Fabrication of Heterojunctions Based on Chemically Deposited Copper Oxide Thin Films for Solar Cell Application

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To fabricate the heterojunction, copper oxide (Cu_2O) layers were deposited by the chemical bath deposition technique using aqueous solutions containing CuSO_4 and Na_2SO_3 without and with adding a small amount of ethylenediamine (EDA). The counterpart of the heterojunction, i.e., a ZnO layer was deposited by electrochemical deposition. Indium-tin-oxide (ITO) coated glass sheet was used as a substrate, and both the substrate ($\text{ZnO}/\text{Cu}_2\text{O}/\text{ITO}$) and superstrate ($\text{Cu}_2\text{O}/\text{ZnO}/\text{ITO}$) structures were fabricated. The Cu_2O films were crystalline with a cubic crystal structure, had Cu/O ratios of 1.7 - 2, and consisted of octahedral particles, whose size was reduced by addition of EDA. The Cu_2O layers exhibited p-type conductivity and photosensitivity. Rectification properties and weak photovoltaic effects were observed for the heterojunctions fabricated using the solution with EDA.

Key words: copper oxide, heterojunction, chemical bath deposition, solar cell.

1. INTRODUCTION

Copper oxide is advantageous for the photovoltaic application since its band gap, absorption coefficient and photosensitive properties are suitable for solar cells. Furthermore, it has low toxicity and good environmental acceptability, is cheap and plentiful. There are many reports on photovoltaic devices using cuprous oxide (Cu_2O) as the active layer¹⁻⁸ because the theoretical energy conversion efficiency of a Cu_2O solar cell is about 20%.¹ Cu_2O -based solar cells have been fabricated by various techniques. Sears et al.² and Mittiga et al.³ fabricated the Cu_2O solar cell by oxidizing copper at high temperature. To deposit ZnO- Cu_2O heterojunctions, Minami et al.⁴ fabricated ZnO by RF magnetron sputtering or pulsed laser deposition on the Cu_2O sheet. Also, ZnO/ Cu_2O heterojunctions have been fabricated using RF-magnetron sputtering by Ishizuka et al.⁵ Some researchers have fabricated heterojunctions based on ZnO and Cu_2O obtained by electrochemical deposition (ECD).⁶⁻⁸ In the previous paper, we reported that the Cu_xO films exhibit p-type conduction and photosensitivity and hence will be suited for heterojunction solar cells.⁹ In the present work, to fabricate the ZnO- Cu_2O heterojunction, Cu_2O layers are deposited by the chemical bath deposition (CBD) technique using aqueous solutions containing CuSO_4 and Na_2SO_3 .⁹ The counterpart of the heterojunction, i.e., a ZnO layer is deposited by ECD. There are several reports on CBD of Cu_2O ,^{10,11} but to the best of our knowledge, a heterojunction based on CBD Cu_2O has never been reported.

2. EXPERIMENTAL PROCEDURE

To fabricate ZnO- Cu_2O heterojunctions, Cu_2O was deposited by CBD and ZnO by ECD. The substrate was indium-tin-oxide (ITO) coated glass sheet. On the surface of the top layer, an indium electrode (1x1 mm size) was deposited by vacuum coating unit. Both the substrate structure In/ZnO/ $\text{Cu}_2\text{O}/\text{ITO}$ and the superstrate

structure In/ $\text{Cu}_2\text{O}/\text{ZnO}/\text{ITO}$ were fabricated.

To deposit Cu_2O thin films, CuSO_4 (20 mmol/L) and Na_2SO_3 (100 mmol/L) were used as a chemical reagent with deionized water. The solution pH was about 7.2 as unadjusted. The amount of the solution was 50 mL. CuSO_4 was first dissolved in the water, and then Na_2SO_3 was added. The solution was stirred for 30 min before deposition. The solution was almost colorless after the stirring. The solution container was put on a heater plate heated to 200 °C, and the solution temperature was increased to a steady-state temperature of 80 °C. The deposition time (time after the container was put on the heater plate) was 30 min. After the deposition experiments, the deposited films were washed softly in pure water and dried naturally in air. To modify the surface morphology, ethylenediamine (EDA) was added to the above working solution. EDA is one of the chemicals commonly used as a complexing agent for metal ions. 0.03 mL or 0.06 mL of EDA was added in the solution just after the stirring. The solution color was light indigo after adding the EDA and it became deep indigo during heating. The deposition time of these samples were 60 min. ZnO- Cu_2O heterojunctions were fabricated with and without EDA addition.

To deposit ZnO layers, a solution containing 100 mmol/L of $\text{Zn}(\text{NO}_3)_2$ was used. A three-electrode cell was used with a saturated calomel electrode (SCE) as the reference electrode. pH was not controlled (~4), deposition voltage (DC) was -1.3V, deposition temperature was 60 °C, and deposition time was 30 s- 10 min.

An Accrettech Surfcom-1400D profile meter was used for measuring the thickness of the films and the heterojunctions. For compositional analysis, Auger electron spectroscopy (AES) measurement was carried out for the Cu_2O films using a JEOL JAMP 7800 at a probe voltage of 10 kV and a current of 2×10^{-8} A. Argon ion etching with an acceleration voltage of 3 kV and a current of 8 mA was used to sputter the film surface.

