

## Research Article

# H<sub>2</sub>O<sub>2</sub> Treatment of Electrochemically Deposited Cu<sub>2</sub>O Thin Films for Enhancing Optical Absorption

Ying Song and Masaya Ichimura

*Department of Engineering Physics, Electronics and Mechanics, Nagoya Institute of Technology,  
Nagoya 466-8555, Japan*

Correspondence should be addressed to Masaya Ichimura; [ichimura.masaya@nitech.ac.jp](mailto:ichimura.masaya@nitech.ac.jp)

Received 12 December 2012; Revised 22 January 2013; Accepted 22 January 2013

Academic Editor: Fahrettin Yakuphanoglu

Copyright © 2013 Y. Song and M. Ichimura. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Cu<sub>2</sub>O is considered to be promising as an absorber layer material of solar cells, but its band gap (about 2.1 eV) is larger than the optimum one (about 1.5 eV). CuO has a smaller band gap of about 1.35 eV. Therefore, we attempted to oxidize Cu<sub>2</sub>O using H<sub>2</sub>O<sub>2</sub> to increase oxygen ratio and decrease band gap. Cu<sub>2</sub>O thin films were deposited on indium-tin-oxide-coated glass from an aqueous solution containing CuSO<sub>4</sub>, lactic acid, and KOH by the galvanostatic electrochemical deposition at 40°C with current density of −1 mA/cm<sup>2</sup>. Then, the as-prepared copper oxide thin film was dipped in H<sub>2</sub>O<sub>2</sub> (30%) at fixed temperature to oxidize for some time. By the H<sub>2</sub>O<sub>2</sub> treatment at room temperature, the oxygen content was increased, and the band gap was decreased.

## 1. Introduction

Solar cell devices can be divided into three major categories: silicon solar cells, inorganic compound semiconductor solar cells, and organic solar cells. At present, crystalline silicon solar cells have high photovoltaic conversion efficiency, but production cost is high. For amorphous silicon solar cells, the production cost can be significantly reduced, but the main problem is that the photovoltaic conversion efficiency is low. Organic solar cells in general have a severe problem of poor stability. As an alternative, compound semiconductor solar cells are considered to increase the conversion efficiency and effectively reduce production cost. CuInSe<sub>2</sub> (CIS) and CdTe solar cells are now in practical use as compound semiconductor solar cells. One of the advantages of CIS and CdTe solar cells compared to silicon-based solar cells is that their absorption coefficients are large so that the film thickness can be small. Moreover, a manufacturing process is not complicated, and hence production cost will be reduced. However, In and Te are rare-earth elements, and Se and Cd are toxic. In contrast, constituent elements of Cu<sub>2</sub>O are abundant, inexpensive, and harmless to a human body. Rühle et al. reviewed recent developments of all-oxide PV systems, which until today were mostly based on Cu<sub>2</sub>O as an absorber [1].

So far, the Cu<sub>2</sub>O/ZnO heterojunction was fabricated by several methods, for example, sputtering technique [2–5], oxidation of metals [6, 7], photochemical deposition [8], and electrochemical deposition (ECD) [9–12]. ECD is a simple technique which can produce films over a large area and be easily scaled up to a commercial process at low cost. We also have been working on ECD of Cu<sub>2</sub>O/ZnO heterostructures [13, 14]. However, one of the shortcomings of Cu<sub>2</sub>O solar cells is that the Cu<sub>2</sub>O band gap (about 2.1 eV) is larger than the optimal value (about 1.5 eV) of a solar cell. Cu<sub>2</sub>O can absorb only the light with wavelength less than 0.6 μm. Thus, if the band gap is decreased, optical absorption of the film and the photocurrent can be increased. Since CuO has a smaller band gap (about 1.35 eV) [15–19], we may be able to reduce the band gap by increasing oxygen content of the film. Recently, it was reported that the performance of the Schottky contact of ZnO can be improved by the surface treatment with boiling hydrogen peroxide [20]. Through the H<sub>2</sub>O<sub>2</sub> treatment, a ZnO<sub>2</sub> layer is formed on the ZnO surface. Thus one can expect that composition of Cu<sub>2</sub>O can be made close to CuO by the H<sub>2</sub>O<sub>2</sub> treatment. In this study, we attempt H<sub>2</sub>O<sub>2</sub> treatment of ECD-Cu<sub>2</sub>O films to reduce the band gap and increase the optical absorption.

