Photovoltaic effect of n-In_2O_3/p-Cu_2O heterojunction thin film cells

Tatsuo NAKAZAWA*, Shin'ichi KURANOUCHI**

Electrical and photovoltaic characteristics of n-In_2O_3/p-Cu_2O heterojunction thin film cells were investigated. Cu_2O semiconducting films were prepared by simple method of thermal oxidation of copper foil in air. Conversion efficiency of 0.57% was obtained under illumination of the sunlight. It is thought that a high series resistance of the diode, which originated from a interface between Cu_2O film and copper foil, causes the poor characteristics.

Photovoltaic characteristics of the cell consisted of relative thick Cu_2O film was improved by a chemical etching for the surface of the film in bromine-methanol solution and a low temperature annealing at 550°C.

1. Introduction

Cuprous oxide (Cu_2O) solar cells have been investigated by various authors[1-6]. Although cuprous oxide has a direct band gap (2.0eV) which is considerably larger than the suitable one for photovoltaic solar energy conversion (1.5eV), it consists of relatively abundant elements and is nontoxic. Up to this time, most cells were prepared by using monocrystalline or polycrystalline Cu_2O platelets thicker than 0.5mm. Thick Cu_2O platelets tend to crack and can be obtained after long time oxidation at high temperature. In order to improve mechanical strength and to reduce the energy consumption, it is desirable to use thin Cu_2O film formed on the copper foil. Some thin film Cu_2O solar cells were investigated by now. They were a Cu/Cu_2O Schottky cell[7], a ZnO/Cu_2O heterojunction cell[8] and a simple structure back wall cell which uses the interfacial barrier of Cu_2O layer and Cu substrate[9]. However, remarkable photovoltaic characteristics have not been reported.

In this paper, we report n-indium oxide (In_2O_3)/p-cuprous oxide (Cu_2O) heterojunction solar cells which consists of thin film Cu_2O (thickness: less than 10μm). It is thought that the heterojunction cells are more stable than the Schottky type cells because both the surface layer and light absorbing layer are consists of oxide semiconductor. Further, larger photocurrent can be expected for heterojunction solar cells due to the window effect. The best cell which consisted of the 3μm thick Cu_2O film substrate showed the conversion efficiency of 0.57% which is one of the largest value for thin film Cu_2O cells.

* Department of Electronics and Computer Science
** Department of Electrical Engineering

2. Experimental procedure

Thin film cuprous oxide layer was formed on a copper foil by thermal oxidation as follows. A copper foil with thickness of 0.5mm was thermally oxidized at 1050°C in air for 1 to 10 min, subsequently annealed at 550°C in air for 15 min before cooled down to room temperature. A polycrystalline Cu_2O layer covered with black CuO was grown on surface of the copper foil. The oxidized foil was chemically etched to remove CuO layer and to treat the Cu_2O surface in following three kinds of solutions, in turn. The solutions are 1) $HCl+FeCl_3+NaCl+H_2O$, 2) $HNO_3+NaCl+H_2O$ and 3) $(NH_4)S_2O_8+H_2O$. Just prior to deposition of In_2O_3 films, the Cu_2O film was etched in the solution of bromine methanol (BM) for 10 sec. Indium oxide films with thickness of about 90 nm were deposited on the Cu_2O layer by reactive evaporation of indium in oxygen partial pressure of 0.1 Pa and at substrate temperature of 200°C[10].

Current-voltage characteristics were measured in the dark using a millivolt ammeter (Kikusui 115A) and a voltage standard (Kikusui 103). Capcacitance-voltage characteristics were measured at 10 kHz using an impedance analyzer (YHP 4192A). Photovoltaic characteristics were measured under illumination of a tungsten lamp and the sunlight using a dc voltage source and an X-Y recorder (Yokogawa 3086). Incident power was measured with a calibrated silicon pn junction solar cell as a standard.

3. Results and discussion

Thickness of thermally grown Cu_2O layer as a function of oxidation time at 1050°C is shown in Fig. 1. The thickness was measured by cylindrical drilling method. A growth rate of Cu_2O layer at 1050°C is estimated about 1.5μm/min. A columnar structure was observed for the Cu_2O layer using an optical microscope. Grain diameter at the surface of the Cu_2O layer increase from 70 to 200μm with the increase of its thickness from 1.5 to 15μm. A conduction type of the Cu_2O layer was always determined as p-type from the polarity of measured thermo-electromotive force by hot probe method.