The Cu/O atomic ratios were calculated using standard CuO. The X-ray diffraction (XRD) measurement was carried out for the Cu_2O films by the RIGAKU RINT-2000 diffractometer using $\text{CuK}\alpha_1$ radiation. The surface morphology of the Cu_2O film was analyzed using a Hitachi S-2000S scanning electron microscope (SEM) at a constant acceleration voltage of 10 kV and a magnification of 2000. To determine the type of conduction and to estimate the photosensitivity of the Cu_2O films, photo electrochemical (PEC) measurements were carried out using the three-electrode cell with the SCE reference electrode. The solution contained 100 mmol/L Na_2SO_3 . The incident light from a xenon lamp (about $100\text{mW}/\text{cm}^2$) was irradiated on the backside of the sample and turned off and on mechanically every 5 s. The current was measured under application of a ramp voltage with a scan rate of 5 mV/s, first in the anodic bias range (0 to +1V) and then in the cathodic bias range (0 to -1V). The photovoltaic properties of the heterojunctions were measured under AM1.5 solar illumination with a power of $100\text{mW}/\text{cm}^2$.

3. RESULTS AND DISCUSSION

3.1 Cu_2O thin films

The chemical reactions of the Cu_2O thin film deposition were completed within 30 minutes without EDA. Thickness of this deposition time depends on the solution amount for a particular solution concentration⁹. The film thickness was around 3 μm for deposition without EDA, 1.2 μm for deposition with 0.03 mL EDA, and 0.5 μm for deposition with 0.06 mL EDA.

The AES results show that only copper and oxygen elements are present in the Cu_2O samples (Fig.1). The near-surface region is more oxygen-rich than the bulk.

Fig. 1. AES spectrum of the film deposited with 0.03 mL EDA.

Fig. 2. XRD pattern of the film deposited with 0.03 mL EDA

The film composition was evaluated from the AES spectra recorded after 10 min sputtering of the surface. For the film deposited without EDA, the Cu/O ratio calculated is 1.8, while it is about 2 for the films deposited with EDA. Thus Cu/O ratio approached to the stoichiometric composition by addition of EDA.

Figure 2 shows the XRD spectrum for the film deposited with EDA. There is no significant difference in either peak position or width between the samples deposited with and without EDA. A peak due to ITO was observed near $2\theta=31^\circ$, and all other dominant peaks are attributed to Cu_2O according to the ICSD standard data. Thus the XRD results show that the films are dominantly cubic crystalline Cu_2O with a lattice parameter 4.25 Å. For the film deposited without EDA,

(a)

(b)

(c)

Fig. 3. SEM photographs of the films deposited (a) without EDA, (b) with 0.03 mL EDA and (c) with 0.06 mL EDA.

the AES results showed the Cu/O ratio ~ 1.8 , but the observed XRD peaks are all attributed to Cu_2O . It has been widely believed that in copper oxide, excess oxygen ions (or copper ion vacancies) are the main sources of acceptors, which produce p-type conductivity.^{12, 13} Our samples are p-type, and thus those Cu-deficiency defects are present in a large number in the crystalline phase of Cu_2O .

Figure 3 (a) shows the SEM photographs of the films deposited (a) without EDA, (b) with 0.03 mL EDA, and (c) with 0.06 mL. The film deposited without EDA consists of octahedral particles, and a similar particle shape was also observed in the previous chemical synthesis works.^{14, 15} Figures 3(b) and (c) show SEM photographs for the films deposited with 0.03 mL and 0.06 mL of EDA, respectively. The morphology reveals the same properties as that of the films deposited without EDA, but the particles size is smaller. This would be because EDA stabilized the copper ions, reduced the reaction rate, and prevented the particles from growing to bigger size. We attempted to measure the band gap by the optical transmission measurement for the films deposited with and without EDA, but the transmission was low, less than 10 %, and a clear absorption edge was not observed. This will be because the light was scattered by the rough surface structure, revealed by the SEM photographs.

Figure 4 shows the PEC measurement results for the films deposited without and with 0.03 mL EDA. It is clear that the current was changed due to the light chopping, and thus the films show good photosensitive behaviors. Under illumination, some carriers were excited in the illuminated region of the film. Then excited minority carriers diffused to the surface during their lifetime to participate in the electrochemical reaction at the electrolyte interface. For our thin films, the photocurrent is negative, and its magnitude is larger under cathodic biasing than under anodic biasing. This implies that the minority carriers generated here are electrons. Thus, the deposited films are p-type semiconductors. Figure 4 shows that the photocurrent is slightly larger for the film deposited with EDA.

