Electrodeposited CuO Photovoltaic Device with Polysiloxane Layer

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1. Introduction

Copper(II) oxide p-type semiconductor\textsuperscript{1} has attracted increasing attention as a photovoltaic layer in solar cells due to its 1.35 eV bandgap energy and high optical absorption coefficient, but the performance was limited at a low level irrespective of the CuO preparation method.\textsuperscript{2}\textsuperscript{3} The CuO layers were prepared by thermal processes including thermal oxidation\textsuperscript{2}\textsuperscript{2} and chemical solution process such as electrodeposition.\textsuperscript{2}\textsuperscript{e} The electrodeposition process has been used for the electroplating of metals in the surface finishing industry, and oxide and compound films for electronic and optical applications can be prepared by the electroplating in addition to metallic layers. The electrodeposition process has several advantages over the thermal processes as demonstrated by the preparation of Cu(In,Ga)Se\textsubscript{2} and Cu_{x}Sn_{y}S\textsubscript{z} precursor\textsuperscript{4} for solar cell applications. The 1.35-eV-bandgap CuO layer with an improved photoactivity has been prepared by electrodeposition in a basic aqueous solution containing copper acetate hydrate and ammonia.\textsuperscript{5} And, the insertion of highly resistive buffer layer\textsuperscript{5} was effective for improving the photovoltaic performance, as reported for the Cu_{x}O/ZnO photovoltaic devices\textsuperscript{6} prepared by electrodeposition.

In this letter, we report the photovoltaic device of an electrodeposited CuO layer with a polysiloxane layer, and its photovoltaic performance of 0.24 V in open-circuit voltage ($V_{oc}$) observed under AM1.5 illumination.

2. Experimental

An aqueous solution containing 0.05 mol L\textsuperscript{-1} copper(II) nitrate hydrate and 0.05 mol L\textsuperscript{-1} ammonium nitrate was used for the electrodeposition of the 1.3-μm-thick-CuO film. The solution pH was adjusted to pH 9 by adding ammonia water. The solution was prepared with reagent grade chemicals and 15-MΩ cm-resistivity distilled water purified by a Millipore Ellix-UV. A (111)-oriented Au coated Si wafer (KOBELCO Research Institute, Inc.) was used as the substrate. The electrodeposition was potentiostatically carried out without stirring at 297 K by anodic polarization at an electric charge of 1 C cm\textsuperscript{-2} and at a potential of 900 mV versus an Ag/AgCl reference electrode. A Pt sheet was used as the counter electrode. Prior to electrodeposition, the Au/Si substrate was rinsed in acetone and then cathodically polarized in an aqueous solution containing pyrophosphate acid and potassium hydroxide for 30 sec. The polysiloxane layers were prepared on the CuO layer by following processes. (i) Spin-coating the tetrahydrofuran (THF) solution with dissolved 0.5-1.5 mass% polymethylphenylsilane (PMPS) (OGSOL, Osaka Gas Chemical, Co., Ltd.), (ii) ultraviolet light irradiation for 30 sec using a high-pressure mercury lamp (USHIO, OPTICA MODULUX, 500W), and (iii) baking at 523 K for 15 min.\textsuperscript{10} The Al electrode was prepared by vacuum evaporation.

The Fourier-transformed infrared spectra were recorded by an attenuated total reflection (ATR) technique using a Thermo Electron Nicolet 4700 FT-IR Spectrometer and a diamond ATR unit (Smiths, Durasamp IR-II\textsuperscript{TM}). The surface and cross-sectional structures were observed using a field emission scanning electron microscope (Hitachi, SU-8000). The current density-voltage curves were measured using a Keithley 2400 source meter in dark and under AM1.5 illumination.

3. Results and discussions

Figure 1 shows the surface and cross-sectional images of the CuO layers with and without the polysiloxane layer prepared with 1.0% PMPS solutions. The CuO layer possessed the (002) "out-of-plane orientation with random in-plane orientation"\textsuperscript{6} and was composed of aggregates of fan-shaped grains with the size of approximately 100-150 nm and a thickness of approximately 15 nm. Fan-shaped CuO grains with sharp edges could also be observed near the surface in the cross-sectional image. The surface morphology of the CuO grains rounded slightly after the polysiloxane layer

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coating, and some pores between the CuO grains were filled with the polysiloxane layer, as represented by arrow. The polysiloxane layer covered the entire of the CuO surface including the area above the grain boundaries, but the estimation of the thickness of the polysiloxane layer was difficult due to the large surface roughness as observed from the cross-sectional image.

