

Article

## Microstructures and Photovoltaic Properties of Zn(Al)O/Cu<sub>2</sub>O-Based Solar Cells Prepared by Spin-Coating and Electrodeposition

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**Abstract:** Copper oxide (Cu<sub>2</sub>O)-based heterojunction solar cells were fabricated by spin-coating and electrodeposition methods, and photovoltaic properties and microstructures were investigated. Zinc oxide (ZnO) and Cu<sub>2</sub>O were used as n- and p-type semiconductors, respectively, to fabricate photovoltaic devices based on In-doped tin oxide/ZnO/Cu<sub>2</sub>O/Au heterojunction structures. Short-circuit current and fill factor increased by aluminum (Al) doping in the ZnO layer, which resulted in the increase of the conversion efficiency. The efficiency was improved further by growing ZnO and Cu<sub>2</sub>O layers with larger crystallite sizes, and by optimizing the Al-doping by spin coating.

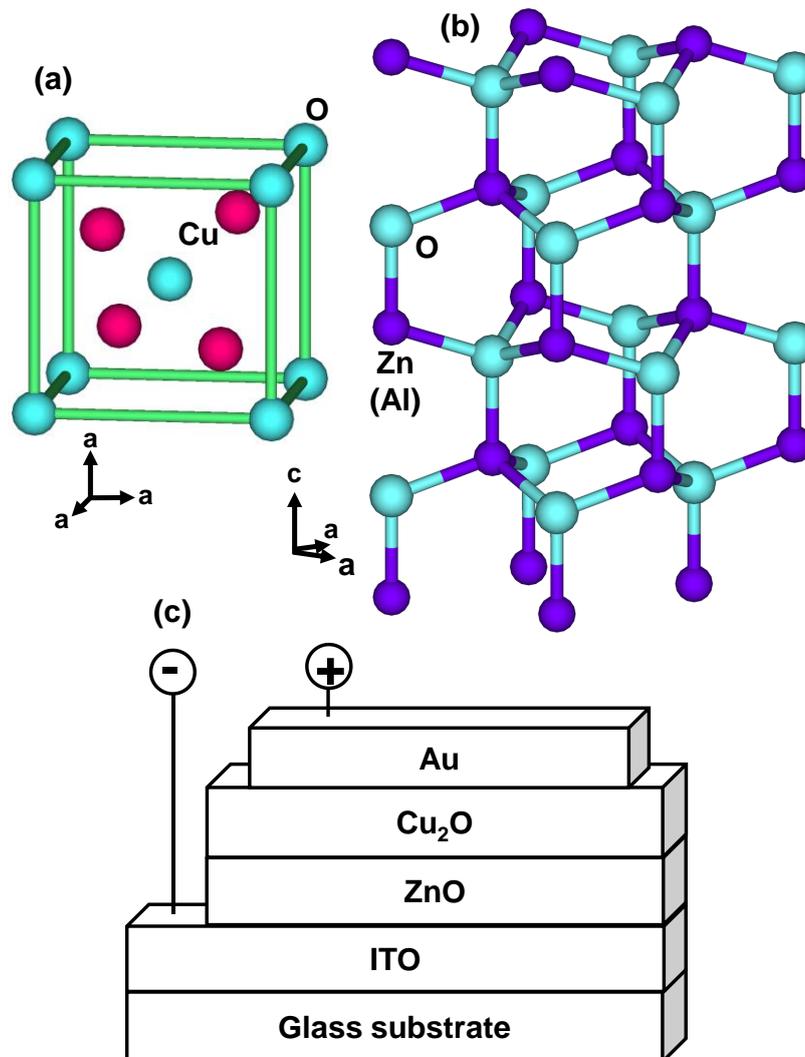
**Keywords:** Cu<sub>2</sub>O; ZnO; photovoltaic cell

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### 1. Introduction

Semiconductor oxides are a promising alternative to silicon based solar cells as they possess high optical absorption, nontoxicity, and have low production costs. Copper oxides (Cu<sub>2</sub>O) are known to be p-type semiconductor oxides, and the crystal structure of Cu<sub>2</sub>O is cubic system with a space group of Pn3m [1], as shown in Figure 1a. The Cu<sub>2</sub>O is a suitable material for high efficiency solar cells because of its direct bandgap of 2.1 eV.