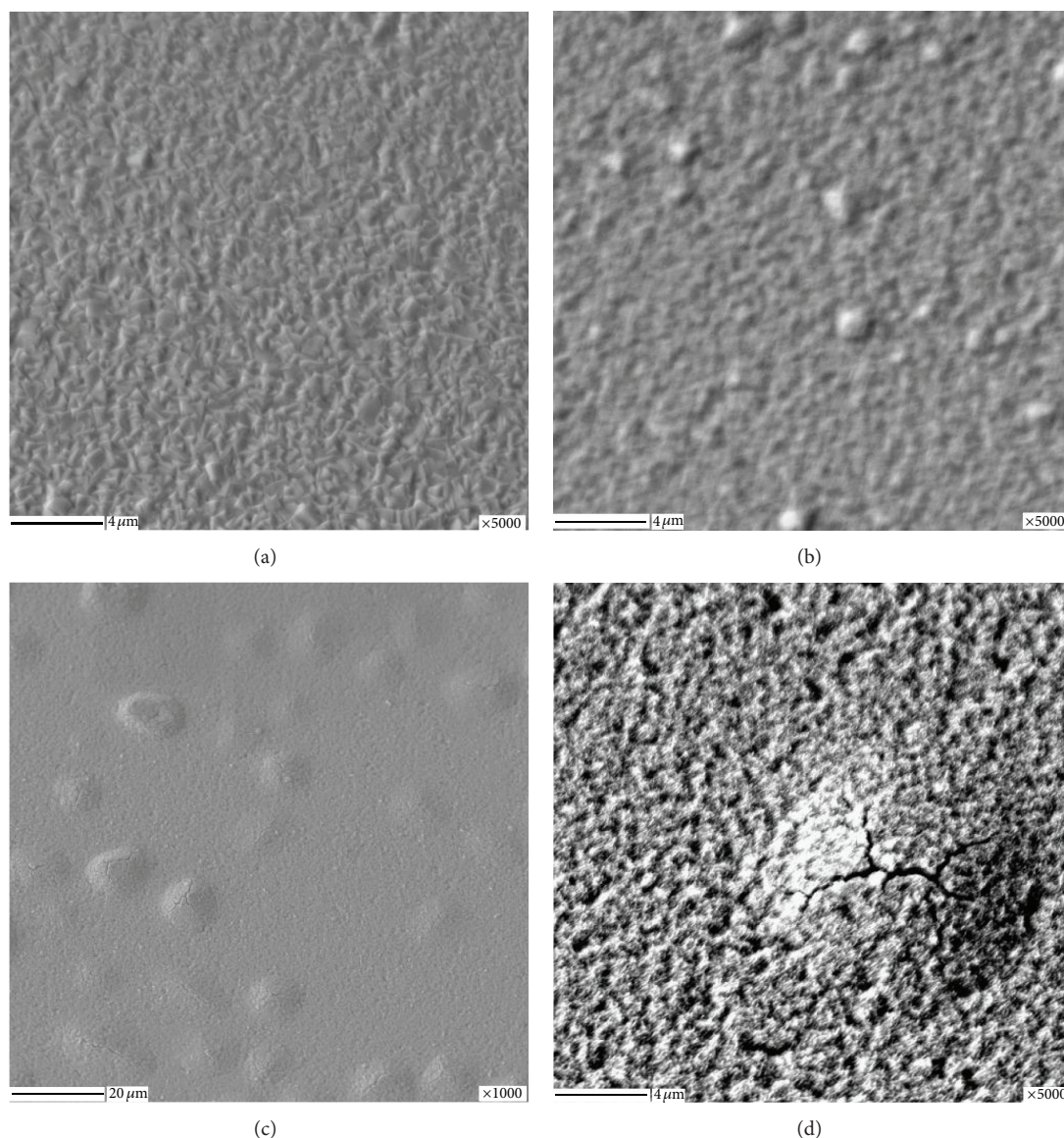


FIGURE 1: (a) SEM images of the as-deposited film. (b) SEM images of the film treated at room temperature for 7 hours. (c) and (d) SEM images of the film treated at room temperature for 24 hours (with different magnifications).

