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Heterostructure Solar Cells Based on Sol-Gel Deposited SnO_2 and Electrochemically Deposited Cu_2O

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ABSTRACT

To fabricate a heterostructure solar cell using environmentally friendly materials and low cost techniques, tin oxide (SnO_2) and cuprous oxide (Cu_2O) were deposited by the sol-gel method and the electrochemical deposition, respectively. The SnO_2 films were deposited from a $SnCl_2$ solution containing ethanol and acetic acid. The Cu_2O films were deposited using a galvanostatic method from an aqueous bath containing $CuSO_4$ and lactic acid at a temperature of 40˚C. The Cu_2O/SnO_2 heterostructure solar cells showed rectification and photovoltaic properties, and the best cell showed a conversion efficiency of 6.6×10^{-2} % with an open-circuit voltage of 0.29 V, a short-circuit current of 0.58 mA/cm^2, and a fill factor of 0.39.

Keywords: Sol-Gel Deposition; Electrochemical Deposition; Cu_2O; SnO_2; Solar Cell

1. Introduction

The production of silicon solar cells is expanding, but not sufficiently fast, because of high cost and large energy consumption for the material purification and cell manufacturing. Thus extensive researches are going on, aiming the development of solar cells using cost-effective and environmentally benign materials prepared by simple low-cost techniques. In this work, we attempt to use tin oxide (SnO_2) deposited by a sol-gel technique for the n-type semiconductor of a solar cell. SnO_2 thin films have been attracting interest since they have many important applications such as gas sensors [1,2] and transparent electrodes [3,4]. SnO_2 films have been fabricated by a number of techniques, including spray pyrolysis [5-6], sputtering [7-9], chemical vapor deposition (CVD) [10-12], and sol-gel deposition [3,13,14]. The sol-gel technique has several advantages, such as easy control of film thickness, ability to coat large area, and cost-effectiveness. In this work, we fabricate heterostructure solar cell based on sol-gel deposited SnO_2. It should be noted here that there are very few reports of application of SnO_2 for n-type layer of a heterostructure solar cell [15-18] although SnO_2 is often used as an electrode material.

On the other hand, cuprous oxide (Cu_2O) has gathered much attention as a p-type absorption layer of solar cells owing to its suitable band gap around 2 eV, material abundance, and non-toxicity. The solar cells based on electrochemically deposited Cu_2O have been fabricated with pn heterojunction with ZnO [19-21], TiO_2 [22,23], and indium-tin-oxide (ITO) [24]. The highest solar conversion efficiency of 1.28% was obtained from ZnO/Cu_2O solar cell [19]. In this work, we attempt fabrication of heterostructure solar cells based on electrochemically deposited Cu_2O and sol-gel deposited SnO_2. One paper has been published on Cu_2O/SnO_2 heterostructure solar cells based on sputtered SnO_2 [16], but to our best knowledge, there are no reports on fabrication of heterostructure cells by a combination of sol-gel deposition of SnO_2 and electrochemical deposition (ECD) of Cu_2O.

2. Experimentals

2.1. SnO_2 Deposition and Characterization

SnO_2 films were deposited by the sol-gel method on ITO coated glass substrates. (For the XRD measurement, we used a glass substrate.) 0.7 M $SnCl_2{\cdot}2H_2O$, 10 mL ethanol and 0.25 mL acetic acid were used as a starting source material, solvent and catalyst, respectively. The coating solution was stirred at 70˚C for 30 min and aged at 40˚C for 3 hours, and then dropped on the ITO substrate, which was rotated at 3000 rpm for 20 sec. Then,

the films were dried at 150˚C for 5 min. The procedures from the spin coating to the drying were repeated 2 - 5 times, and then the film was annealed in air at 300˚C for 1 hour.

The compositional analysis was carried out by Auger electron spectroscopy (AES) using the model JEOL JAMP 7800. Profile meter Accretech Surfcom-1400D was used to measure the thickness of the film. The X-ray diffraction (XRD) measurement was carried out by the Rigaku SmartLab X-ray diffractometer using CuKα_1 radiation. The optical transmission measurement was performed using a JASCO-570 spectrometer with the ITO substrate as the reference. In addition, the conduction type and photosensitivity of the films were examined by means of the photoelectrochemical (PEC) measurements. The PEC measurement was carried out using the three-electrode cell with saturated calomel electrode (SCE) as the reference electrode. The deposited film was used as the working electrode, and 100 mM of Na_2SO_3 was used for the electrolyte. The backside of the sample was illuminated by pulsed light coming from a Xe lamp (about 100 mW/cm^2). The incident light was turned off and on mechanically every five seconds. A ramp voltage was applied between the working and the reference electrodes, and the released current was monitored.