Figure 2 shows open circuit voltage V_{oc} and short circuit current I_{sc} for the In_2O_3/Cu_2O heterojunction cells as a function of the thickness of Cu_2O layer. The thickness was estimated from its oxidation time using the growth rate of 1.5μm/min. In the figure, dots show the data of cells which were fabricated on the BM etched Cu_2O substrates, on the other hand, open-circles show the data of cells which were fabricated on the substrates without the BM etching. The value of short-circuit current decreased with the increase of the thickness of Cu_2O substrate. The value of open-circuit voltage, however, was only slightly affected by the thickness of the substrate. It is evident that the photovoltaic characteristics of the cells were improved by the BM etching. Olsen et al. reported that the significant progress was observed with Cu-Cu_2O frontwall cells by introducing the interfacial layer of Cu-Br which was formed after the treatment of Cu_2O in bromine

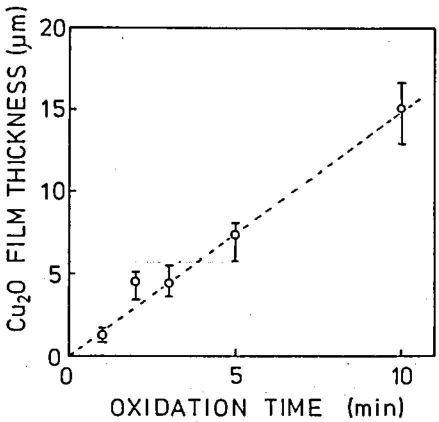

Fig. 1 Thickness of Cu_2O film as a function of oxidation time.

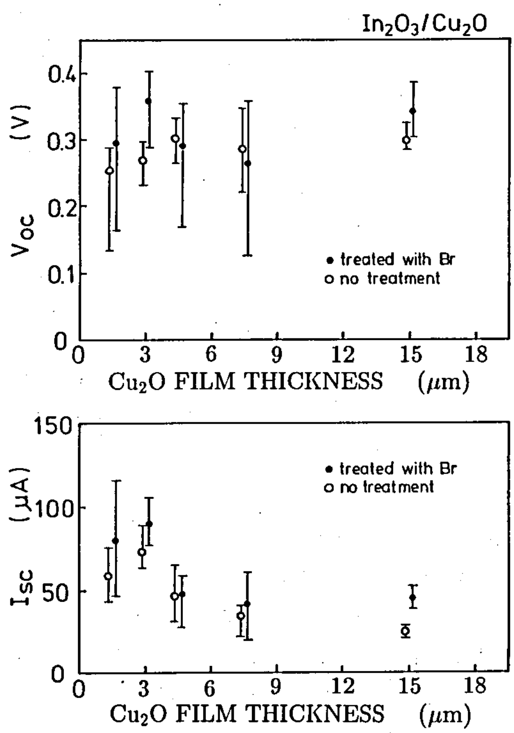

Fig. 2 Open circuit voltage V_{oc} and short circuit current I_{sc} for In_2O_3/Cu_2O heterojunction cells which fabricated on thermally grown Cu_2O film with vairious thickness.

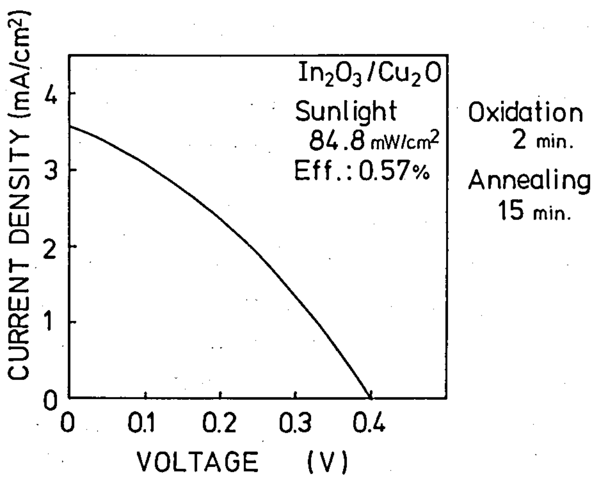

Fig. 3 Photovoltaic output of In_2O_3/Cu_2O heterojunction cell under illumination of the sunlight.

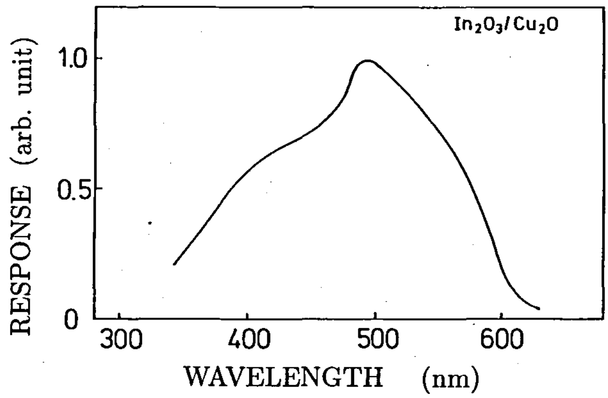

Fig. 4 Spectral response of In_2O_3/Cu_2O heterojunction cell.

solution[6]. In our cells, it is thought that the output characteristics was improved by forming of a similar interfacial layer after the BM etching.