Figure 2 shows the FT-IR spectra for the polysiloxane-layer-stacked CuO layer prepared from 1.0% PMPS solutions. It was confirmed that the CuO layer did not possess an absorption band at the wave number ranging from 800 to 1400 cm\(^{-1}\). The strong absorption band at wavenumber around 1070 cm\(^{-1}\) was identified as the stretching vibration of Si-O and Si-O-Si bonding\(^{10,11}\). The weak absorption band at around 1260 cm\(^{-1}\) was identified as the stretching vibration of Si-C bonding. Indeed, polysiloxane is represented by the chemical formula of \([\{\text{CH}_3\}_2\text{Si-O}\]\(_n\), formed by ultraviolet-light induced decomposition of the polymethylphenylsilane (PMPS), and involved both Si-O and Si-C bonding\(^{12,13}\). The detection of both Si-C and Si-O-Si bonding by FT-IR measurements indicated the formation of the polysiloxane layer on the CuO layer.

Figure 3 shows the current density-voltage curves recorded for Al/CuO/Au heterostructures without and with the polysiloxane layer in the dark and under AM1.5 G illumination. An almost linear proportionality was observed for the polysiloxane-free Al/CuO/Au heterostructure. Since it was predicted that the ohmic and Schottky contacts were formed between the Au/CuO and CuO/Al hetero-interfaces from the energy states as already reported\(^{14}\), the ohmic behavior could be due to the electrical contact between the Au and Al metal layers through the pores of the CuO layer. The polysiloxane-free Al/CuO/Au heterostructure showed an ohmic behavior even under AM1.5 illumination, and no photocurrent density was observed.

The rectification feature in dark was improved by the insertion of the polysiloxane layer, and the rectification ratio of the current densities at +1 V and −1 V was estimated to be 1.7, although a large leakage current density remained. The polysiloxane layer prepared on a quartz glass substrate, in the same manner, showed a bandgap energy of 3.7 eV from the optical absorption spectrum. (not shown) The location of Fermi level is not clear at present, but the polysiloxane/Al interface could be an ohmic contact because polysiloxane is not a p-type semiconductor. The polysiloxane layer could partly make contact under the Au layer through the pores in the CuO layer like the Au/CuO/Al heterostructure, and the carrier could be transported through the polysiloxane layer by tunneling effect. The electrical characteristics observed for the Al/polysiloxane/CuO/Au diode originated from the polysiloxane/CuO and polysiloxane/Au interfaces.

The Al/Polysiloxane/CuO/Au diode showed photovoltaic performance under AM1.5 irradiation. The open-circuit voltage \(V_{oc}\),
short-circuit current density \( (J_{sc}) \), and Fill factor \( (FF) \) were estimated to be 0.24 V, 0.067 \( \mu A \) cm\(^{-2}\), and 0.29, respectively. The conversion efficiency was calculated to be \( 4.6 \times 10^{-7}\% \). The \( V_{oc} \) value was much larger than 0.28 mV reported for the electrodeposited CuO-PV-device\(^{2}\) and slightly lower than 0.37 V for the thermally-prepared CuO/ZnO-PV-device.\(^{3}\) The conversion efficiency was much lower than 0.05 % for the thermally prepared CuO/ZnO-PV-device.\(^{3}\) Since the CuO layer was reduced to metallic Cu during the preparation of Ga: ZnO window by sputtering, the Al/poly-siloxane/CuO/Au diode did not possess a transparent conductive window and this hindered the collection of carriers generated by photons. The CuO and polysiloxane layers showed very high resistivities of \( 2.2 \times 10^7 \) \( \Omega \) cm\(^{-1}\) and over \( 10^9 \) \( \Omega \) cm, respectively. Since the carriers collected by the Al electrode originated from the part in the vicinity of the Al electrode, the practical \( J_{sc} \) value would be higher than that measured in this study in the case of possessing a transparent conductive window. Thus, the insertion of the transparent conductive window, optimization of the device structure, and improvements of the qualities of the CuO and polysiloxane layers are necessary to improve the overall photovoltaic performance.

4. Conclusions

The polysiloxane/CuO diodes were constructed by electrodeposition of the (002)-oriented CuO layer followed by the preparation of polysiloxane layer using polymethylphenylsilane (PMPS) which showed a rectification feature in dark, along with the photovoltaic performance of 0.24 V in \( V_{oc} \) under AM1.5 illumination.

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