Fabrication and characterization of CuO/ZnO solar cells

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Abstract. Cuprous oxide (CuO) and zinc oxide (ZnO) heterojunction solar cells fabricated on indium tin oxide-coated glass were studied. CuO and ZnO films were deposited using a galvanostatic method. Structural, morphological and optoelectronic properties of the CuO/ZnO heterojunction were studied by using X-ray diffraction, atomic force microscopy and light current-voltage characteristics.

1. Introduction
Solar cell technology for future energy resources has been progressed recently. Silicon is used as the semiconductor material for conventional solar cells, but silicon is expensive and the cost reduction of the solar cells is one of the most important issues. Oxide semiconductors are one of the alternatives to silicon solar cells, and copper oxides such as CuO and Cu$_2$O are one of the candidate materials. The features of copper oxide semiconductors are relatively higher optical absorption, low cost of raw materials and non-toxic. CuO and Cu$_2$O are p-type semiconductors with band gap energies of 1.5 eV and 2.0 eV, respectively, which are close to the ideal energy gap of 1.4 eV for solar cells and allows for good solar spectral absorption. The highest efficiency of ~2 % for Cu$_2$O solar cells has been obtained by using the high temperature annealing method [1]. Cu$_2$O/ZnO thin film solar cells have also been studied and reported [2,3]. However, the solar cells with a CuO/ZnO structure have not been reported.

The purpose of the present work is to fabricate and characterize solar cells with CuO/ZnO structures. The band gap energy of CuO is ~1.5 eV, which is closer to the ideal band gap of 1.4 eV. Zinc oxide (ZnO) is an n-type semiconductor with a wide band gap of ~3.37 eV, which can be applied to solar cells [4].

2. Experimental procedures
CuO layers were prepared on pre-cleaned indium tin oxide (ITO) glass plate by electro deposition using platinum as counter electrode. Copper(II) sulfate (CuSO$_4$, 0.4 mol/L, Wako 97.5%) and l-lactic acid (3 mol/L, Wako) were dissolved into distilled water. pH of the electrolyte solution was adjusted to 12.5 by adding NaOH. The temperature of electrolyte solution was kept at 65 °C during electro deposition. Preparation of CuO layers were carried out at voltages of +0.70 V and quantity of electric charge of 2.2 C cm$^{-2}$. After the deposition, the sample was rinsed with water and transferred into the ZnO electro deposition bath. ZnO layers were galvanostatically electro-deposited from 0.025 M aqueous solution of Zn(NO$_3$)$_2$ on the ITO/CuO substrate. The sample thickness ranged between 1 and 2 μm depending on the deposition time and current. Finally, the substrates were rinsed with water, dried and placed into the vacuum chamber to obtain a vacuum of ~10$^{-4}$ Torr.
with air and quickly transferred into a thermal evaporator for the vacuum deposition of the aluminum (Al) back contact. Structure of heterojunction solar cells were denoted as ITO/CuO/ZnO/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, Electric, XES-301S). The solar cells were illuminated through the side of the ITO substrate, 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). Microstructures of the copper oxides were investigated by X-ray diffractometer (XRD, PHILIPS X’Pert-MPD System) with CuKα radiation operating at 40 kV and 40 mA.

3. Results and discussion

The measured parameters of the solar cells are summarized in Table 1. Thicknesses of CuO were ~1 μm and ~2 μm for 5 min and 10 min, respectively. A solar cell with a CuO/ZnO structure provided a power conversion efficiency (η) of 1.1×10⁻⁴ %, fill factor (FF) of 0.25, short-circuit current density (Jsc) of 1.6 mA cm⁻² and open-circuit voltage (Voc) of 2.8 × 10⁻⁴ V. The photocurrent was observed under illumination, and the CuO/ZnO structure showed characteristic curves with short-circuit current and open-circuit voltage. Figure 2 shows measured optical absorption of thin films. The CuO and ZnO thin films shows high optical absorption in the range of 400 nm and 800 nm.

Transmittance spectrum of 100 nm thick CuO film, deposited on ITO, is presented in Fig. 3(a). From this spectrum, the optical absorption coefficients (α) of this film was determined from the spectral transmittance using the next equation, \( \alpha = 1/d \cdot \ln(1/T) \). Where d is the film thickness and T is the transmittance [5]. For determination of the optical band gap energy (Eg), the method based on the relation of \( a h v = A(hv-E_g)^{n/2} \) was used, where n is a number that depends on the nature of the transition. In this case, its value was found to be 1, which corresponds to direct band to band transition.