## 2. Experimental Procedure

An aqueous solution used for the deposition of  $\text{Cu}_2\text{O}$  contained 0.2 mol/L  $\text{CuSO}_4$  and 1.6 mol/L lactic acid. pH of the solution was adjusted to 12.5 by adding KOH.  $\text{Cu}_2\text{O}$  was deposited galvanostatically at  $40^\circ\text{C}$  with a current density of  $-1 \text{ mA/cm}^2$ . The sample was deposited for 10 min. The indium-tin-oxide-(ITO-) coated glass sheets with sheet resistance about  $8-9 \Omega/\text{square}$  were used as substrates. Then, the as-prepared  $\text{Cu}_2\text{O}$  thin film is dipped in  $\text{H}_2\text{O}_2$  (30%) for some time. After the treatment, the sample was washed with pure water.

The structural, compositional, and optical properties of the films were characterized by various techniques. Profile meter Accretech Surfcom-1400D was used to measure the

thickness of the thin film. The optical transmission measurement was performed using a JASCO-570 spectrometer with the substrate as the reference. The photoconductivity of the film was examined by means of the photoelectrochemical (PEC) measurement [21, 22]. The PEC measurement was carried out using the three-electrode cell with saturated calomel electrode (SCE) as a reference electrode. The deposited film was used as a working electrode and 100 mM of  $\text{Na}_2\text{SO}_4$  was used as an electrolyte. The incident light from a xenon lamp (about  $100 \text{ mW/cm}^2$ ) was irradiated on the backside of the sample and turned off and on mechanically every five seconds. The current was measured under application of a ramp voltage with a scan rate of  $5 \text{ mV/s}$ , first in the cathodic bias range (from 0 to  $-0.5 \text{ V}$ ) and then in the anodic bias range (from 0 to  $+0.5 \text{ V}$ ). The Auger electron spectroscopy

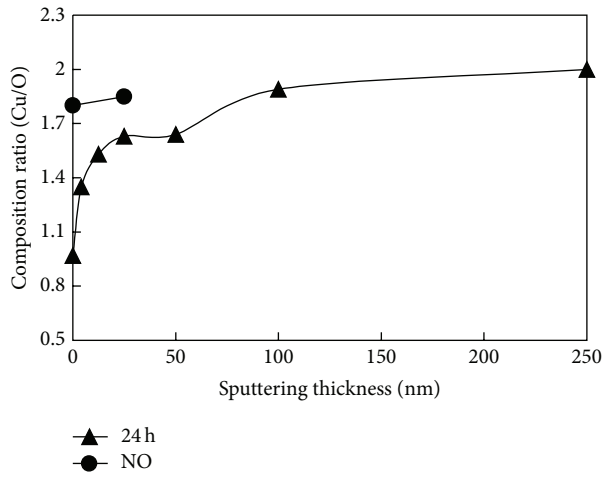


FIGURE 2: Change of Cu/O composition ratio with depth for the as-deposited film and the film treated at room temperature for 24 hours.

