Fabrication and characterization of copper oxides/fullerene solar cells prepared by an electrodeposition method

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Copper oxide based solar cells with fullerene (C60) were fabricated on indium tin oxide (ITO) by an electrodeposition method. Cell performance of the solar cells with the Cu2O/C60 and CuO/C60 structures were investigated. A photovoltaic device based on an ITO/Cu2O/C60 heterojunction structure provided short-circuit current density of 67 μA cm−2 and open circuit voltage of 0.20 V under an air mass 1.5 illumination. The microstructures of the Cu2O and CuO layers were examined, and the energy levels of the present solar cells were also discussed.

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1. Introduction

Oxide-based semiconductors are a promising alternative to silicon-based solar cells because they possess high optical absorption and are composed of low cost materials. Copper oxides of CuO and Cu2O are known to be p-type semiconductor oxides. They are suitable materials for high efficiency solar cells because their direct bandgaps of ~1.5 and ~2.1 eV, respectively, are close to the ideal energy gap for solar cells, and well matched with the solar spectrum. A maximum efficiency of ~2% has been obtained for Cu2O solar cells using high-temperature annealing and vacuum evaporation techniques. Solar cells of Cu2O and ZnO fabricated by electro deposition and photochemical deposition methods have also been reported. Although CuO has been used as a hole transfer layer and barrier layer for dye-sensitized solar cells, few solar cells have been reported using copper oxides as a p-type semiconductor active layer. The use of Cu2O and CuO are advantageous because of its simple production method for solar cells. The purpose of the present work was to fabricate Cu2O/C60 and CuO/C60 thin film solar cells by electrodeposition, and to investigate the effect of Cu2O and C60 layers on their electronic properties. Fullerene (C60) is a good electron acceptor, and has been used as the n-type semiconductor active layer for organic thin film solar cells. The electrodeposition method has advantages of low cost and low temperature method. Cu2O and CuO thin films prepared by electrodeposition method have also been previously reported. Cu2O/C60 solar cells in the present study were investigated by structural analysis and measurements of optical absorption and photovoltaic activity.

2. Experimental procedures

Cu2O and CuO layers were prepared on pre-cleaned indium tin oxide (ITO) glass plate by electrodeposition using platinum counter electrode. Copper(II) sulfate (CuSO4, 0.4 mol/L, Wako 97.5%) and l-lactic acid (3 mol/L, Wako) were dissolved into distilled water. The electrolyte pH was adjusted to 12.5 by adding NaOH. The electrolyte temperature was kept at 65°C during electrodeposition. Preparation of Cu2O layers were carried out at voltages ranging from −0.25 to −0.45 V and quantity of electric charge of 1.6–2.4 C cm−2. CuO layers were also prepared at voltages of +0.70 V and quantity of electric charge of 2.2 C cm−2. A C60 layer of thickness ~100 nm was prepared on a Cu2O and CuO layers by vacuum evaporation from C60 powder. Aluminum (Al) metal contacts were deposited as top electrodes. Structure of heterojunction solar cell were denoted as ITO/Cu2O/C60/Al and ITO/CuO/C60/Al, with a schematic illustration as shown in Fig. 1.

Current density–voltage (J–V) characteristics (Hokuto Denko Corp., HSV-100) of the solar cells were measured both in the dark and under illumination at 100 mW/cm2 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 cm2. Optical absorption of the solar cells was investigated by means of UV visible spectroscopy (Hitachi, Ltd., U-4100). The microstructures of the copper oxides were investigated by X-ray diffractometer (XRD, PHILIPS X’Pert-MPD System) with Cu Kα radiation operating at 40 kV and 40 mA, and transmission electron microscopy (TEM) operating at 200 kV (Hitachi, Ltd., H-8100).

Fig. 1. (Color online) Structure of ITO/PEDOT:PSS/Cu oxides:C60/Al heterojunction solar cells.
Table 1. Measured parameters of solar cells

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voltage (V)</th>
<th>Charge (C cm^{-2})</th>
<th>η (%)</th>
<th>FF</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (µA cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_{2}O/ITO</td>
<td>-0.25</td>
<td>2.2</td>
<td>2.1 x 10^{-4}</td>
<td>0.25</td>
<td>0.06</td>
<td>14</td>
</tr>
<tr>
<td>Cu_{2}O/ITO</td>
<td>-0.35</td>
<td>2.2</td>
<td>4.2 x 10^{-5}</td>
<td>0.31</td>
<td>0.20</td>
<td>67</td>
</tr>
<tr>
<td>Cu_{2}O/ITO</td>
<td>-0.45</td>
<td>2.2</td>
<td>1.2 x 10^{-4}</td>
<td>0.25</td>
<td>0.012</td>
<td>21</td>
</tr>
<tr>
<td>CuO/ITO</td>
<td>-0.35</td>
<td>1.6</td>
<td>7.0 x 10^{-7}</td>
<td>0.24</td>
<td>1.3 x 10^{-3}</td>
<td>2.2</td>
</tr>
<tr>
<td>CuO/ITO</td>
<td>-0.35</td>
<td>1.9</td>
<td>3.7 x 10^{-6}</td>
<td>0.26</td>
<td>0.076</td>
<td>0.18</td>
</tr>
<tr>
<td>CuO/ITO</td>
<td>-0.35</td>
<td>2.4</td>
<td>5.4 x 10^{-5}</td>
<td>0.25</td>
<td>0.25</td>
<td>0.88</td>
</tr>
<tr>
<td>CuO/ITO</td>
<td>+0.70</td>
<td>2.2</td>
<td>9.0 x 10^{-5}</td>
<td>0.21</td>
<td>0.24</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. 2. (Color online) Measured J-V characteristic of solar cell with Cu_{2}O/C_{60} structure in the dark and under illumination.