**Figure 1.** Crystal structures of (a)  $\text{Cu}_2\text{O}$  and (b)  $\text{ZnO}$ ; (c) Device structure of  $\text{ZnO}/\text{Cu}_2\text{O}$  heterojunction solar cells.



A maximum efficiency of 5.38% has been obtained for  $\text{Cu}_2\text{O}$  solar cells fabricated by high-temperature annealing and pulsed laser deposition [2].  $\text{Cu}_2\text{O}$ -based solar cells fabricated by electrodeposition and photochemical deposition have been reported [3–12], and zinc oxide ( $\text{ZnO}$ )/ $\text{Cu}_2\text{O}$  thin film solar cells prepared by electrodeposition have also been reported [13–22]. Electrodeposition is a low-temperature method for solar cell fabrication with a low process cost. Izaki *et al.* [3] reported high conversion efficiency of 1.28% for electrodeposited  $\text{ZnO}/\text{Cu}_2\text{O}$  solar cells using an electrolyte containing KOH for  $\text{Cu}_2\text{O}$  deposition. Conversion efficiencies of 1.06 and 0.88% were also reported for p- $\text{Cu}_2\text{O}/\text{n-Cu}_2\text{O}$  [12] and  $\text{ZnO}/\text{Cu}_2\text{O}$  [11] solar cells prepared by electrodeposition. Progress of the conversion efficiency up to 1.43% for electrodeposited  $\text{ZnO}/\text{Cu}_2\text{O}$  solar cells was also reported by using an electrolyte containing LiOH for  $\text{Cu}_2\text{O}$  deposition [23].

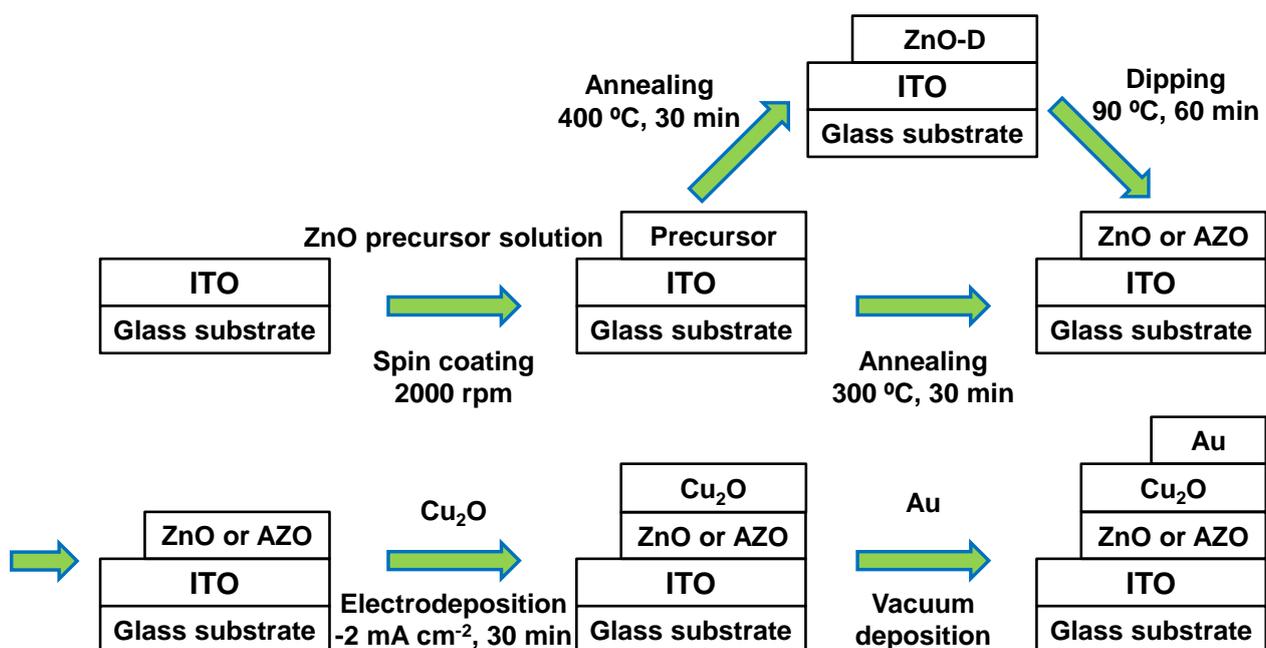
The purpose of the present work was to fabricate  $\text{ZnO}/\text{Cu}_2\text{O}$  thin-film solar cells by spin-coating and electrodeposition and to investigate the effect of doping element into the  $\text{ZnO}$  layers.  $\text{ZnO}$  is a good electron acceptor with a hexagonal crystal system (space group P63mc) [24] as shown in Figure 1b, and has been used as an n-type semiconductor active layer for inorganic thin-film solar cells [25–30]. To improve the carrier transport in the  $\text{ZnO}$  structure, aluminum (Al) was selected in the present work

