRD, Philips, X’Pert-MPD System) with CuK\(_\alpha\) radiation operating at 40 kV and 40 mA, and scanning electron microscope (SEM) operating at 15 kV (Jeol, JEM-6380).

### 3. Results and discussion

J-V characteristics of ZnO/Cu\(_2\)O structure under illumination at 100 mW cm\(^{-2}\) by using an AM 1.5 solar simulator are shown in Figure 2. The photocurrent was observed under illumination, and the CuO/ZnO structure showed characteristic curves with short-circuits current and open-circuit voltage. A solar cell with a FTO/ZnO/Cu\(_2\)O structure provided power conversion efficiency (\(\eta\)) of 0.25 %, fill factor (FF) of 0.33, and short-circuit current density (\(J_{SC}\)) of 2.7 mA cm\(^{-2}\) and open-circuit voltage (\(V_{OC}\)) of 0.28 V. Measured parameters of the present copper oxides-based solar cells are summarized in Table 1.

**Table 1.** Measured parameters of the present solar cells.

| Sample | \(V_{OC}\) (V) | \(J_{SC}\) (mA cm\(^{-2}\)) | FF   | \(\eta\) (%) |
|--------|----------------|----------------------------|------|--------------|
| ITO/ZnO(10 mA cm\(^{-2}\))/Cu\(_2\)O | 0.063          | 0.45                       | 0.26 | 7.3\times10\(^{-3}\) |
| ITO/ZnO(5 mA cm\(^{-2}\))/Cu\(_2\)O | 0.20           | 1.38                       | 0.26 | 6.9\times10\(^{-2}\) |
| FTO/ZnO(5 mA cm\(^{-2}\))/Cu\(_2\)O | 0.28           | 2.7                        | 0.33 | 0.25         |
| ITO/ZnO(5 mA cm\(^{-2}\))/CuO    | 0.017          | 2.4\times10\(^{-3}\)     | 0.25 | 1.0\times10\(^{-5}\) |
Figure 2. J-V characteristics of solar cells with ITO or FTO/ZnO(5 mA cm\(^{-2}\) or 10 mA cm\(^{-2}\))/Cu\(_2\)O(1.5 mA cm\(^{-2}\))/Au structures in the under AM 1.5 illumination.

Figure 3 shows optical absorption of the Cu\(_2\)O, ZnO and CuO thin films. Absorption peaks at \(\sim\)360 nm and \(\sim\)530 nm were due to CuO, and peaks at \(\sim\)330 nm and \(\sim\)470 nm were due to Cu\(_2\)O thin film, and a peak at \(\sim\)350 nm corresponded to ZnO.

Figure 3. Absorption spectra of active layers

Figure 4. IPCE spectrum of solar cell with ZnO/Cu\(_2\)O structure.
An IPCE spectrum of a solar cell with the ZnO/Cu$_2$O structure is shown in Figure 4. The IPCE profile well corresponds to absorption spectra of ZnO and Cu$_2$O thin films, which indicated that excitons form effectively at active layers by illumination of light.

All the crystalline components in the Cu$_2$O, CuO and ZnO thin films were investigated by XRD, as shown in Figure 5 (a), (b) and (c). Diffraction peaks corresponding to Cu$_2$O and CuO and ZnO were observed for the Cu$_2$O and CuO and ZnO thin films, and they consisted of cuprite phase with cubic system (space group of Pn3m and lattice parameter of $a = 0.427$ nm) and cupric phase with monoclinic system (space group of C2/c and lattice parameter of $a = 0.433$ nm, $b = 0.343$ nm, $c = 0.509$ nm) and hexagonal system (space group of P63mc and lattice parameter of $a = 0.326$ nm, $c = 0.522$ nm). As current density increased which ZnO (002) orientation raised. The fact observed influence of c axis growth by electrodeposition. The particle size was estimated using Scherrer’s equation: $D = 0.9 \lambda / B \cos \theta$, where $\lambda$, $B$, and $\theta$ represent the wavelengths of the X-ray source, the full width at half maximum, and the Bragg angle, respectively. The crystallite sizes of Cu$_2$O and CuO and ZnO were determined to be 53.0 nm, 20.0 nm and 52.0 nm, respectively.

**Figure 5.** XRD pattern of (a) Cu$_2$O and (b) CuO thin films and (c) ZnO thin film prepared under different currents by electrodeposition.
Figures 6 (a) and (b) are SEM images of Cu2O and ZnO thin films and (c) is cross-section image of FTO/ZnO/Cu2O thin film, respectively. The SEM image indicated Cu2O and growth of ZnO polycrystals with sizes of 2.5 µm and 1~2 µm, respectively. The cross-section indicated of Cu2O and ZnO film thicknesses are ~2.5 µm and ~ 2.0 µm, respectively.

Figure 6. SEM image of (a) Cu2O and (b) ZnO and (c) cross section of ZnO/Cu2O thin films.

Energy level diagram of ZnO/Cu2O and ZnO/CuO solar cells is summarized as shown in Fig. 7 (a) and 7 (b). Previously reported values were used for the energy levels [9-14]. It has been reported that $V_{OC}$ is nearly proportional to the band gap of the semiconductors [15], and control of the energy levels is important to increase efficiency.
Cu$_2$O and CuO based solar cells prepared by an electrodeposition method were investigated in the present work. The low conversion efficiency of the present solar cells would be due to large thickness of ZnO thin films. Optimization of thickness of active layers could increase the efficiency of the solar cells.

4. Conclusion

ZnO/Cu$_2$O/Au and ITO/ZnO/CuO/ heterojunction solar cells were produced and characterized. A device based on the ZnO/Cu$_2$O structure fabricated by an electrodeposition method which provided $\eta$ of 0.25 $\%$, FF of 0.33 , $J_{sc}$ of 2.7 mAcm$^{-2}$ and $V_{oc}$ of 0.28 V. XRD indicated active layer deposited and orientation. As current density increased ZnO (002) orientation raised. The fact observed influence of c axis growth by electrodeposition. C axis growth would influence interfacial area lead to decrease of $V_{oc}$. Optimization of electrodeposition condition would improve the efficiencies of the solar cells.

Acknowledgements

The authors would like to thank Profs. B. Jeyadevan and H. Miyamura for support of XRD and SEM.

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