

## Photon-Assisted Electrodeposition of <0001>-n-ZnO/<111>-p-Cu<sub>2</sub>O Photovoltaic Devices with TiO<sub>2</sub> Intermediate Layer

Mohd Zamzuri<sup>1,2, a</sup>, Junji Sasano<sup>1, b</sup>, Fariza Binti Mohamad<sup>3, c</sup>,

Masanobu Izaki<sup>1, d</sup>

<sup>1</sup>Department of Mechanical Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tenpaku, Toyohashi, Aichi 441-8580, Japan

<sup>2</sup>School of Manufacturing Engineering, Universiti Malaysia Perlis, Kampus Tetap Pauh Putra, Jalan Arau-Changlun, 02600, Arau, Perlis, Malaysia

<sup>3</sup>Faculty of Electrical & Electronic, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

<sup>a</sup>zamzuri@tf.me.tut.ac.jp, <sup>b</sup>sasano@me.tut.ac.jp,

<sup>c</sup>farizabm@uthm.edu.my, <sup>d</sup>m-izaki@me.tut.ac.jp

**Keywords:** Photon-assisted electrodeposition, ZnO/Cu<sub>2</sub>O heterojunction, TiO<sub>2</sub> layer, Sol-gel method

**Abstract.** The <111>-Cu<sub>2</sub>O/<0001>-ZnO photovoltaic (PV) device has been constructed by a electrodeposition of Cu<sub>2</sub>O layer followed by a photon-assisted electrochemical reaction in aqueous solutions, and the effect of the insertion of the TiO<sub>2</sub> layer prepared by a sol-gel technique on the photovoltaic performance was investigated. The structural, optical, and electrical characterizations were carried out with XRD, FE-SEM, UV-Vis-NIR spectrophotometer, and solar simulator. The performance of AZO/<0001>-ZnO/TiO<sub>2</sub>/<111>-Cu<sub>2</sub>O PV-devices changed depending on the preparation condition for the TiO<sub>2</sub> layer, and the short-circuit current density of 4.86 mAcm<sup>-2</sup> has been obtained for the PV device prepared under optimized condition.

### Introduction

A photovoltaic device composed of p-Cu<sub>2</sub>O and n-ZnO semiconductors has received broad attention as a candidate of the next generation thin film solar cell, because of the nontoxicity, abundance, theoretical conversion efficiency of around 18% [1], and an absorption coefficient higher than a single crystalline Si [2]. The Cu<sub>2</sub>O layers for the photovoltaic application have been prepared by several techniques such as a thermal oxidation of a metallic Cu sheet [3], RF magnetron sputtering [4], and electrodeposition [5]. The ZnO layers have been prepared by electrodeposition in an aqueous solution containing either zinc nitrate [6] or zinc chloride [7] as well as gas-phase deposition techniques such as sputtering, molecular beam epitaxy, and laser ablation techniques. 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, as demonstrated for the CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub> solar cell production. The conversion efficiency, however, was limited at 1.28% for the randomly oriented Cu<sub>2</sub>O/ZnO heterojunction diode prepared only by electrodeposition [8]. The quality of the Cu<sub>2</sub>O layer was improved by using an electrochemical heteroepitaxial growth [9], and a photon-assisted electrochemical growth of the ZnO layer without the reduction of Cu<sub>2</sub>O to metallic Cu was developed [10]. Here, we prepare <0001>ZnO/<111>Cu<sub>2</sub>O PV device by the heteroepitaxial and photon-assisted electrochemical process, and the effects of the insertion of a TiO<sub>2</sub> layer prepared by a sol-gel process were investigated by the structural, optical, and electrical characterizations.

## Experimental Procedures

The  $\text{Cu}_2\text{O}$  layer was deposited potentiostatically at  $-0.5$  V referenced to Ag/AgCl electrode on the Au(111)/Si(100) substrate at an electric charge of  $1.7 \text{ coulomb cm}^{-2}$  with a potentiostat in an alkaline aqueous solution containing a  $0.4$  M copper(II) acetate monohydrate, and  $3$  M lactic acid at  $328$  K. The solution was prepared with reagent grade chemicals and de-ionized (DI) water, and KOH was added for the pH adjustment to  $12.5$ . A Pt plate was used as the counter electrode. The  $\text{TiO}_2$  layer was deposited on the  $\text{Cu}_2\text{O}$  layer by using spin coating technique at  $5000$  rpm for  $15$  sec with  $3\%$  and  $5\%$  of  $\text{TiO}_2$  sol at substrate temperature of  $65^\circ\text{C}$ . The ZnO layer was stacked on the  $\text{TiO}_2$  layer at a potential of  $-0.06$  V referenced to the Ag/AgCl for the deposition time of  $30$  min in a simple aqueous solution containing  $0.08$  M zinc nitrate hydrate at  $336$  K with light irradiation. The  $200\text{-nm}$ -thick ZnO:Al layer was deposited using radio frequency (rf) magnetron sputtering with AZO target. The substrate temperature was  $25^\circ\text{C}$ , pressure chamber of  $1.0$  Pa, and the rf power of  $100$  W. Structural, optical, and electrical characterizations were performed by XRD, FE-SEM, UV-Vis-NIR spectrophotometer, and Keithley 2400 source meter under illumination with  $100 \text{ mWcm}^{-2}$  power.