for doping element at the Zn sites in the ZnO structure. The Al-doped ZnO (AZO) materials have also been reported for solar cell materials [31–35]. Spin coating is a low-cost method, and electrodeposition is a method for homogeneous thin film formation, which is essential for the mass production of any solar cells. The low cost methods have been already reported [3,36,37], and the spin coating of Al-doped ZnO in the present work would be also one of the useful and easy fabrication methods. In the present work, The ZnO/Cu<sub>2</sub>O solar cells prepared in the present study were investigated by structural analysis, optical absorption, and photovoltaic measurements.

## 2. Experimental Procedures

A thin layer of zinc oxide (ZnO) was prepared by a sol-gel method [38,39]. A 2-methoxyethanol (0.97 mL, Wako, Osaka, Japan) solution containing zinc acetate dihydrate (0.1098 g/mL, Wako, 99%) and monoethanolamine (0.03 mL, Nacalai Tesque, Kyoto, Japan) was spin-coated at 2000 rpm on a pre-cleaned indium-doped tin oxide (ITO, Xin Yan Technology, Kowloon, Hong Kong,  $\sim 10 \Omega/\square$ ) glass substrate. Aluminum nitrate enneahydrate (0.105 g, Wako, 98.0%) was also added into the above solution to form AZO layers with a composition of Al<sub>3</sub>Zn<sub>97</sub>. To form ZnO layers by a dipping method (ZnO-D), the spin-coated and annealed sample was also dipped in a solution (50 mL) of zinc nitrate hexahydrate (0.185 g, Wako, 99%) and hexamethylenetetramine (0.0876 g, Nacalai Tesque, Kyoto, Japan) at 90 °C for 60 min, and rinsed by distilled water and dried in air. Then, the ZnO layers were annealed at 300 °C for 60 min. The device process is schematically illustrated in Figure 2. The film thicknesses were measured by an atomic force microscope (AFM, SPA400-AFM, Hitachi High-Technologies, Tokyo, Japan), and the thickness of the ZnO and AZO was  $\sim 200$  nm.

**Figure 2.** Device fabrication process ZnO/Cu<sub>2</sub>O heterojunction solar cells.



A Cu<sub>2</sub>O layer was prepared on the ZnO layer by electrodeposition method using a platinum counter electrode. Copper (II) sulfate (CuSO<sub>4</sub>, 5.107 g, Wako, 97.5%) and L-lactic acid (80 mL, Wako) were dissolved in distilled water. The pH of the electrolyte was adjusted to 12.5 by the addition of NaOH (Wako). The electrolyte temperature was kept at 65 °C during electrodeposition. The electrodeposition of Cu<sub>2</sub>O layer was carried out at a current density of 2 mA cm<sup>-2</sup> using a potentio/galvanostat (Model 1110, Husou, Kanagawa, Japan). The film thickness of the Cu<sub>2</sub>O layer was measured to be ~1.5 μm. Gold (Au) metal contacts were deposited as top electrodes. The structure of the heterojunction solar cells is thus ITO/ZnO/Cu<sub>2</sub>O/Au, which is shown in Figure 1c as a schematic illustration.

