Sputtered AZO on <111>-oriented Cu2O photovoltaic device with improved performance

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Abstract. Electrodeposited Cu2O/AZO photovoltaic (PV) device are promising low-cost solar cell. Both layer of Cu2O and AZO heterojunction architectures are studied as a function of AZO target-Cu2O substrate distance during sputtering process to mitigate the damage at the interface. The Cu2O/AZO PV device has been constructed by electrodeposition of a <111>-p-Cu2O layer on an Au (111)/Si wafer substrate followed by stacking the AZO layer using a sputtering technique. The Cu2O/AZO PV device showed a photovoltaic performance under AM1.5 illumination, and the performance changed depending on the target-substrate distance. It is shown that an increase in target-substrate distance during stacking the AZO layer by sputtering mitigated the damage at the Cu2O/AZO interface. As a result, we were able to improve the Voc and power conversion efficiency from 0.16 V and 0.46 % to 0.30 V and 0.64 %, respectively.

1. Introduction

Cuprous oxide (Cu2O) is a p-type semiconductor with the band-gap energy of 2.1 eV [1] and has received broad attention as a light-absorbing layer in a photovoltaic device [2-7], because of its non-toxicity, abundance, and theoretical conversion efficiency of 18%. The Cu2O layers have been prepared by several techniques such as a thermal oxidation of a metallic Cu sheet in air at 1273 K [8], RF magnetron sputtering [9], radical oxidation [10], sol-gel spin coating [11] and electrodeposition in an aqueous solution [12]. The conversion efficiency of 6.1% has been reported for the AZO/Al-doped Ga2O3/Na-doped Cu2O PV device using the thermal oxidation of metallic Cu sheet in air followed by a pulse-laser deposition of Ga2O3 and AZO layers [13]. In contrast, the electrodeposition process in aqueous solutions is a well-known technique due to several advantages such as low-fabrication cost, low temperature, ambient pressure processing, controllable film thickness, and possible large scale deposition. The intrinsically p-type nature, self-compensation problems, and low dopant solubility have inhibited the synthesis of n-type Cu2O to give efficient homojunctions [14-15]. The conversion
efficiency, however, was limited at 1.28% for the randomly oriented Cu$_2$O/ZnO PV device prepared by only electrodeposition [16], and the poor performance was originated from the low mobility relating to the diffusion length of minority carrier. The highly $<111>$-oriented Cu$_2$O layer has been prepared by electrodeposition of the (111)-Au/Si wafer substrate, and showed the increased mobility. The (111)-Cu$_2$O/ZnO PV device was fabricated by stacking the n-ZnO layer on the Cu$_2$O layer with a conventional and photon-assisted electrodeposition process, and the photovoltaic performance was discussed clearly [17]. The performance, however, was poor compared to the electrodeposition Cu$_2$O/ZnO PV device.

Here, we demonstrate the preparation of $<111>$-Cu$_2$O/Al-doped ZnO (AZO) PV device by the electrodeposition of the Cu$_2$O layer followed by stacking the AZO layer by a sputtering, and reports the effects of target-substrate distance of sputtered AZO layer on the photovoltaic performance. The structural, optical, and electrical characterizations for the Cu$_2$O/AZO PV device were carried out by X-ray diffraction (XRD), scanning electron microscopy (FE-SEM) observations, and measurements of electrical properties. The $<111>$-Cu$_2$O/AZO PV device revealed the photovoltaic performance with conversion efficiency of 0.64%.

2. Experimental Section

The Cu$_2$O layer was deposited potentiostatically at −0.5 V referenced to Ag/AgCl electrode on the Au(111)/Si(100) substrate at a constant electric charge of 1.7 C.cm$^{-2}$ with a potentiostat (Hokuto Denko, HABF-501A) in an alkaline aqueous solution containing a 0.4 M copper(II) acetate monohydrate (Cu(CH$_3$COO)$_2$·H$_2$O, Nacalai Tesque, Inc.) and 3 M lactic acid (Kanto Chemical, Co., Inc.) at 328 K. The solution was prepared with deionized (DI) water purified by an Elix-UV system (Millipore), and KOH was added for the pH adjustment to 12.5. The Au(111)/Si(100) substrate (Kobelco Research Inst. Inc.) was composed of 0.5μm-sputtered Au layer on a single-crystal Si(100) wafer, and prior to the electrodeposition, the Au(111)/Si(100) substrate was rinsed with acetone, polarized in 1 M NaOH and rinsed with distilled water. A Pt plate was used as the counter electrode. The AZO layer was sputtered on the Cu$_2$O layer by using radio frequency (rf) magnetron sputtering (ULVAC, RFS-200) with AZO target (99%). The substrate temperature was 25°C, pressure chamber of 1.0 Pa, and the rf power of 100 W for 60 sec. The distance between AZO target and Cu$_2$O layer substrate varied from 30 to 50 mm. The photovoltaic device was fabricated by stacking a 100-nm-thick-Al electrode by vacuum evaporation (ULVAC, VPC-260F) on the top of the AZO/Cu$_2$O heterostructures.