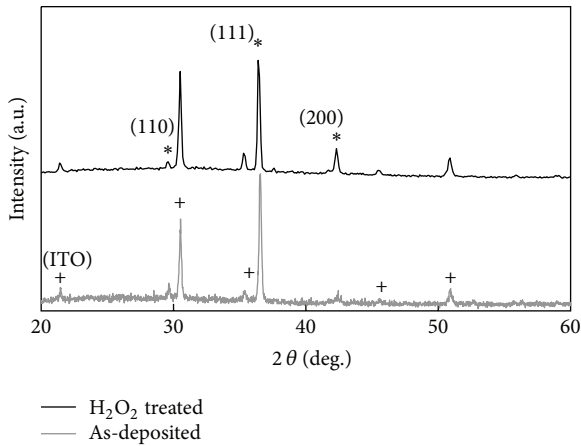


FIGURE 3: XRD of the as-deposited film and the film treated at room temperature for 24 hours. The peaks labeled “\*” are attributed to Cu<sub>2</sub>O, and the others to ITO.

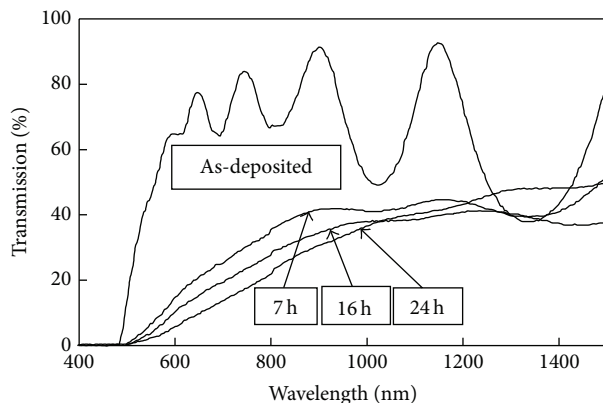


FIGURE 4: Optical transmission of the as-deposited film and the film treated at room temperature for various time.

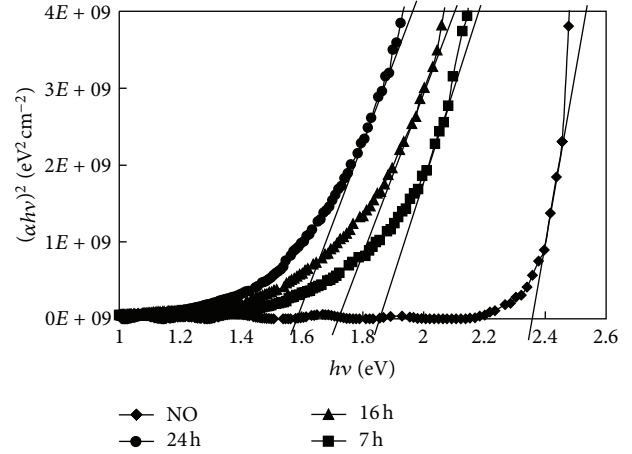


FIGURE 5: Plot of  $(\alpha h\nu)^2$  versus  $h\nu$  for the as-deposited film and the film treated at room temperature for various time.

(AES) analysis and scanning electron microscopy (SEM) observation were carried out using the model JEOL JAMP-9500F at probe voltage 10 kV. Argon ion etching with an acceleration voltage of 2 kV and a ion current of 2.6  $\mu$ A was used to sputter the film surface. The composition ratio was calculated by using a standard CuO compound. Furthermore, the X-ray diffraction (XRD) measurement was carried out by the Rigaku SmatLab X-ray diffractometer using Cu K $\alpha_1$  radiation at 40 kV/30 mA.

### 3. Results and Discussion

**3.1. Treatment at Room Temperature.** Figures 1(a) and 1(b) show the SEM images of the untreated Cu<sub>2</sub>O thin film and the film treated at room temperature for 7 hours, respectively, and Figures 1(c) and 1(d) show those of the film treated at room temperature for 24 hours (with different magnifications). The thickness of the as-deposited film was about 0.6  $\mu$ m, and the thickness was not changed significantly by the room temperature treatment. No significant change was observed for the surface of the sample treated for 7 hours compared with the untreated film. However, for the 24-hour-treated film, we can see bumps on the surface, where adhesion to the substrate was apparently weakened with narrow cracks generated on the surface, as shown in Figure 1(d).