Current density–voltage (J-V) characteristics of the solar cells were measured (HSV-110, Hokuto Denko, Tokyo, Japan) in the dark and under illumination at 100 mW cm<sup>-2</sup> using an AM 1.5 solar simulator (XES-301S, San-ei Electric, Osaka, Japan). The solar cells were illuminated through the side of the FTO substrates and the illuminated area was 0.16 cm<sup>2</sup>. Optical absorption of the thin films was investigated by UV–visible spectroscopy (V-670, Jasco, Tokyo, Japan) using the reflection spectra, and the thin films were illuminated through the side of the ITO substrates. The microstructures of the solar cells were investigated by X-ray diffractometry (X'Pert-MPD System, Philips, Amsterdam, The Netherlands) with CuKα radiation operating at 40 kV and 40 mA.

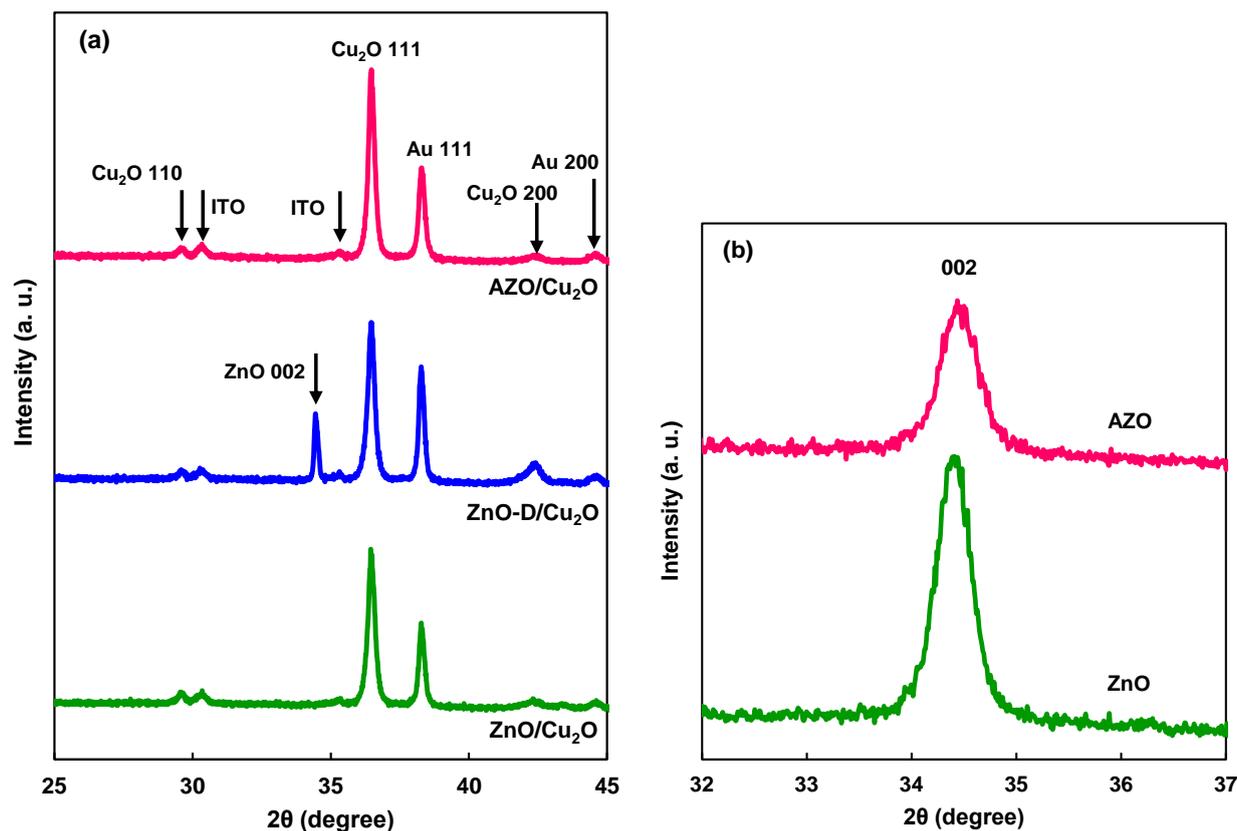
### 3. Results and Discussion

X-ray diffraction (XRD) patterns of ZnO/Cu<sub>2</sub>O-based solar cells are shown in Figure 3a. Diffraction peaks due to Cu<sub>2</sub>O, ZnO, Au electrode and ITO substrate are observed in the XRD pattern. A strong diffraction peak of ZnO 002 is observed only for the ZnO-D/Cu<sub>2</sub>O cell, which indicates the highly-oriented c-axis of ZnO perpendicular to the ITO substrate. No sharp peak due to ZnO was observed for the ZnO/Cu<sub>2</sub>O and AZO/Cu<sub>2</sub>O solar cells.