## Results and Discussion

Figure 1 shows X-ray diffraction patterns of ZnO/ $\text{Cu}_2\text{O}$  heterojunction structure before and after inserting the  $\text{TiO}_2$  sol concentration of  $3\%$  and  $5\%$ . Three diffraction peaks assigned as the ZnO(0002) [11],  $\text{Cu}_2\text{O}(111)$  [12], and Au(111) planes could be observed on the XRD pattern before and after inserting the  $\text{TiO}_2$ . No obvious peaks identified as the  $\text{TiO}_2$  could be observed on the XRD patterns. The ZnO peak intensity decreased as the  $\text{TiO}_2$  sol concentration increased.

Figure 2 shows FE-SEM images of the ZnO layers before and after stacking the  $\text{TiO}_2$  layer with sol concentrations of  $3\%$  and  $5\%$ . The  $\text{Cu}_2\text{O}$  layers deposited on the Au(111) layer were composed of aggregates of hexagonal columnar grains grown in direction perpendicular to the Au(111) substrate surface, and the thickness was estimated to be about  $2.4 \mu\text{m}$ . The hexagonal columnar ZnO grains with the width of approximately  $150$  nm grew in the direction normal to the surface and hexagonal facets corresponding to the (0001) plane was observed on the surface image without the  $\text{TiO}_2$  layer. The  $\text{TiO}_2$  layer thickness was estimated to be about  $100$  nm at  $5\%$   $\text{TiO}_2$  sol and decreased at  $3\%$   $\text{TiO}_2$  sol. For the  $\text{TiO}_2$  layer prepared at  $5\%$ , ZnO grains with the width of approximately  $90$  nm were grown in the direction normal to the surface, and some pores could be observed between the ZnO grains. The width changed to  $110$  nm at  $3\%$  as shown in Fig. 2 (b). The thickness of the ZnO layer was estimated to be around  $200$  nm.

Figure 3 shows the absorption spectra for ZnO/ $\text{Cu}_2\text{O}$  PV devices after depositing  $\text{TiO}_2$  layer with  $3\%$  and  $5\%$   $\text{TiO}_2$  sol. The  $\text{Cu}_2\text{O}$  film showed an absorption edge at  $600$  nm, and the interference fringe pattern was observed at a wavelength less than  $600$  nm, indicating the formation of  $\text{Cu}_2\text{O}$  layer with the characteristic bandgap energy of  $2.1$  eV.

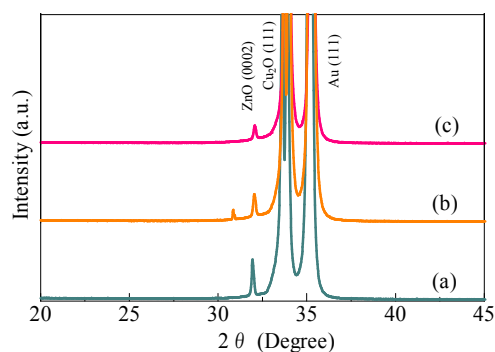


Fig. 1 XRD patterns for ZnO/Cu<sub>2</sub>O PV devices on Au substrate before (a) and after inserting TiO<sub>2</sub> layers at 3% (b) and 5% sol (c).

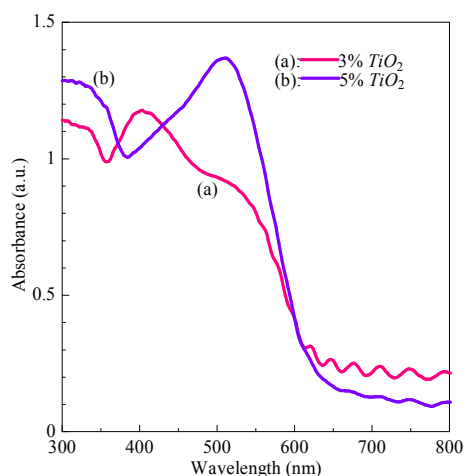


Fig. 3 Absorption spectra for ZnO/Cu<sub>2</sub>O PV devices with inserting the TiO<sub>2</sub> layer of 3% (a) and 5% sol (b).

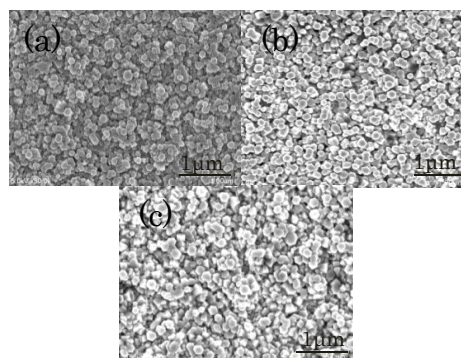


Fig. 2 FESEM images of ZnO prepared without (a) and with TiO<sub>2</sub> layers with 3% (b) and 5 % sol (c).