2.2. Cu_2O/SnO_2 Heterostructure Fabrication and Characterization

The heterostructure solar cells were fabricated by depositing Cu_2O by ECD on the SnO_2 film. We used a solution containing 0.2 M $CuSO_4$ and 1.6 M lactic acid. pH of the solution was adjusted to 12.5 by adding KOH. Cu_2O was deposited galvanostatically at 40˚C with a current density of −1.0 mA/cm^2. All samples were deposited for 10 min. Indium metal electrodes were deposited by thermal evaporation on the Cu_2O layer. The electrode size is 1 mm^2. Photovoltaic properties were characterized using an AM 1.5 solar simulator. The radiation power of light was about 100 mW/cm^2. The light was illuminated on the ITO side (SnO_2 side) of the sample.

3. Results and Discussion

3.1. SnO_2 and Cu_2O Films

The thickness of the SnO_2 film was about 0.6 μm when the coating-drying cycle was repeated 3 times. The film is transparent in the visible range, and the band gap obtained from the optical transmission spectrum is 3.9 eV. The differential AES spectrum of the prepared film is shown in **Figure 1**. The O/Sn composition ratio obtained from it is about 2, *i.e.*, the film is almost stoichiometric. A weak chlorine signal was observed near 190 eV. The XRD pattern of the film deposited on the glass substrate is shown in **Figure 2**. The pattern shows three characteristic XRD peaks of SnO_2 with a broad background signal due to glass. The SnO_2 peaks are broad, which indicates that the SnO_2 film consists of nano crystallites.

The PEC results for the SnO_2 film are shown in **Figure 3**. The current was not changed by illumination for the cathodic scan, while during the anodic scan, the current was changed due to the light chopping. When the junction of the semiconductor-electrolyte is illuminated, photogenerated electrons/holes are separated in the space charge region. The photogenerated minority carriers

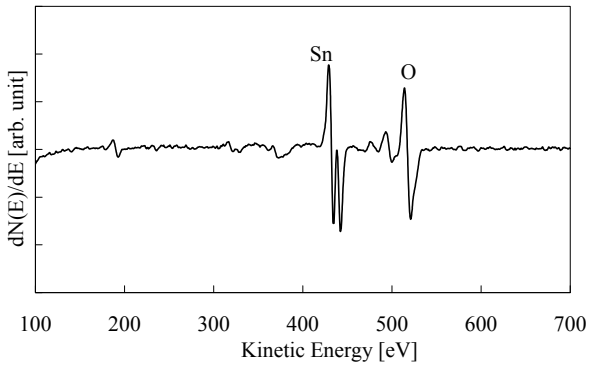

Figure 1. AES spectrum for sol-gel deposited SnO_2.

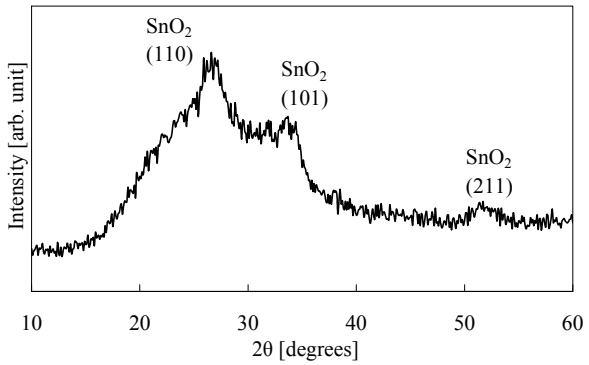

Figure 2. X-ray diffraction pattern of sol-gel deposited SnO_2.

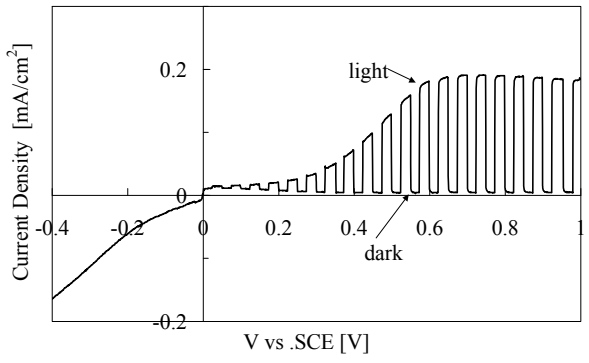

Figure 3. Photoelectrochemical measurement results for SnO_2.

arrive at the interface of the semiconductor-electrolyte to participate in the electrochemical reaction at the film/ electrolyte interface. The current becomes more positive under the light illumination during the anodic scan. This implies that the minority carriers generated here are holes. Thus, the prepared film is n-type semiconductor.