To investigate the microstructure of ZnO, XRD patterns of spin-coated ZnO and AZO thin films prepared on the glass plates were also measured as shown in Figure 3b, which indicates 002 diffraction peaks of ZnO and AZO. Lattice constants and crystallite sizes of ZnO are summarized as listed in Table 1, and the crystallite sizes were 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. A crystallite size of ZnO in the ZnO-D sample is the largest, which indicates the crystal growth of ZnO during annealing and dipping the substrate. A lattice constant  $c$  of ZnO in the AZO sample is the smallest, which suggests Al doping at the Zn sites in the ZnO crystal because the ionic radius of Al<sup>3+</sup> (0.054 nm) is smaller compared with that of Zn<sup>2+</sup> (0.074 nm).

Table 2 shows lattice constants and crystallite sizes of Cu<sub>2</sub>O determined from the XRD measurements. All cells have almost the same lattice constants as the reported Cu<sub>2</sub>O structure [1], which indicates the high crystallinity of the present Cu<sub>2</sub>O layers. Diffraction intensity ratios  $I_{111}/I_{200}$  of Cu<sub>2</sub>O on the ZnO for all the devices were larger compared to the normal randomly oriented powder samples. As listed in Table 2, Cu<sub>2</sub>O crystals on the AZO are highly oriented along the [111] direction. The crystallite size of the Cu<sub>2</sub>O on the ZnO-D was found to be the largest compared with those of other cells.

**Figure 3.** X-ray diffraction (XRD) patterns of (a) Cu<sub>2</sub>O-based solar cells and (b) ZnO and Al-doped ZnO (AZO) thin films.



**Table 1.** Lattice constants and crystallite sizes of ZnO.

ZnO formation	Lattice constant <i>c</i> (nm)	Crystallite size (nm)
ZnO	0.5211	25
ZnO-D	0.5208	104
AZO	0.5203	22
ZnO [24]	0.52066	–