Figure 2 shows the change of Cu/O composition ratios with the sputtering time. For the as-deposited sample, the composition ratio of the films is 1.8. For the sample treated for 24 hours, the Cu/O composition ratio near the surface is close to unity, and the composition ratio was increased with increasing sputtering thickness. Thus, the surface of the Cu<sub>2</sub>O thin film was converted to CuO by the H<sub>2</sub>O<sub>2</sub> treatment while the inner portion of the samples was not affected.

Figure 3 shows the XRD spectra of the as-deposited and H<sub>2</sub>O<sub>2</sub>-treated samples. The Cu<sub>2</sub>O films are polycrystalline and have cubic-cuprite structure with weak preferential orientation along (111). We did not find any peaks of other phases such as CuO even after the H<sub>2</sub>O<sub>2</sub> treatment. This



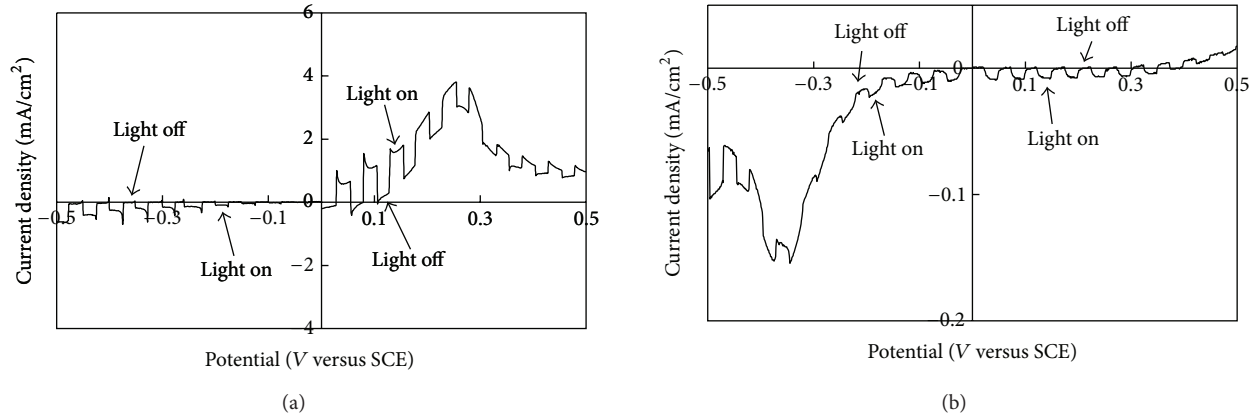


FIGURE 6: PEC results of (a) the as-deposited film and (b) the film treated at room temperature for 24 hours.

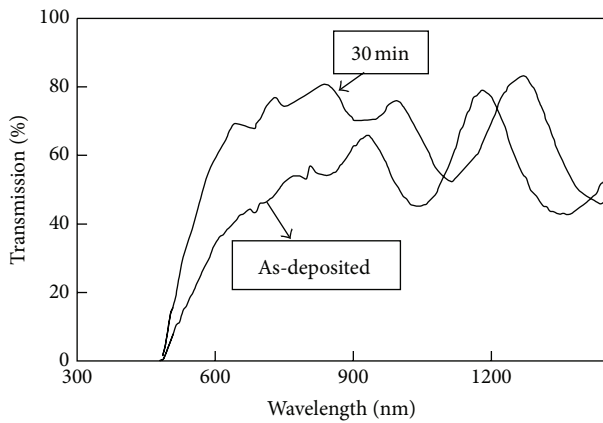


FIGURE 7: Optical transmission of the as-deposited film and the film treated at 60°C for 30 min.

would be because the CuO layer formed near the surface by the  $H_2O_2$  treatment is too thin or does not have crystallinity.