Figure 3(b) is a Tauc plot, which shows \( (a h v)^2 \) versus hv for the CuO film. The intersection of the straight line with the hv-axis determines the optical band gap energy Eg [6]. It was found to be ~2.1 eV which is lower than the ideal band gap of the CuO crystal. Because of the small band gap energy, the open-circuit voltage would be low.

| Deposition time of CuO (min) | Voc (mV) | Jsc (mA/cm²) | FF  | η (%)  |
|-----------------------------|---------|-------------|-----|--------|
| 5                           | 0.28    | 1.9         | 0.25| 1.1×10⁻⁴ |
| 10                          | 0.18    | 0.017       | 0.25| 1.1×10⁻⁷ |
Figure 2. Optical absorption of thin films prepared by electrodeposition.

Figure 3. (a) Optical transmission spectrum of CuO film and (b) Tauc plot for CuO film.

All the crystalline components in the CuO and ZnO thin films were investigated by XRD, as shown in Fig. 4. Diffraction peaks corresponding to CuO and ZnO are observed in thin films, which consisted of cupric phase with monoclinic system (space group of C2/c and lattice parameter of $a=0.4653$ nm, $b=0.3410$ nm, $c=0.5018$ nm, $\beta=99.481^\circ$). The particle size was estimated using Scherrer’s equation: $D=\frac{0.9\lambda}{B\cos\theta}$, where $\lambda$, $B$, and $\theta$ represent the wavelength of the X-ray source, the full width at half maximum (FWHM), and the Bragg angle, respectively [7]. The crystallite sizes of CuO and ZnO were determined to be 49.0 nm and 82.0 nm, respectively. Lattice constants of CuO and ZnO were summarized as listed in Table 1 and Table 2, comparing with reported values [8,9]. From the lattice constants, the crystal structures of CuO and ZnO have some crystal distortions. To increase the efficiency of the CuO/ZnO solar cells, small grain size of ZnO and higher crystallinity of CuO would be necessary.

Energy level diagram of the CuO/ZnO solar cell is summarized as shown in Fig. 5. Previously reported values were used for the energy levels [7,8]. It has been reported that $V_{oc}$ is nearly
proportional to the band gap of the semiconductors, and control of the energy level is important to increase efficiency [9]. Compared to silicon with an indirect transition band structure, CuO with a direct transition band structure is more suitable for the optical absorption property. In addition, the ultrathin film of the CuO layers could provide efficient charge injection because of the high optical absorption.

![Figure 4](image_url) Figure 4. XRD patterns of (a) CuO and (b) ZnO thin films.

| Table 2. Lattice constants of CuO. |
|-----------------------------------|
| a (nm) | b (nm) | c (nm) |
| Present data | 0.5122 | 0.4732 | 0.5182 |
| Reference [8] | 0.4679 | 0.3426 | 0.5127 |

| Table 3. Lattice constants of ZnO. |
|-----------------------------------|
| a (nm) | c (nm) |
| Present data | 0.2816 | 0.5213 |
| Reference [9] | 0.3257 | 0.5213 |

![Figure 5](image_url) Figure 5. Energy diagram of ITO/CuO/ZnO/Al heterojunction solar cells.
In the present work, the $V_{oc}$ is not so high compared to Fig. 5. Microstructures of CuO and ZnO thin films in the present work were found to have some crystal distortion, which would result in the reduction of electrical transport. If the crystal qualities of the CuO and ZnO thin films are increased, $V_{oc}$ would be improved.

4. Conclusion

ITO/CuO/ZnO/Al solar cells were produced and characterized, which provided $\eta$ of $1.1 \times 10^{-4}$ %, FF of 0.25, $J_{sc}$ of 1.6 mAcm$^{-2}$ and $V_{oc}$ of $2.8 \times 10^{-4}$ V. The CuO/ZnO structure showed high optical absorption in the range of 400 nm and 800 nm, and the $E_g$ of CuO was found to be $\sim 1.2$ eV from the Tauc plot, which is smaller than that of the ideal band gap of the CuO crystal and the open-circuit voltage would be decreased. A crystallite size of CuO was determined to be 49.0 nm, and higher crystallinity of CuO would increase the efficiency of the CuO/ZnO solar cells. The energy level of the present solar cell was proposed, and separated holes could transfer from the valence band of the CuO to the ITO, and separated electrons could transfer from the conduction band of the CuO to the Al electrode, respectively. Formation of the CuO/ZnO active layer with homogeneous distributed CuO nanoparticles would improve the efficiencies of the solar cells.

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