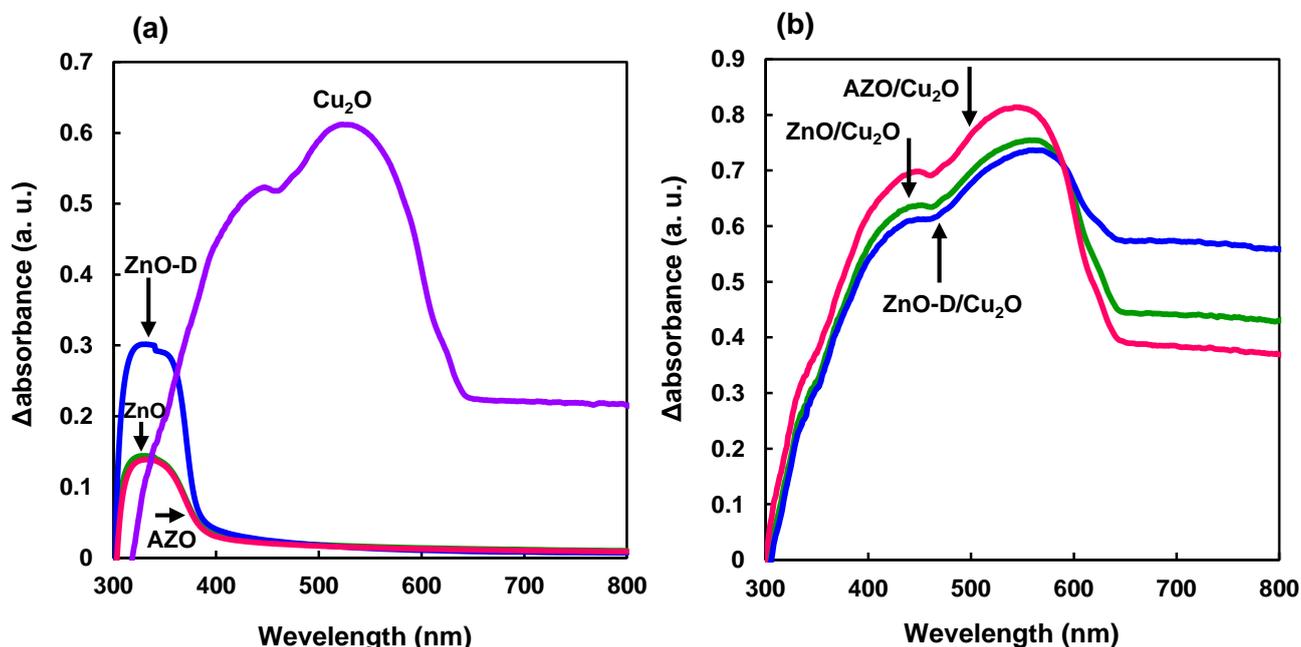
**Table 2.** Lattice constants and crystallite sizes of Cu<sub>2</sub>O.

Cu <sub>2</sub> O formation	Lattice constant <i>a</i> (nm)	Crystallite size (nm)	I <sub>111</sub> /I <sub>200</sub>
Cu <sub>2</sub> O on ZnO	0.4268	52	19.9
Cu <sub>2</sub> O on ZnO-D	0.4268	189	8.63
Cu <sub>2</sub> O on AZO	0.4268	86	35.7
Cu <sub>2</sub> O [1]	0.42696	–	2.7

Figure 4a shows optical absorption of the Cu<sub>2</sub>O and ZnO thin films. Absorption edges at ~630 nm and ~390 nm in Figure 4a are due to Cu<sub>2</sub>O and ZnO structure, which correspond to energy gaps of ~2.0 and ~3.2 eV, respectively. Figure 4b shows the optical absorption of the solar cells. The ZnO/Cu<sub>2</sub>O structures show high absorption in the range of 400–600 nm, which are due to Cu<sub>2</sub>O crystals. The origin of the absorption background observed above the wavelength of ~650 nm might be light scattering by Cu<sub>2</sub>O grains with the large grain size. The reason for the variation in its dependence

on types of ZnO would be due to the film thickness. The absorbance difference of the three types of solar cells would be related to the  $I_{111}$  orientations of  $\text{Cu}_2\text{O}$  grains. As the  $I_{111}$  orientations of  $\text{Cu}_2\text{O}$  layers increased, the absorptions also increased, which would be due to the light confinement by the arrangement of the  $\text{Cu}_2\text{O}$  grain with preferred orientations.

**Figure 4.** Optical absorption of (a)  $\text{Cu}_2\text{O}$ , ZnO, ZnO-D and AZO and (b) ZnO/ $\text{Cu}_2\text{O}$ -based solar cells.