Figure 4 shows the comparative results of the optical transmission of the  $Cu_2O$  sample treated for 7, 16, and 24 hours at room temperature. From the figure, it was confirmed that by extending the treatment time, the optical absorption is increased further. The sample absorbed light of wavelength less than 560 nm completely; the absorption edge is around 1000 nm when treated for 24 hour. Figure 5 shows the plot of  $(\alpha h\nu)^2$  versus  $h\nu$ . The apparent band gap can be estimated from extrapolation of a straight line part of the curve to the photon energy axis. For the samples treated for 24 hours, the band gap seems to be about 1.6 eV. From these results, we can conclude that  $Cu_2O$  thin films can be oxidized to have a smaller band gap by the  $H_2O_2$  treatment at room temperature.

Figure 6(a) shows the PEC measurement results of the as-deposited sample. In the PEC measurement, the current was measured under chopped illumination. Relative change in the carrier concentration due to the illumination is larger for the minority carriers than for the majority carriers, and thus

the photocurrent due to photo-generated minority carriers is observed clearly. Thus negative photocurrent is generally significant for a p-type sample, and positive photocurrent for an n-type sample. For the as-deposited samples, the negative photocurrent (under cathodic bias) and the positive photocurrent (under anodic bias) were observed, and thus the conduction type is close to intrinsic. Figure 6(b) shows the PEC measurement results of the sample treated for 24 hours. The photocurrent is negative even under anodic bias. This indicates that the treated sample exhibited clearer p-type character.

**3.2. Treatment at Higher Temperatures.** As shown in the previous section, the  $H_2O_2$  treatment at room temperature is effective to modify the composition and enhance the optical absorption, but the treatment time needs to be longer than several hours. For the practical application, shorter treatment time would be preferable. Thus we tried the  $H_2O_2$  treatment at higher temperatures.

Figure 7 shows the optical transmission of the samples treated at 60°C for 30 minutes. From the figure, we can conclude that the optical absorption of the sample was not increased by the  $H_2O_2$  treatment at 60°C for 30 min.

Figures 8(a) and 8(b) show the SEM images of the thin films treated at 60°C and at 90°C for 30 min, respectively. It can be seen that the surface of the sample was partly broken (holes were formed) when treated at 90°C. Similar damages were observed for the film treated at 70°C and 80°C. Thus, we can conclude that the  $H_2O_2$  treatment at higher temperatures is not useful for the modification of the film composition.

## 4. Conclusions

$Cu_2O$  thin films have been deposited electrochemically onto ITO-coated glass. Then, the thin film was dipped in  $H_2O_2$  (30%) at fixed temperature for oxidization. By the  $H_2O_2$  treatment at room temperature for 7, 16, and 24 hours, the oxygen content of surface was increased and the apparent band gap of the samples was decreased. Thus this treatment can be used to enhance optical absorption of the  $Cu_2O$  films