Structural characterization was carried out by X-ray Diffractometer (XRD, Rigaku RINT 2500) operated at 20 kV and 10 mA using Cu Kα radiation. The observation of surface and cross-sectional morphology of the layers was carried out with a field emission scanning electron microscope (FE-SEM, Hitachi High Technology SU8000) at an operating voltage of 3 kV. Optical absorption spectra were recorded using a UV-Vis-NIR spectrophotometer (Hitachi High-Technology UV-4100) with an integrating sphere. The photoluminescence spectrum was recorded with fluorescent spectroscopy (Hitachi, F-7000) at room temperature. The current density-voltage curve in the dark and under AM1.5 illumination with 100 mWcm$^{-2}$ in power was recorded using a solar simulator (Bunko Keiki, OTENTOSUN-III) and a Keithley 2400 source meter.

3. Results and Discussion

3.1. Characteristic of the Cu$_2$O layer prepared on the (111)Au/Si substrate.

The X-ray diffraction pattern of the Cu$_2$O layer with electric charges of 1.7 C.cm$^{-2}$ prepared on the (111)-Au/Si substrate is shown in Fig. 1. Only two peaks seen in X-ray diffraction pattern could be assigned to the (111) plane of Au with a face-centered cubic lattice and (111) plane of Cu$_2$O with the characteristic cubic cupric structure. The lattice parameter calculated from the Cu$_2$O (111) peak was

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Figure 1. X-ray diffraction pattern of the Cu$_2$O layer with electric charges of 1.7 C.cm$^{-2}$ prepared on the (111)-Au/Si substrate.

Figure 2. FE-SEM image of the Cu$_2$O layer with electric charges of 1.7 C.cm$^{-2}$ prepared on the (111)-Au/Si substrate.

4.267 Å, which almost agreed with the standard value of 4.269 Å tabulated in the ICDD card [18]. The electrodeposition of Cu$_2$O layer had no effect on the intensity and angles of the (111)-Au peaks.

Fig. 2 shows the FE-SEM images of the Cu$_2$O layer with electric charges of 1.7 C.cm$^{-2}$ prepared on the (111)-Au/Si substrate. The Cu$_2$O layers deposited on the Au(111) layer were composed of aggregates of the hexagonal columnar grains grown in direction perpendicular to the Au(111) substrate surface, and the thickness was estimated to be about 2.0 μm. The triangular facet corresponding to the (111)-plane of the Cu$_2$O crystal was obviously observed in the plan-view FE-SEM image even after stacking the AZO layer, and the surface morphology was similar to the typical pyramidal-shape-Cu$_2$O layer prepared on a conductive glass substrate as already reported [19].
The pyramidal-shape of Cu$_2$O grains was approximately 0.4 μm corresponding to the electric charge of 1.7 C.cm$^{-2}$. No defects such as pores were observed throughout the layer thickness.

Fig. 3 show the absorption spectra and the correlation of absorption coefficient and photon energy for the (111)-Cu$_2$O layer prepared on the (111)-Au/Si substrate. The Cu$_2$O layer showed an absorption edge around 600 nm, and the interference fringe pattern was obviously observed at a wavelength less than 600 nm, indicating the formation of a homogeneous Cu$_2$O layer. The absorption coefficient was calculated from the absorbance and thickness obtained with a SEM observation. The optical bandgap energy ($E_g$) was estimated by extrapolating the linear part with the assumption of a direct optical transition [20] for Cu$_2$O layer and was measured to be approximately 2.0 eV.

