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Electrochemically deposited Cu_2O thin films on thermally oxidized Cu_2O sheets for solar cell applications

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ABSTRACT

This paper deals with homoepitaxial growth of Cu_2O 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_2O thin film prepared by epitaxial growth. Such a film was formed at 70 °C on a degenerated p-type Cu_2O:Na (p^+-type Cu_2O: 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_2O thin film (58.8 nm) was larger than that of the film produced on FTO (SnO_2: F) (14.6 nm). A photoelectric conversion efficiency of 2.36% was achieved for the AZO/p-type Cu_2O thin film/p^+-type Cu_2O:Na heterojunction solar cell in which a degenerated Al-doped ZnO (AZO) thin film was prepared as the transparent electrode layer on the Cu_2O thin film by pulse laser deposition. Furthermore, photoelectric conversion efficiency of 4.41% was achieved for the AZO/n-type $Ga_{0.975}Al_{0.025}O$/p-type Cu_2O/p^+-type Cu_2O:Na heterojunction solar cell with n-type $Ga_{0.975}Al_{0.025}O$ film inserted between the AZO and p-type Cu_2O thin film. This clearly shows that the Cu_2O thin film produced by epitaxial growth on a p^+-type Cu_2O:Na (p^+-type Cu_2O: Na) substrate is superior as an active layer.

1. Introduction

Cu_2O is an attractive selection for the active layer of solar cells because copper (Cu), the primary raw material of Cu_2O, is non-toxic and inexpensive, and Cu_2O is a direct transition semiconductor with a bandgap of 2.1 eV. Furthermore, heterojunction solar cells using Cu_2O 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_2O functions as an acceptor, Cu_2O shows p-type conductivity. In other words, it would be extremely difficult to realize n-type Cu_2O [4,5]. Consequently, research on Cu_2O solar cells focuses on the R&D of n-type semiconductor/p-type Cu_2O heterojunction solar cells consisting of p-type Cu_2O active layers and other n-type semiconductor materials [6,7]. The production of n-type semiconductor/p-type Cu_2O heterojunction solar cells reported in a large number of scientific papers used, as the active layer, p-type Cu_2O sheets fabricated by thermal oxidation or Cu_2O thin films prepared with an electrochemical deposition (ECD) method [8–18].

Among n-type semiconductor/p-type Cu_2O heterojunction solar cells that use Cu_2O thin film as the active layer produced by EDC, Isaki et al. reported a 1.28% conversion efficiency for p-type Cu_2O/n-type ZnO/FTO solar cells in 2007 [8]. These cells were fabricated by growing an n-type ZnO film and Cu_2O thin film (mobility [μ]: 1.8 $cm^2/V\,s$) on a glass substrate with an F-doped SnO_2 (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_2O thin films as the active layer was reported by a research group led primarily by Buonassisi [16,17]. They prepared a Cu_2O thin film (μ: 8 $cm^2/V\,s$) 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_2O_3) 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_2/AZO/ZTO/Cu_2O and MgF_2/AZO/Ga_2O_3/Cu_2O 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_2O, Therefore, it is important to use a high-quality Cu_2O thin film as the active layer [9]. Crystallinity and hole mobility of Cu_2O thin film significantly

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affect the diffusion length of the decimal carrier. Consequently, it is indispensable to use a Cu_2O thin film having a superior crystallinity (high hole mobility) in order to realize a high conversion efficiency of Cu_2O solar cells. A high hole mobility ([μ]: 90 $cm^2/V\,s$) of Cu_2O thin film produced by epitaxial growth on an 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 Cu_2O thin films through epitaxial growth. Thus, we can expect improvement in the conversion efficiency by using Cu_2O thin film, produced by epitaxial growth, having high crystallinity and hole mobility for the active layer. The ECD method of depositing p-type Cu_2O thin films is widely known. At present, however, there has been no report of epitaxial growth on a p^+-type Cu_2O:Na substrate by ECD.

This paper describes a homoepitaxial growth of Cu_2O thin films by ECD on a degenerated p^+-type Cu_2O:Na substrate with 10^{19} cm^{-3} hole concentration (p). Properties of the Cu_2O 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 Cu_2O heterojunction solar cells using the p-type Cu_2O thin film produced for the active layer were studied.