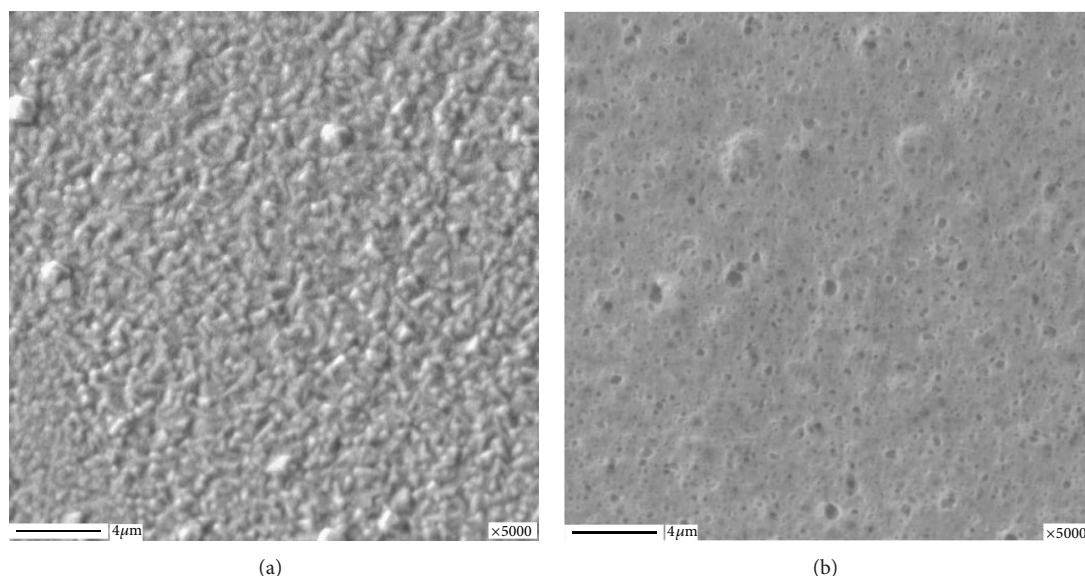


FIGURE 8: SEM images of (a) the film treated at 60°C and (b) the film treated at 90°C for 30 min.

for solar cell application. The samples were partially broken by the  $\text{H}_2\text{O}_2$  treatment at higher temperatures (70–90°C), and thus the treatment at low temperature is preferable.

## Acknowledgments

The authors would like to thank Dr. M. Kato for his useful discussion and Mr. H. Zhang for his useful suggestion on the  $\text{H}_2\text{O}_2$  treatment.

## References

- [1] S. Rühle, A. Y. Anderson, H.-N. Barad et al., “All-oxide photo-voltaics,” *The Journal of Physical Chemistry Letters*, vol. 3, no. 24, pp. 3755–3764, 2012.
- [2] S. M. Chou, M. H. Hon, I. C. Leu, and Y. H. Lee, “Al-Doped  $\text{ZnO}/\text{Cu}_2\text{O}$  heterojunction fabricated on (200) and (111)-orientated  $\text{Cu}_2\text{O}$  substrates,” *Journal of the Electrochemical Society*, vol. 155, no. 11, pp. H923–H928, 2008.
- [3] T. Minami, T. Miyata, K. Ihara, Y. Minamino, and S. Tsukada, “Effect of  $\text{ZnO}$  film deposition methods on the photovoltaic properties of  $\text{ZnO}-\text{Cu}_2\text{O}$  heterojunction devices,” *Thin Solid Films*, vol. 494, no. 1-2, pp. 47–52, 2006.
- [4] S. Ishizuka, K. Suzuki, Y. Okamoto et al., “Polycrystalline  $\text{n-ZnO}/\text{p-Cu}_2\text{O}$  heterojunctions grown by RF-magnetron sputtering,” *Physica Status Solidi C*, vol. 1, no. 4, pp. 1067–1070, 2004.
- [5] K. Akimoto, S. Ishizuka, M. Yanagita, Y. Nawa, G. K. Paul, and T. Sakurai, “Thin film deposition of  $\text{Cu}_2\text{O}$  and application for solar cells,” *Solar Energy*, vol. 80, no. 6, pp. 715–722, 2006.
- [6] A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi, “Copper oxide transistor on copper wire for e-textile,” *Applied Physics Letters*, vol. 98, no. 19, Article ID 192102, 3 pages, 2011.
- [7] T. Minami, Y. Nishi, T. Miyata, and J. I. Nomoto, “High-efficiency oxide solar cells with  $\text{ZnO}/\text{Cu}_2\text{O}$  heterojunction fabricated on thermally oxidized  $\text{Cu}_2\text{O}$  sheets,” *Applied Physics Express*, vol. 4, no. 6, Article ID 062301, 3 pages, 2011.
- [8] M. Izaki, K. T. Mizuno, T. Shinagawa, M. Inaba, and A. Tasaka, “Photochemical construction of photovoltaic device composed of p-copper(I) oxide and n-zinc oxide,” *Journal of the Electrochemical Society*, vol. 153, no. 9, pp. C668–C672, 2006.
- [9] M. Izaki, T. Shinagawa, K. T. Mizuno, Y. Ida, M. Inaba, and A. Tasaka, “Electrochemically constructed p- $\text{Cu}_2\text{O}/\text{n-ZnO}$  heterojunction diode for photovoltaic device,” *Journal of Physics D*, vol. 40, no. 11, pp. 3326–3329, 2007.
- [10] S. S. Jeong, A. Mittiga, E. Salza, A. Masci, and S. Passerini, “Electrodeposited  $\text{ZnO}/\text{Cu}_2\text{O}$  heterojunction solar cells,” *Electrochimica Acta*, vol. 53, no. 5, pp. 2226–2231, 2008.
- [11] J. Katayama, K. Ito, M. Matsuoka, and J. Tamaki, “Performance of  $\text{Cu}_2\text{O}/\text{ZnO}$  solar cell prepared by two-step electrodeposition,” *Journal of Applied Electrochemistry*, vol. 34, no. 7, pp. 687–692, 2004.
- [12] D. K. Zhang, Y. C. Liu, Y. L. Liu, and H. Yang, “The electrical properties and the interfaces of  $\text{Cu}_2\text{O}/\text{ZnO}/\text{ITO}$  p-i-n heterojunction,” *Physica B*, vol. 351, no. 1-2, pp. 178–183, 2004.
- [13] M. Ichimura and Y. Song, “Band alignment at the  $\text{Cu}_2\text{O}/\text{ZnO}$  heterojunction,” *Japanese Journal of Applied Physics*, vol. 50, no. 5, Article ID 051002, 6 pages, 2011.
- [14] Y. Song and M. Ichimura, “Improvement of electrochemically deposited  $\text{Cu}_2\text{O}/\text{ZnO}$  heterojunction solar cells by modulation of deposition current,” *Japanese Journal of Applied Physics*, vol. 51, no. 10, Article ID 10NC39, 5 pages, 2012.
- [15] M. Izaki, “Effects of annealing on optical and electrical characteristics of p-type semiconductor copper (II) oxide electrodeposits,” *Thin Solid Films*, vol. 520, no. 7, pp. 2434–2437, 2012.
- [16] M. Izaki, Y. Yamane, J. Sasano, T. Shinagawa, and M. Inoue, “Direct preparation of 1.35-eV-bandgap  $\text{CuO}:\text{S}$  film by chemical bath deposition,” *Electrochemical and Solid-State Letters*, vol. 14, no. 3, pp. D30–D32, 2011.
- [17] P. Poizot, C. J. Hung, M. P. Nikiforov, E. W. Bohannon, and J. A. Switzer, “An electrochemical method for  $\text{CuO}$  thin film deposition from aqueous solution,” *Electrochemical and Solid-State Letters*, vol. 6, no. 2, pp. C21–C25, 2003.