The film thickness of ECD-Cu_2O was about 0.7 μm and the direct band gap obtained from the optical transmission was about 2.5 eV. The PEC results for the Cu_2O film are shown in **Figure 4**. The current was not changed by illumination for the anodic scan, and thus only the results for the cathodic scan are shown there. Negative photo current was observed, which implies that the minority carriers generated here are electrons. Thus, the prepared film is a p-type semiconductor with a good photosensitivity.

3.2. Cu_2O/SnO_2 Heterostructures

The heterostructures were fabricated with SnO_2 as a window layer and Cu_2O as an absorption layer. **Figure 5** shows I-V characteristic of the Cu_2O/SnO_2 heterostructure cell fabricated by repeating the coating-drying cycle 3 times for the SnO_2 deposition. The rectification and photovoltaic behaviors appeared. The heterostructure cells were fabricated with different repetition time of the coating-drying cycle, and the photovoltaic properties of all the samples are shown in **Table 1**. The properties strongly depends on the repetition number of the coating-drying cycle, and the highest efficiency of 6.6×10^{-2} % was obtained with three times repetitions. The reason for dependence on the repetition number is not understood. The film thickness increases in proportion to the repetition number, and too large thickness may results in generation of defects such as crack because of strain.

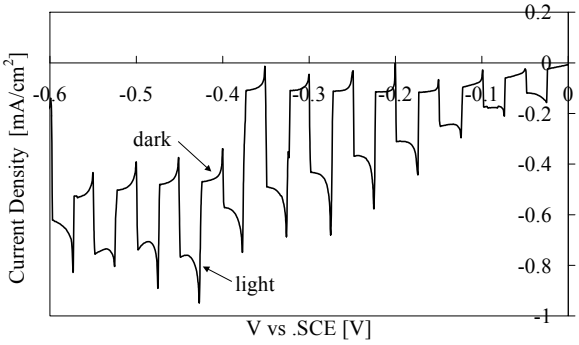

Figure 4. Photoelectrochemical measurement results for ECD-Cu_2O.

Table 1. Photovoltaic properties for the Cu_2O/SnO_2 heterostructure cells.

Number of coating-drying cycles for SnO_2	Open circuit voltage [mV]	Short circuit current [mA/cm^2]	Fill factor	Efficiency [%]
2	20	3.2×10^{-1}	0.25	1.6×10^{-3}
3	290	5.8×10^{-1}	0.39	6.6×10^{-2}
4	75	4.9×10^{-1}	0.27	1.0×10^{-2}
5	10	7.8×10^{-2}	0.27	2.3×10^{-4}

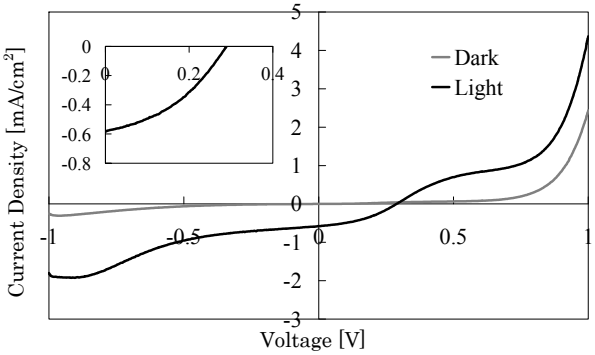

Figure 5. I-V characteristic of the heterostructure cell consisting of sol-gel deposited SnO_2 and ECD-Cu_2O. The coating-drying cycle was repeated 3 times in the sol-gel process. The inset is an expanded figure of photovoltaic properties.

Since each of the layers in the heterostructure showed fairly high photosensitivity as shown in **Figures 3** and **4**, the poor photovoltaic characteristics will be due to some disorder at the interface. Apparently, the SnO_2 layer did not dissolve in the Cu_2O deposition solution, but we cannot exclude possibility that the SnO_2 surface reacted with the Cu_2O deposition solution, to form a thin defective layer. Another possible reason of the poor performance is the Cu_2O/electrode interface. The forward characteristics under the illumination is not a simple diode curve but has a plateau around 0.7 V. This may be due to non-ohmic characteristics of the interface with the electrode.

4. Conclusion

SnO_2 films have been deposited by the sol-gel method. The films showed clear n-type conduction and photosensitivity. We have fabricated Cu_2O/SnO_2 heterostructure cells by depositing Cu_2O by ECD on the sol-gel deposited SnO_2 layer. Rectification property was observed, and the best cell showed an efficiency of 6.6×10^{-2} % under AM1.5 illumination.

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