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# Electrochemically deposited Cu<sub>2</sub>O thin films on thermally oxidized Cu<sub>2</sub>O sheets for solar cell applications

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## ABSTRACT

This paper deals with homoepitaxial growth of Cu<sub>2</sub>O thin films using the electrochemical deposition (ECD) method. It also discusses the photovoltaic properties of solar cells that use the active layer of p-type Cu<sub>2</sub>O thin film prepared by epitaxial growth. Such a film was formed at 70 °C on a degenerated p-type Cu<sub>2</sub>O:Na (p<sup>+</sup>-type Cu<sub>2</sub>O: Na) substrate, and this film produced on a substrate with a (110) plane orientation was oriented only in the (110) plane. The crystallite size of the produced Cu<sub>2</sub>O thin film (58.8 nm) was larger than that of the film produced on FTO (SnO<sub>2</sub>: F) (14.6 nm). A photoelectric conversion efficiency of 2.36% was achieved for the AZO/p-type Cu<sub>2</sub>O thin film/p<sup>+</sup>-type Cu<sub>2</sub>O:Na heterojunction solar cell in which a degenerated Al-doped ZnO (AZO) thin film was prepared as the transparent electrode layer on the Cu<sub>2</sub>O thin film by pulse laser deposition. Furthermore, photoelectric conversion efficiency of 4.41% was achieved for the AZO/n-type Ga<sub>0.975</sub>Al<sub>0.025</sub>O/p-type Cu<sub>2</sub>O/p<sup>+</sup>-type Cu<sub>2</sub>O:Na heterojunction solar cell with n-type Ga<sub>0.975</sub>Al<sub>0.025</sub>O film inserted between the AZO and p-type Cu<sub>2</sub>O thin film. This clearly shows that the Cu<sub>2</sub>O thin film produced by epitaxial growth on a p<sup>+</sup>-type Cu<sub>2</sub>O:Na (p<sup>+</sup>-type Cu<sub>2</sub>O: Na) substrate is superior as an active layer.

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## 1. Introduction

Cu<sub>2</sub>O is an attractive selection for the active layer of solar cells because copper (Cu), the primary raw material of Cu<sub>2</sub>O, is non-toxic and inexpensive, and Cu<sub>2</sub>O is a direct transition semiconductor with a bandgap of 2.1 eV. Furthermore, heterojunction solar cells using Cu<sub>2</sub>O could theoretically realize a photoelectric conversion efficiency of 20% (under AM1 illumination) [1–3]. On the other hand, because the intrinsic defect (Cu Vacancy) of Cu<sub>2</sub>O functions as an acceptor, Cu<sub>2</sub>O shows p-type conductivity. In other words, it would be extremely difficult to realize n-type Cu<sub>2</sub>O [4,5]. Consequently, research on Cu<sub>2</sub>O solar cells focuses on the R&D of n-type semiconductor/p-type Cu<sub>2</sub>O heterojunction solar cells consisting of p-type Cu<sub>2</sub>O active layers and other n-type semiconductor materials [6,7]. The production of n-type semiconductor/p-type Cu<sub>2</sub>O heterojunction solar cells reported in a large number of scientific papers used, as the active layer, p-type Cu<sub>2</sub>O sheets fabricated by thermal oxidation or Cu<sub>2</sub>O thin films prepared with an electrochemical deposition (ECD) method [8–18].

Among n-type semiconductor/p-type Cu<sub>2</sub>O heterojunction solar cells that use Cu<sub>2</sub>O thin film as the active layer produced by EDC, Isaki et al. reported a 1.28% conversion efficiency for p-type Cu<sub>2</sub>O/n-type ZnO/FTO solar cells in 2007 [8]. These cells were fabricated by growing an n-type ZnO film and Cu<sub>2</sub>O thin film (mobility [μ]: 1.8 cm<sup>2</sup>/V s) on a glass substrate with an F-doped SnO<sub>2</sub> (FTO) transparent electrode [8]. In 2013, Fujimoto reported that a conversion efficiency of 1.43% was reached by optimizing the deposition process used to produce the above heterojunction solar cells [9]. The highest conversion efficiency for solar cells using Cu<sub>2</sub>O thin films as the active layer was reported by a research group led primarily by Buonassisi [16,17]. They prepared a Cu<sub>2</sub>O thin film (μ: 8 cm<sup>2</sup>/V s) by ECD on a quartz substrate with Au electrodes deposited. After that, they fabricated heterojunction solar cells where various types of n-type semiconductor layers (ZnO, Zn–Sn–O (ZTO), Ga<sub>2</sub>O<sub>3</sub>) and Al-doped ZnO (AZO) transparent electrodes were grown at low temperature by the Atomic Layer Deposition (ALD) method. Conversion efficiencies of 3.06% and 3.97% were reported for MgF<sub>2</sub>/AZO/ZTO/Cu<sub>2</sub>O and MgF<sub>2</sub>/AZO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterostructure solar cells, respectively [16,17]. It has been reported that because the conversion efficiency of solar cells is significantly affected by the crystallinity of Cu<sub>2</sub>O, Therefore, it is important to use a high-quality Cu<sub>2</sub>O thin film as the active layer [9]. Crystallinity and hole mobility of Cu<sub>2</sub>O thin film significantly