3.2 Characteristics of the (111)-Cu$_2$O/AZO photovoltaic device

Fig. 4 show the schematic illustration of cell configuration of substrate type Cu$_2$O/AZO PV device and the cross-section of SEM images of the Cu$_2$O layers before and after stacking the AZO layer for 60 sec by using r.f. magnetron sputtering with different target-substrate distance of 30 and 50 mm. The AZO layer could be observed on the cross-sectional images after sputtering for 60 sec on both target-substrate distances. The AZO layer was found to be deposited on the entire surface of the Cu$_2$O layer. And, the thickness was estimated to be about 50 nm from the cross-sectional images, irrespective of the target-substrate distance during sputtering process. No voids could be observed between the Cu$_2$O layer and AZO layer. Despite of different in target-substrate distance during sputtering of AZO layer, no obvious changes could be seen at the Cu$_2$O/AZO interface.
Figure 4. (a) Schematic illustration of cell configuration of substrate type Cu$_2$O/AZO PV device and (b) the cross-section SEM images of the Cu$_2$O layers before and after stacking the AZO layer with target-substrate distance of (c) 30 mm and (d) 50 mm.

Figure 5. Absorption spectra for Cu$_2$O/AZO PV device with target-substrate distance of (a) 30 and (b) 50 mm.
Fig. 5 shows the optical absorption spectra for Cu$_2$O/AZO PV device with target-substrate distance of 30 and 50 mm. An absorption edge was also observed at a wavelength around 380 nm that originated from the AZO layer in addition to that for the Cu$_2$O layer. By stacking AZO layer on the Cu$_2$O layer, the PV device was observed to absorb more light compared to the bare Cu$_2$O layer. The Cu$_2$O/AZO PV device with target-substrate distance of 50 mm exhibited higher absorption spectra compared to that of target-substrate distance of 30 mm at wavelength around 380 nm. The increase in the absorbance was attributed to the scattering effect at the Cu$_2$O/AZO heterointerface.

Fig. 6 shows current density-voltage curves of the Cu$_2$O/AZO PV devices with different target-substrate distance during sputtering process of AZO layer under AM 1.5 illumination (100 mWcm$^{-2}$). All of the Cu$_2$O/AZO PV devices showed the photovoltaic performance. The Cu$_2$O/AZO PV device showed a strong dependence on the target-substrate distance of Cu$_2$O/AZO layer. The Cu$_2$O/AZO PV device with target-substrate distance of 30 mm exhibited a short-circuit current density (Jsc) of 8.85 mAcm$^{-2}$ with a fill factor (FF) of 0.33, open-circuit voltage (Voc) of 0.16 V, and a power conversion efficiency (PCE) of 0.47%.

By increasing the target-substrate distance during stacking the AZO layer to 50 mm, the photovoltaic performance was found to produce the highest PCE of 0.64% with Voc and Jsc of 0.30 V and 5.64 mAcm$^{-2}$ respectively. This dramatic improvement has been attributed to the quality of the <111>-Cu$_2$O/AZO heterojunction formed. The Voc increased from 0.16 V to 0.30 V by increasing the target-substrate distance from 30 mm to 50 mm. The increase of target-substrate distance is speculated to mitigate the AZO ions impact on the Cu$_2$O layer substrate, resulting in better Cu$_2$O/AZO heterointerface quality [21]. The sputtered AZO layer was found to completely cover the entire <111>-oriented Cu$_2$O layer, forming an abrupt interface for the efficient transfer of the generated carrier out from the Cu$_2$O layer.
4. Conclusion
The substrate-type Cu$_2$O/AZO photovoltaic (PV) device has been constructed by electrodeposition of the <111>-p-Cu$_2$O layer on an Au (111)/Si wafer substrate followed by stacking the AZO layer by sputtering. The <111>-oriented Cu$_2$O layer was prepared by electrodeposition on <111>Au/Si wafer substrate in an alkaline solution containing copper acetate and lactic acid. The PV device was fabricated by stacking the top Al electrode by evaporation. The thickness of Cu$_2$O layer was maintained by controlling the electric charge during the electrodeposition process. All <111>- Cu$_2$O/AZO PV devices showed photovoltaic performance under AM1.5 illumination, and the performance changed depending on the target-substrate distance during stacking the AZO layer by sputtering, resulting in the increase in quality of the Cu$_2$O/AZO interface. The highest photovoltaic performance of 0.64% with short-circuit current density of 5.64 mAcm$^{-2}$ and open-circuit voltage of 0.30 V could be obtained for the substrate-type <111>-Cu$_2$O/AZO PV device prepared with target-substrate distance of 50 mm and Cu$_2$O layer thickness of 2.0 μm. Although, further improvement is needed, these results show the importance of the heterointerface state including band alignment and the viability of the oxide-based photovoltaic devices to be the next generation thin film solar cells.

5. References
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