3. Results and discussion

The measured parameters of the solar cells are summarized in Table 1. A solar cell with a Cu_{2}O/C_{60} structure provided the highest power conversion efficiency (η) of 4.2 x 10^{-5}%, fill factor (FF) of 0.31, short-circuit current density (J_{sc}) of 67 µA cm^{-2} and open-circuit voltage (V_{oc}) of 0.20 V.

J-V characteristics of the Cu_{2}O/C_{60} structure (η = 4.2 x 10^{-5}%), which was prepared at voltage of -0.35 V and charge of 2.2 C cm^{-2}, in the dark and under illumination are shown in Fig. 2. The photocurrent was observed under illumination, and the Cu_{2}O/C_{60} structure showed characteristic curves with short-circuit current and open-circuit voltage.

Figure 3 shows measured optical absorption of the solar cells. The Cu_{2}O/C_{60} and CuO/C_{60} structure shows high absorption in the range of 300 and 800 nm. In Fig. 3(a), absorption peaks at 362 and 526 nm for the Cu_{2}O/C_{60} structure was due to Cu_{2}O. For Fig. 3(b), absorption peaks at 368 and 506 nm for the CuO/C_{60} structure corresponds to CuO.

All the crystalline components in the Cu_{2}O and CuO thin films were investigated by XRD, as shown in Fig. 4. Diffraction peaks corresponding to Cu_{2}O and CuO were observed for the Cu_{2}O and CuO thin films, and they consisted of cuprite phase with cubic system (space group of Pn3m and lattice parameters of
est 0.3410 nm, crystal wa
group on nanocompos
te the size of Cu2O:C60

The TEM

Fig. 5. (a) TEM image and (b) electron diffraction pattern of Cu2O:C60
structure.

![TEM image](image1)

![Diffraction pattern](image2)

(a)

\[ a = 0.4250 \text{ nm} \]

cubic phase with monoclinic system (space group of C2/C and lattice parameter of \( a = 0.4653 \text{ nm}, \ b = 0.3410 \text{ nm}, c = 0.5018 \text{ nm}, \beta = 99.48^\circ \)). The particle size was estimated using Scherrer's equation: \( D = \frac{0.94}{\beta \cos \theta} \), where \( \lambda \), \( \beta \), and \( \theta \) represent the wavelength of the X-ray source, the full width at half maximum, and the Bragg angle, respectively. The crystalite sizes of Cu2O and CuO were determined to be 42.5 and 41.3 nm, respectively.

Figures 5(a) and 5(b) show a TEM image and a selected area electron diffraction pattern of the Cu2O thin film, respectively. The TEM image indicated aggregated Cu2O nanocrystals with the size of ~50 nm. The Debye–Scherrer rings in Fig. 5(b) indicate nanocrystal structures of Cu2O. Optimization of the nanocomposite structure with Cu2O would increase the efficiencies of the solar cells.

Energy level diagram of Cu2O:C60 and CuO:C60 solar cells is summarized as shown in Fig. 6. Previously reported values were used for the energy levels.13,14,15 It has been reported that \( \eta_{\text{eff}} \) is nearly proportional to the band gap of the semiconductors,16 and control of the energy levels is important to increase efficiency. Compared to a Si semiconductor with an indirect transition band structure, Cu2O and CuO with a direct transition band gap are more suitable for the optical absorption property. In addition, ultrathin films of the Cu2O and CuO layers could provide efficient charge injection because of the high optical absorption. Although ZnO has been mainly used as an n-type semiconductor for Cu2O-based solar cells,11-13 C60 was applied instead of ZnO in the present work. The advantages of the present C60 are a good electronic acceptable material for solar cells.

Cu2O and CuO based solar cells produced by an electrodeposition method without vacuum evaporation were investigated in the present work. The low conversion efficiency of the present solar cells would be due to presence of Cu impurities in the active layer. Depositing films with pure copper oxide layers could increase the efficiency of the solar cells.

4. Conclusions

ITO/Cu2O/C60/Al and ITO/CuO/C60/Al solar cells were produced and characterized. A device based on the Cu2O/C60 structure fabricated by an electrodeposition method which provided \( \eta = 4.2 \times 10^{-3}, FF = 0.31, J_{SC} = 67 \mu A cm^{-2} \) and \( V_{OC} = 0.20 \text{ V} \). XRD and TEM results indicated the presence of Cu2O and CuO particles. Energy level diagram was proposed, and separated holes could transfer from the valence band of the Cu2O to the ITO, and separated electrons could transfer from the conduction band of the Cu2O to the Al electrode, respectively. Introduction of a new electrode and optimization of electrodeposition conditions would improve the efficiencies of the solar cells.

References