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affect the diffusion length of the decimal carrier. Consequently, it is indispensable to use a  $\text{Cu}_2\text{O}$  thin film having a superior crystallinity (high hole mobility) in order to realize a high conversion efficiency of  $\text{Cu}_2\text{O}$  solar cells. A high hole mobility ( $[\mu]$ :  $90 \text{ cm}^2/\text{V s}$ ) of  $\text{Cu}_2\text{O}$  thin film produced by epitaxial growth on an  $\text{MgO}$  substrate using the PLD method was achieved by Hosono et al. in 2008 [19]. This means high hole mobility and high-quality film properties can be obtained for  $\text{Cu}_2\text{O}$  thin films through epitaxial growth. Thus, we can expect improvement in the conversion efficiency by using  $\text{Cu}_2\text{O}$  thin film, produced by epitaxial growth, having high crystallinity and hole mobility for the active layer. The ECD method of depositing p-type  $\text{Cu}_2\text{O}$  thin films is widely known. At present, however, there has been no report of epitaxial growth on a  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate by ECD.

This paper describes a homoepitaxial growth of  $\text{Cu}_2\text{O}$  thin films by ECD on a degenerated  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate with  $10^{19} \text{ cm}^{-3}$  hole concentration (p). Properties of the  $\text{Cu}_2\text{O}$  thin film produced were evaluated using a scanning electron microscope (SEM) and X-ray diffraction equipment (XRD). In addition, a photovoltaic properties of n-type semiconductor/p-type  $\text{Cu}_2\text{O}$  heterojunction solar cells using the p-type  $\text{Cu}_2\text{O}$  thin film produced for the active layer were studied.

## 2. Experimental

P-type  $\text{Cu}_2\text{O}$  thin film was prepared on a  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate by ECD. A degenerated  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  sheet used both as the electrode and as the substrate was fabricated by heating a  $\text{p}^+$ -type  $\text{Cu}_2\text{O}$  sheet, which was fabricated by thermal oxidation of Cu together with an Na compound at  $800^\circ\text{C}$  for 30 h in an Ar atmosphere, cooling down to  $500^\circ\text{C}$ , and then quick-cooling in the atmosphere [20]. Typical electrical properties (at room temperature) of the fabricated  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate are a hole concentration of  $2\text{--}5 \times 10^{19} \text{ cm}^{-3}$ , a mobility ( $\mu$ ) of  $5\text{--}8 \text{ cm}^2/\text{V s}$ , and a specific resistance ( $\rho$ ) of  $0.02\text{--}0.04 \Omega \text{ cm}$ . Before using it as an electrode, the  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate was wet-etched to remove the  $\text{CuO}$  layer on the surface [21]. The technique reported by McShane et al. was referred to for the production conditions (solution, current density) of p-type  $\text{Cu}_2\text{O}$  thin film [22]. For the growth, a mixed aqueous solution of  $\text{NaOH}$ ,  $\text{CuSO}_4$  (concentration of  $0.20 \text{ mol/l}$ ), and  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$  (concentration of  $3.00 \text{ mol/l}$ ) was used, and the pH was adjusted to 12.0. A Pt plate was used for the material for the positive electrode and the  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate was used for the negative electrode, or F-doped  $\text{SnO}_2$  (FTO) was used as the reference.  $\text{Cu}_2\text{O}$  thin film was deposited by applying voltage between the electrodes with a constant current density of  $0.25 \text{ mA/cm}^2$  at a solution temperature of  $70^\circ\text{C}$ . Properties of the  $\text{Cu}_2\text{O}$  thin film produced were evaluated using SEM and XRD equipment. In order to evaluate film properties of the thin film produced by ECD, photovoltaic properties were evaluated by fabricating an n-type semiconductor/p-type  $\text{Cu}_2\text{O}$  heterojunction solar cell consisting of a p-type  $\text{Cu}_2\text{O}$  thin film and an n oxide semiconductor. Fig. 1 shows the two types of solar cells fabricated in the research. Fig. 1(a) shows the cross-sectional structure of an Al-doped  $\text{ZnO}(\text{n}^+\text{-type AZO})/\text{p-type Cu}_2\text{O}/\text{p}^+\text{-type Cu}_2\text{O}:\text{Na}$  heterojunction solar cell. A  $200\text{-}\mu\text{m}$ -thick degenerated  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  sheet was used as the substrate. A p-type  $\text{Cu}_2\text{O}$  film was prepared as the active layer on  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$ , and AZO was further prepared both as the n-type semiconductor layer and as the transparent electrode layer on top of it. Fig. 1(b) shows an AZO/n-type  $\text{Ga}_{0.975}\text{Al}_{0.025}\text{O}/\text{p-type Cu}_2\text{O}/\text{p}^+\text{-type Cu}_2\text{O}:\text{Na}$  heterojunction solar cell. The  $\text{Ga}_{1-x}\text{Al}_x\text{O}$  ( $=\text{Al}/[\text{Ga}+\text{Al}]$ ) thin film functions as the n-type layer. Gold (Au) is prepared as the rear electrode on the back side of each solar cell. Next, an n-type  $\text{Ga}_{0.975}\text{Al}_{0.025}\text{O}$  thin film or an AZO thin film was deposited on the deposited p-type