The highest photovoltaic output was obtained for the cell which was prepared using a 3μm thick Cu_2O layer as the substrate. Photovoltaic characteristics of the cell under illumination of the sunlight is shown in Fig. 3 The open-circuit voltage of 400 mV, the short-circuit current density of 3.58mA/cm^2 and the fill factor of 0.399 were obtained under incident solar power of 84.8mW/cm^2. The conversion efficiency was 0.57% which is one of the largest value for the thin film Cu_2O cells.

Figure 4 shows a spectral response of the In_2O_3/Cu_2O cell. The response was observed in the wavelength between 0.35 and 0.62μm and reached to the peak at about 0.5μm. The cutoff wavelengths, 0.35μm and 0.62μm, correspond to the energy gap of the In_2O_3 and the Cu_2O, respectively. The peak wavelength (0.5μm) corresponds to the peak of AM2 spectrum. The response of the In_2O_3/Cu_2O cell in the short wavelength region was improved by window effect of the transparent conductive indium oxide film as compared with that reported for the cells which consisted of semitransparent metal surface layer and Cu_2O[7].

Electrical and photovoltaic properties of the In_2O_3/Cu_2O cells are summarized in tables 1 and 2. The cells were fabricated on the BM etched Cu_2O layers with various thicknesses. Saturation current density J_0 and the acceptor concentration of the Cu_2O layer N_A were derived from the dark current-voltage characteristics and the $1/C^2$ versus V plots of capacitance-voltage characteristics, respectively. We define a *"rectification ratio"* as a ratio of currents at the bias of + 1 and −1 V. A series resistance of the diode R_s was calculated using the equation, $R_s=V_d(I_{sc})-V_{oc}/I_{sc}$, which was proposed by Rajkanan et al[11]., where $V_d(I_{sc})$is the bias voltage which gives the same current with I_{sc} in the dark. Photovoltaic characteristics were measured under illumination of the sunlight. The incident power of the sunlight P_{in} is shown in the table 2. Besides the short

Table 1 : Photovoltaic properties of the cells based on Cu_2O thin films with various thickness

Thickness of Cu_2O (μm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	P_{in} (mW/cm^2)	conversion efficiency (%)
1.5	0.355	3.43	0.257	88.3	0.33
3	0.400	3.58	0.339	84.8	0.57
4.5	0.375	2.00	0.252	89.3	0.21
7.5	0.380	1.71	0.250	82.4	0.20
15	0.405	1.44	0.243	88.1	0.16

Table 2 : Electrical properties of the cells

Thickness of Cu_2O (μm)	J_o (A/cm^2)	N_A (cm^{-3})	rectification ratio (at 1V)	R_s (Ω)
1.5	2.8×10^{-4}	7.2×10^{14}	2.6	1500
3	2.6×10^{-5}	5.9×10^{14}	6.8	2500
4.5	3.3×10^{-5}	5.1×10^{14}	4.0	8500
7.5	5.7×10^{-5}	5.7×10^{14}	2.8	8500
15	4.6×10^{-5}	1.1×10^{14}	2.2	12000

circuit current density J_{sc} and the fill factor FF, the rectification ratio tends to decrease with the increase of the Cu_2O thickness. This tendency seems to be caused by the increase of series resistance R_S. Therefore, the thinner Cu_2O films, which have relative low series resistance, thought to be useful for substrates of solar cells. However, the photovoltaic characteristics of the cells which fabricated on the too thin Cu_2O films were rather poor due to the increase of J_0. As shown in table 1, values of J_0 for the cell fabricated on 1.5μm thick Cu_2O film is about ten times larger than that for the cell based on 3μm thick Cu_2O film. It is thought that J_0 increases because of the increase of harmful shuntpathes in the too thin film. Consequently, in this research, the 3μm thick Cu_2O film was the most suitable substrate for the solar cell.

The series resistance of the cell is thougho to originate rather from the high contact resistance between Cu_2O layer and Cu foil than the bulk resistance of Cu_2O film, because the measured bulk resistance of the Cu_2O platelets was relative low (on the order of 10^3 Ωcm). This undesirable series resistance can be reduced by annealing at low temperature (550°C) in air after oxidation. To study the effect of low temperature (LT) annealing, thicker Cu_2O films with thickness of about 4.5μm were prepared by the oxidation of the copper foil at 1050°C for 3min. These samples were annealed at 550°C (LT annealing) in various times in air just after the oxidation.