2. Experimental

P-type Cu_2O thin film was prepared on a p^+-type Cu_2O:Na substrate by ECD. A degenerated p^+-type Cu_2O:Na sheet used both as the electrode and as the substrate was fabricated by heating a p^+-type Cu_2O sheet, which was fabricated by thermal oxidation of Cu together with an Na compound at 800 °C for 30 h in an Ar atmosphere, cooling down to 500 °C, and then quick-cooling in the atmosphere [20]. Typical electrical properties (at room temperature) of the fabricated p^+-type Cu_2O:Na substrate are a hole concentration of 2–5 × 10^{19} cm^{-3}, a mobility (μ) of 5–8 $cm^2/V\,s$, and a specific resistance (p) of 0.02–0.04 Ω cm. Before using it as an electrode, the p^+-type Cu_2O:Na substrate was wet-etched to remove the 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 Cu_2O thin film [22]. For the growth, a mixed aqueous solution of NaOH, $CuSO_4$ (concentration of 0.20 mol/l), and $CH_3CH(OH)COOH$ (concentration of 3.00 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 p^+-type Cu_2O:Na substrate was used for the negative electrode, or F-doped SnO_2 (FTO) was used as the reference. Cu_2O thin film was deposited by applying voltage between the electrodes with a constant current density of 0.25 mA/cm^2 at a solution temperature of 70 °C. Properties of the Cu_2O 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 Cu_2O heterojunction solar cell consisting of a p-type Cu_2O 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 AI-doped ZnO(n^+-type AZO)/p-type Cu_2O/p^+-type Cu_2O:Na heterojunction solar cell. A 200-μm-thick degenerated p^+-type Cu_2O:Na sheet was used as the substrate. A p-type Cu_2O film was prepared as the active layer on p^+-type Cu_2O: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 $Ga_{0.975}Al_{0.025}O$/p-type Cu_2O/p^+-type Cu_2O:Na heterojunction solar cell. The $Ga_{1-X}Al_XO$ (=Al/[Ga+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 $Ga_{0.975}Al_{0.025}O$ thin film or an AZO thin film was deposited on the deposited p-type Cu_2O film by the PLD method using an ArF excimer laser (wavelength: 193 nm, energy: 350 mJ, repetition frequency: 20 Hz). An n-type $Ga_{0.975}Al_{0.025}O$ sintered target and an AZO sintered target were prepared by forming the mixed powders using a cold-pressing method followed by sintering. N-type $Ga_{0.975}Al_{0.025}O$ thin films or AZO films were prepared at room temperature (not heated intentionally) on p-type Cu_2O thin films. AZO thin films of 200–300 nm in thickness were prepared at an oxygen pressure of 0.2 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 ρ of 0.8–1 × 10^{-4} Ωcm and an electron concentration (n) of 5 × 10^{20} cm^{-3}. The photovoltaic properties of the Cu_2O-based solar cells (electrode area: 3.14 mm^2) were evaluated by exposing only the AZO transparent electrode area to AM 1.5 G solar illumination (100 mW/cm^2) at 25 °C.

3. Results and discussion

3.1. Epitaxial growth of Cu_2O thin film on p^+-type-Cu_2O:Na substrate

A Cu_2O thin film of 2.0 μm in thickness was prepared on a p^+-type Cu_2O:Na substrate with a constant current density of 0.25 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 p^+-type Cu_2O:Na substrate surface. Fig. 2(b) and (c) show an surface and a cross-sectional SEM image of the Cu_2O thin film/p^+-type Cu_2O: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 Cu_2O thin film/FTO/glass after the thin film was prepared, and Fig. 2(f) shows a cross-sectional SEM image. Cu_2O 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 Cu_2O thin film/p^+-type Cu_2O:Na, the p^+-type Cu_2O:Na substrates, and the p-type Cu_2O thin film/FTO/glass substrates, respectively. The Cu_2O thin film prepared on the p^+-type Cu_2O:Na substrate shown in Fig. 3(I) showed (110) plane orientation only. As shown in Fig. 3(II), the p^+-type Cu_2O:Na substrate also showed (110) plane orientation only. It is therefore assumed that the Cu_2O thin film deposited has grown in the same orientation as that of the p^+-type Cu_2O:Na substrate. On the other hand, Cu_2O thin film prepared on the FTO/glass shows not only the diffraction peak of the FTO (SnO_2) substrate but also the diffraction peak originating from the Cu_2O thin film were observed. In addition, the Cu_2O 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 Cu_2O thin films, they were evaluated by the grazing-incidence X-ray diffraction method. Fig. 4(I) shows a diffraction profile of the Cu_2O thin film/p^+-type Cu_2O:Na substrate measured by the grazing-incidence X-ray diffraction method with an X-ray incidence angle of 0.4°. Fig. 4(II) also shows the X-ray diffraction profile for a p^+-type Cu_2O:Na substrate, while Fig. 4(III) shows the X-ray diffraction spectrum of a p-type Cu_2O thin film/FTO/glass substrate. In all cases, diffraction peaks originating from the Cu_2O were observed, as clearly shown in the figures. The (110) crystal plane was only detected for the Cu_2O thin film deposited on the