$\text{Cu}_2\text{O}$  film by the PLD method using an ArF excimer laser (wavelength:  $193 \text{ nm}$ , energy:  $350 \text{ mJ}$ , repetition frequency:  $20 \text{ Hz}$ ). An n-type  $\text{Ga}_{0.975}\text{Al}_{0.025}\text{O}$  sintered target and an AZO sintered target were prepared by forming the mixed powders using a cold-pressing method followed by sintering. N-type  $\text{Ga}_{0.975}\text{Al}_{0.025}\text{O}$  thin films or AZO films were prepared at room temperature (not heated intentionally) on p-type  $\text{Cu}_2\text{O}$  thin films. AZO thin films of  $200\text{--}300 \text{ nm}$  in thickness were prepared at an oxygen pressure of  $0.2 \text{ Pa}$ . Electrical properties of AZO thin films were evaluated under the previously mentioned device fabrication conditions using the film simultaneously deposited on OA-10 glass (Nippon Electric Glass Co., Ltd.). The AZO film produced has a  $\rho$  of  $0.8\text{--}1 \times 10^{-4} \Omega \text{ cm}$  and an electron concentration ( $n$ ) of  $5 \times 10^{20} \text{ cm}^{-3}$ . The photovoltaic properties of the  $\text{Cu}_2\text{O}$ -based solar cells (electrode area:  $3.14 \text{ mm}^2$ ) were evaluated by exposing only the AZO transparent electrode area to AM 1.5 G solar illumination ( $100 \text{ mW/cm}^2$ ) at  $25^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Epitaxial growth of $\text{Cu}_2\text{O}$ thin film on $\text{p}^+$ -type- $\text{Cu}_2\text{O}:\text{Na}$ substrate

A  $\text{Cu}_2\text{O}$  thin film of  $2.0 \mu\text{m}$  in thickness was prepared on a  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate with a constant current density of  $0.25 \text{ mA/cm}^2$ . The film was also deposited on an FTO coated glass (FTO/glass) under the same conditions. Fig. 2(a) shows an SEM image of the  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate surface. Fig. 2(b) and (c) show a surface and a cross-sectional SEM image of the  $\text{Cu}_2\text{O}$  thin film/ $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate after the thin film was prepared, respectively. Fig. 2(d) also shows an SEM image of the FTO/glass surface. Fig. 2(e) shows the p-type  $\text{Cu}_2\text{O}$  thin film/FTO/glass after the thin film was prepared, and Fig. 2(f) shows a cross-sectional SEM image.  $\text{Cu}_2\text{O}$  thin films were prepared on all of the substrates, but a comparison of Fig. 2(b) and (e) shows that the morphologies of the film surfaces after deposition differ significantly depending on the substrate. Thus, the crystallinity of the films is possibly affected by the substrates used for deposition. To evaluate the crystallographic properties of the films, the orientation of planes was first evaluated using the XRD method (out-of-plane). Fig. 3(I), (II) and (III) show X-ray diffraction profiles of the  $\text{Cu}_2\text{O}$  thin film/ $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$ , the  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrates, and the p-type  $\text{Cu}_2\text{O}$  thin film/FTO/glass substrates, respectively. The  $\text{Cu}_2\text{O}$  thin film prepared on the  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate shown in Fig. 3(I) showed (110) plane orientation only. As shown in Fig. 3(II), the  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate also showed (110) plane orientation only. It is therefore assumed that the  $\text{Cu}_2\text{O}$  thin film deposited has grown in the same orientation as that of the  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate. On the other hand,  $\text{Cu}_2\text{O}$  thin film prepared on the FTO/glass shows not only the diffraction peak of the FTO ( $\text{SnO}_2$ ) substrate but also the diffraction peak originating from the  $\text{Cu}_2\text{O}$  thin film were observed. In addition, the  $\text{Cu}_2\text{O}$  thin film produced on the FTO/glass was non-oriented. These results suggest that this method consequently include the crystallinity of the substrate layer. In order to study the crystallographic properties of the  $\text{Cu}_2\text{O}$  thin films, they were evaluated by the grazing-incidence X-ray diffraction method. Fig. 4(I) shows a diffraction profile of the  $\text{Cu}_2\text{O}$  thin film/ $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate measured by the grazing-incidence X-ray diffraction method with an X-ray incidence angle of  $0.4^\circ$ . Fig. 4(II) also shows the X-ray diffraction profile for a  $\text{p}^+$ -type  $\text{Cu}_2\text{O}:\text{Na}$  substrate, while Fig. 4(III) shows the X-ray diffraction spectrum of a p-type  $\text{Cu}_2\text{O}$  thin film/FTO/glass substrate. In all cases, diffraction peaks originating from the  $\text{Cu}_2\text{O}$  were observed, as clearly shown in the figures. The (110) crystal plane was only detected for the  $\text{Cu}_2\text{O}$  thin film deposited on the

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