Figure 5 shows the photovoltaic characteristics of the cells which were fabricated on the Cu_2O substrates treated at 550°C for 15, 30 or 120min. It was shown in the figure that

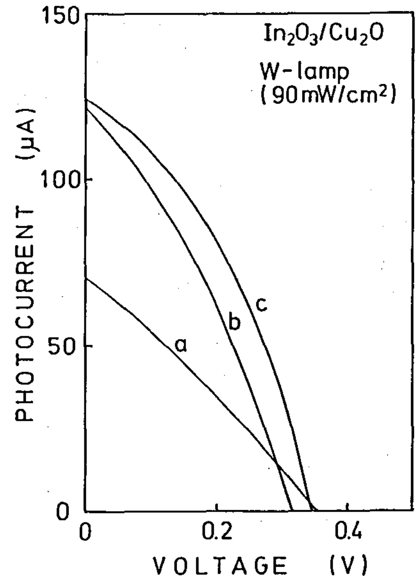

Fig. 5 Photovoltaic output of the In_2O_3/Cu_2O cells fablicated on 4.5μm thick Cu_2O films with low temperature annealing in (a)15min, (b)30min and (c)120min.

the short circuit current density, the fill factor and consequently the conversion efficiency were improved by the long time LT annealing. Table 3 summarize the electrical and photovoltaic characteristics of the cells which are the same as that shown in Fig. 5. Series resistance of the film decreased with the increase of the annealing time. The value of R_s of the 4.5μm thick Cu_2O film with 120min LT annealing, and consequentry the output characteristics, became nealy equal to those of the 3μm thick film with 15min LT annealing. Figure 6 shows the photovoltaic characteristics of the cell fabricated on the 4.5μm thick substrate with the 120min LT annealing. The open-circuit voltage of 0.385 V, the short-circuit current density of 2.7mA/cm^2 and the fill factor of 0.351 were obtained under illumination of the sunlight (71.6mW/cm^2). The conversion efficiency was 0.51%.

The effect of the LT annealing is thought as follows. The significant strain was introduced near the interface of the oxide film and the base copper foil due to the rapid oxidation of the surface of copper foil at 1050°C. It would be one of the main causes of

Table 3 : Electrical properties of the cells with LT annealing

Annealing Time (min)	J_o (A/cm^2)	N_A (cm^{-3})	rectification ratio (at 1V)	R_s (Ω)
15	3.3×10^{-5}	4.3×10^{14}	4.0	8500
30	3.4×10^{-5}	5.0×10^{14}	4.0	4000
120	1.0×10^{-5}	7.2×10^{14}	18.1	1900

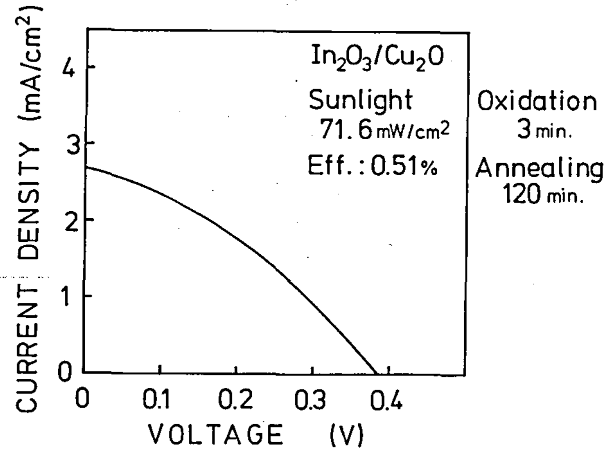

Fig. 6 Photovoltaic octput of In$_2$O$_3$/Cu$_2$O heterojunc-tion cell, which consists of 4.5μm thick Cu$_2$O film with low temperature annealing in 120min, under ilumination of the sunlight.

the high series resistance. The LT annealing for the oxidized sample would be improve the crystallinity of the Cu$_2$O layer and decrease the undesirable effect of the strain. Trivich et al. reported that the low temperature heat treatment improves the diffusion length of crystalline Cu$_2$O[4]. The longer time is required to improve the characteristics of the thicker Cu$_2$O layer by the LT annealing.

4. Summary

The n-In$_2$O$_3$/p-Cu$_2$O heterojunction thin film cells were investigated. The Cu$_2$O films were prepared by simple thermal oxidation technique. The conversion efficiency of 0.57% was obtained under solar illumination of 84.8mW/cm^2. It is thought that the high series resistance of the diode and the interfacial reaction cause the poor characteristics.

The cell characteristics were improved by the etching of Cu$_2$O surface in bromine-methanol solution and the heat treatment at low temperature (550°C).

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