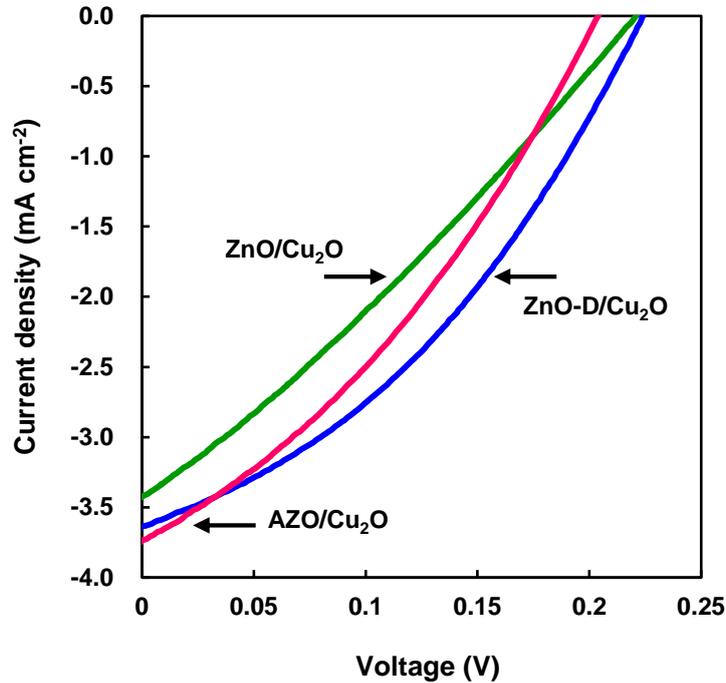
The J-V characteristics of the ZnO/ $\text{Cu}_2\text{O}$  structures under illumination at  $100 \text{ mW cm}^{-2}$  obtained using an AM 1.5 solar simulator are shown in Figure 5. The photocurrent was observed under illumination, and the ZnO/ $\text{Cu}_2\text{O}$  structure showed characteristic curves with regard to the short-circuit current and open-circuit voltage. A solar cell with the ITO/ZnO-D/ $\text{Cu}_2\text{O}$ /Au structure provided the highest power conversion efficiency ( $\eta$ ) of 0.30%, a fill factor (FF) of 0.37, a short-circuit current density ( $J_{\text{SC}}$ ) of  $3.6 \text{ mA cm}^{-2}$ , and an open-circuit voltage ( $V_{\text{OC}}$ ) of 0.24 V. The measured parameters of these ZnO/ $\text{Cu}_2\text{O}$ -based solar cells are summarized in Table 3.

An energy level diagram of the present ZnO/ $\text{Cu}_2\text{O}$ -based solar cells is summarized as shown in Figure 6. Measured and previously reported values were used for the energy levels [6,7]. Light was irradiated from the ITO substrate side, and was absorbed in the  $\text{Cu}_2\text{O}$  layer. Charges were excited in the  $\text{Cu}_2\text{O}$  layer, and were separated at the ZnO/ $\text{Cu}_2\text{O}$  interface. Electrons are transported to the ITO substrate, and holes are transported to the Au electrode. It has been reported that  $V_{\text{OC}}$  is nearly proportional to the band gap of the semiconductors [22], and control of the energy levels is important to increase efficiency.

In the present work, Al-doping to ZnO and dipping method for ZnO after spin-coating ZnO were found to be effective in improving the conversion efficiency of the ZnO/ $\text{Cu}_2\text{O}$  solar cells. The Al-doping at the Zn sites in the ZnO structure improve the carrier transport in the ZnO structure, which would result in the increase of short-circuit current as listed in Table 3. In addition, the  $\text{Cu}_2\text{O}$  prepared

on the AZO provided the highest  $I_{111}/I_{200}$ , which indicates the formation of the highest {111}-oriented  $\text{Cu}_2\text{O}$  crystallites.

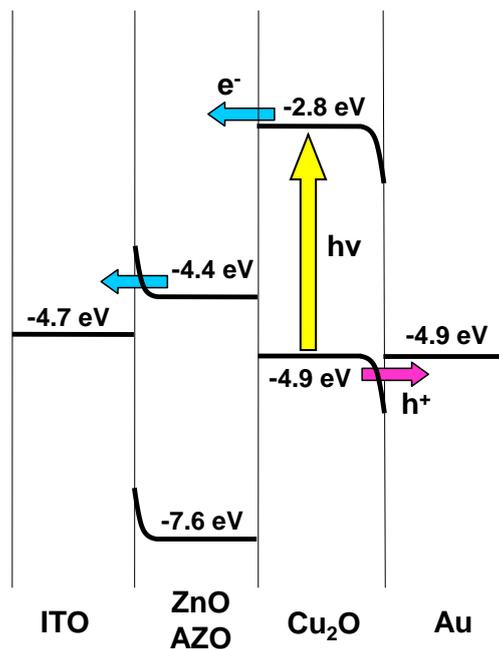
**Figure 5.** J-V characteristic of ZnO/ $\text{Cu}_2\text{O}$ -based solar cells.