- [18] K. Nakaoka, J. Ueyama, and K. Ogura, "Photoelectrochemical behavior of electrodeposited CuO and Cu<sub>2</sub>O thin films on conducting substrates," *Journal of the Electrochemical Society*, vol. 151, no. 10, pp. C661–C665, 2004.
- [19] V. Dhanasekaran, T. Mahalingam, R. Chandramohan, J.-K. Rhee, and J. P. Chu, "Electrochemical deposition and characterization of cupric oxide thin films," *Thin Solid Films*, vol. 520, no. 21, pp. 6608–6613, 2012.
- [20] A. Nakamura and J. Temmyo, "Schottky contact on ZnO nanocolumnar film with H<sub>2</sub>O<sub>2</sub> treatment," *Journal of Applied Physics*, vol. 109, no. 9, Article ID 093517, 7 pages, 2011.
- [21] A. Paracchino, J. C. Brauer, J.-E. Moser, E. Thimsen, and M. Graetzel, "Synthesis and characterization of high-photoactivity electrodeposited Cu<sub>2</sub>O solar absorber by photoelectrochemistry and ultrafast spectroscopy," *The Journal of Physical Chemistry C*, vol. 116, no. 13, pp. 7341–7350, 2012.
- [22] K. L. Hardee and A. J. Bard, "Semiconductor electrodes. X. Photoelectrochemical behavior of several polycrystalline metal oxide electrodes in aqueous solutions," *Journal of the Electrochemical Society*, vol. 124, no. 2, pp. 215–224, 1977.