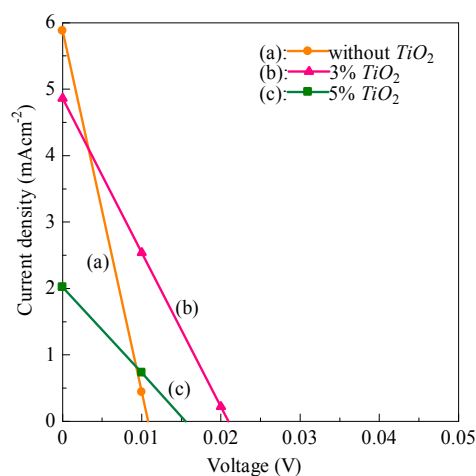


Fig. 4 J-V curve of the AZO/ZnO/Cu<sub>2</sub>O PV cells without (a) and with inserting the TiO<sub>2</sub> layer of 3% (b) and 5% sol (c).

An absorption edge was also observed at a wavelength around 380 nm originated from the ZnO layer in addition to that for the Cu<sub>2</sub>O layer. An absorption edge assigned as the TiO<sub>2</sub> layer also observed at a wavelength around 350 nm corresponding to the characteristic bandgap energy of 3.5 eV.

To demonstrate the effect of the TiO<sub>2</sub> buffer layer on ZnO/Cu<sub>2</sub>O PV cell performance, we fabricate ZnO/Cu<sub>2</sub>O PV cells by inserting 3% and 5% TiO<sub>2</sub> layer. Figure 4 shows the current density-voltage curves for the AZO/ZnO/Cu<sub>2</sub>O PV cells with and without TiO<sub>2</sub> layers under AM 1.5G illumination (100 mWcm<sup>-2</sup>). The PV device without TiO<sub>2</sub> exhibited a conversion efficiency of 0.004 % with 0.01 V open current voltage (V<sub>oc</sub>) and 5.87 mAcm<sup>-2</sup> short-circuit current (J<sub>sc</sub>). The performance of AZO/ZnO/TiO<sub>2</sub>/Cu<sub>2</sub>O PV devices strongly depended on TiO<sub>2</sub> sol concentration closely relating to the TiO<sub>2</sub> layer thickness and the resultant ZnO layer. The AZO/ZnO/TiO<sub>2</sub>/Cu<sub>2</sub>O PV device prepared at 3% TiO<sub>2</sub> sol showed an improved conversion efficiency of 0.03 %, although the J<sub>sc</sub> decreased slightly. The low V<sub>oc</sub> suggested the electrical shorting thorough the pores between the deposited ZnO grains. Further improvement of the quality including the homogeneity and energy state is indispensable to raise the photovoltaic performance.

## Conclusion

The effects of the inserted TiO<sub>2</sub> layer at the electrodeposited ZnO/Cu<sub>2</sub>O PV devices on the photovoltaic performance were investigated by structural, optical, and electrical characterizations. The insertion of the TiO<sub>2</sub> layer by a sol-gel process resulted in the improvement of the photovoltaic performance to 0.03% with Voc of 0.02 V, Jsc of 4.86 mAcm<sup>-2</sup>, and FF of 0.25.

## Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (25281062) from the Japan Society of the Promotion of Science.

## References

- [1] J.J. Lofeski, J. Appl. Phys. 27 (1956) 777.
- [2] M.A.Green, M. J. Keevers, Prog. Photovoltaics. 3 (1995)189.
- [3] J. Herion, E. A. Niekisch, G. Scharl, Solar Energy Mater. 4 (1980) 101.
- [4] V. F. Drobný, D. L. Pulfrey, Thin Solid Films 61 (1979) 89.
- [5] T. D.Golden, M. G. Shumsky, Y. Zhou, R. F. VanderWerf, R. A.Van Leeuwen, J. A. Switzer, Chem. Mater. 8 (1996) 2499.
- [6] M. Izaki, T. Omi, Appl. Phys. Lett. 68 (1996) 2439.
- [7] M. Izaki, T. Omi, J. Electrochem. Soc. 144 (1997) L3.
- [8] M. Izaki, T. Shinagawa, K. Mizuno, Y. Ida, M. Inaba, A. Tasaka, J. Phys. D: Appl. Phys. 40 (2007) 3326.
- [9] T. Shinagawa, M. Onoda, B. M. Fariza, J. Sasano, M. Izaki, J. Mater. Chem. A 1 (2013) 9182.
- [10] B. M. Fariza, J. Sasano, T. Shinagawa, S. Watase, M. Izaki, Thin Solid Films 520 (2012) 2261.
- [11] Joint Committee on Powder Diffraction Standards, Powder Diffraction File, International Data for Diffraction Data, Newtown Square, PA, 1992, pp 41-1445.
- [12] Joint Committee on Powder Diffraction Standards, Powder Diffraction File, International Data for Diffraction Data, Newtown Square, PA, 1992, pp 5-667.