**Table 3.** Measured parameters of the present ZnO/ $\text{Cu}_2\text{O}$ -based solar cells.

Devices	$J_{SC}$ ( $\text{mA cm}^{-2}$ )	$V_{OC}$ (V)	FF	$\eta$ (%)	$R_s$ ( $\Omega \text{ cm}^2$ )	$R_{sh}$ ( $\Omega \text{ cm}^2$ )
ZnO/ $\text{Cu}_2\text{O}$	3.4	0.22	0.29	0.22	53	94
ZnO-D/ $\text{Cu}_2\text{O}$	3.6	0.22	0.37	0.30	32	150
AZO/ $\text{Cu}_2\text{O}$	3.7	0.20	0.34	0.26	32	100

**Figure 6.** Energy level diagram of ZnO/ $\text{Cu}_2\text{O}$ -based solar cells.



The ZnO layer prepared by a dipping method after spin-coating provided the largest crystallite size of ZnO and high 002-orientation, which indicates the crystal growth of ZnO during the dipping. A nanorod structure of ZnO might be formed by the dipping method [39], which could be also explained from optical absorption in Figure 3a. The Cu<sub>2</sub>O prepared on the ZnO-D also provided the largest crystallite size, which would result in an increase in the shunt resistance ( $R_{sh}$ ) and a decrease in the series resistance ( $R_s$ ) of the ZnO-D/Cu<sub>2</sub>O solar cell, as listed in Table 3. The increase in the  $R_{sh}$  and the decrease in the  $R_s$  indicate increase of carrier separation and decrease of inner electrical resistance. The ZnO-D/Cu<sub>2</sub>O solar cell provided the highest fill factor in the present work, which indicates suppression of carrier recombination at the ZnO/Cu<sub>2</sub>O interface. A decrease in the leakage current and an increase in  $R_{sh}$  resulted in the improved photoelectric parameters.

Thickness effects were discussed in the previous works [36,37,40], and the effect of thickness reduction or decomposition of ZnO during electrodeposition of Cu<sub>2</sub>O layer, which would be dependent on the several electrodeposition conditions. Optimization of thickness of active layers in the present solar cells could increase the efficiency of the solar cells.

In the present work, a simple spin-coating technique was applied for thin film coatings of ZnO layer. Al doping in the ZnO layer by simply adding aluminum nitrate enneahydrate to zinc acetate dehydrate solution resulted in the increase of the conversion efficiency. In addition, a simple dipping method in a zinc nitrate hexahydrate solution was applied to form ZnO layers on the spin-coated ZnO layer, which also resulted in the efficiency increase. These simple fabrication methods are useful for the fabrication of preliminary solar cells with a new structure.

#### 4. Conclusions

ITO/ZnO(Al)/Cu<sub>2</sub>O/Au-based heterojunction solar cells were fabricated by spin-coating and electrodeposition, and the photovoltaic properties and microstructures were investigated. The conversion efficiency was improved by aluminum doping in the ZnO layer, which was attributed to the increase of short-circuit current and fill factor. The efficiencies were improved further by growing the ZnO and Cu<sub>2</sub>O layers with larger crystallite sizes and high [002]-orientation of ZnO crystal, which resulted in the increase of fill factor. The present method of spin-coating using aluminum doping and electrodeposition is expected for the simple fabrication method for Cu-based solar cells.

#### Author Contributions

Takeo Oku wrote the manuscript and summarized the project. Tetsuya Yamada fabricated and characterized the solar cells, and summarized the results. Kazuya Fujimoto developed the deposition method for Cu<sub>2</sub>O layers by the electrochemical deposition. Tsuyoshi Akiyama also developed the Cu<sub>2</sub>O deposition method, and supported the project.

#### Conflicts of Interest

The authors declare no conflict of interest.

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