3.2 ZnO- Cu_2O heterojunctions

Before fabricating the heterostructure, we deposited Cu_2O and ZnO layers separately on ITO and confirmed that the interface with ITO has the ohmic character for both Cu_2O and ZnO. Figure 5 shows the I-V characteristics of the heterojunctions, for which the Cu_2O layers were deposited without EDA. The sample structure is the substrate structure for Fig. 5(a) and the superstrate structure for Fig. 5(b). The ZnO layer thickness is about 0.2 μm for deposition time of 30 s, about 1 μm for deposition time of 2.5 min and about 2 μm for deposition time of 10 min. In the substrate structure, the heterojunction of the shorter ZnO deposition time showed better rectification. On the other hand, better rectification appeared for the superstrate structure for which the ZnO deposition time was longer. However, photovoltaic properties have not been observed for those samples deposited without EDA.

Figure 6 shows I-V characteristics of the superstrate heterostructures with Cu_2O films deposited with (a) 0.03 mL EDA and (b) 0.06 mL EDA. The ZnO deposition

Fig. 4. PEC measurement results for the Cu_2O films deposited without and with 0.03 mL EDA.

Fig. 5. I-V characteristics for (a) the substrate and (b) superstrate structure heterojunctions with two different ZnO deposition times. Cu_2O was deposited without EDA.

Fig. 6. I-V characteristics for the superstrate structure heterojunctions with Cu_2O deposited with 0.03 mL EDA and 0.06 mL EDA.

time is 2.5 min. The rectification properties are not good, but weak photovoltaic effects appeared for these samples. Figures 7(a) and 7(b) show I-V characteristics with and without AM1.5 illumination for the superstrate structure with Cu₂O layers deposited using (a) 0.03 mL and (b) 0.06 mL of EDA. For the samples deposited with EDA, the particle size is smaller and adhesion is better than for the films deposited without EDA. Surface roughness and porous nature will be the main cause for absence of the photovoltaic effects for the samples deposited without EDA. We also fabricated the substrate structure based on the films deposited with EDA, but photovoltaic effects were not observed.

Although the photovoltaic effects were observed for the samples deposited with EDA, the efficiency is still very low, 0.002 % with $V_{oc}=0.1$ V, $I_{sc}=0.07$ mA/cm² and F.F.=0.27 for Fig.7(a) and 0.0007 % with $V_{oc}=0.014$ V, $I_{sc}=0.19$ mA/cm² and F.F.=0.25 for Fig.7(b). To improve further, a more compact and dense Cu₂O film needs to be fabricated by, for example, using other additives to the solution.

4. CONCLUSIONS

The Cu₂O layers have been deposited by CBD using aqueous solutions containing CuSO₄ and Na₂SO₃ without and with adding small amount of EDA. The Cu₂O films are crystalline with a cubic crystal structure, have Cu/O ratios of 1.7 - 2, and consist of octahedral particles, whose size is reduced by addition of EDA. To fabricate pn heterojunctions, ZnO layers have been deposited by electrochemical deposition. Rectification properties and weak photovoltaic effects are observed for the heterojunctions fabricated using the solution with EDA. Our technique is a very low-cost technique, using those inexpensive source chemicals and the simple apparatus. Therefore our CBD technique is potentially suitable for commercial production of solar cells.

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REFERENCES

- [1] A. E. Rakhshani, *Solid-State Electronics*, **29**, 7-17 (1986).
- [2] W. M. Sears, E. Fortin and J. B. Webb, *Thin Solid Films*, **103**, 303-309 (1983).
- [3] A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi, *Appl. Phys. Lett.*, **88**, 163502 (2006).
- [4] T. Minami, H. Tanaka, T. Shimakawa, T. Miyata and H. Sato, *Jpn. J. Appl. Phys.*, **43**, L917-L919 (2004).
- [5] S. Ishizuka, K. Suzuki, Y. Okamoto, M. Yanagita, T. Sakurai, K. Akimoto, N. Fujiwara, H. Kobayashi, K. Matsubara and S. Niki, *Phys. Stat. Sol.*, (c) **1**, 1067-1070

Fig. 7. Photovoltaic properties for the Cu₂O/ZnO (superstrate structure) heterojunctions for which Cu₂O was deposited with (a) 0.03 mL EDA and (b) 0.06 mL EDA.

(2004).

- [6] J. Katayama, K. Ito, M. Matsuoka and J. Tamaki, *J. Appl. Electrochem.*, **34**, 687-692 (2004).
- [7] S. S. Jeong, A. Mittiga, E. Salza, A. Masci and S. Passerini, *Electrochimica Acta*, **53**, 2226-2231 (2008).
- [8] M. Izaki, T. Shinagawa, K. Mizuno, Y. Ida, M. Inaba, and A. Tasaka, *J. Phys. D: Appl. Phys.*, **40**, 3326-3329. (2007)
- [9] M. Muhibbullah and M. Ichirura, *Jpn. J. Appl. Phys.*, **49**, 081102 (2010).
- [10] M. Ristov, G. I. Sinadinovski, and I. Grozdanov, *Thin Solid Films* **123**, 63-67 (1985) 63.
- [11] M. T. S. Nair, L. Guerrero, O. L. Arenas, and P. K. Nair, *Appl. Surf. Sci.* **150** 143-151 (1999).
- [12] V.F. Drobny and D.L. Pulfrey, *Thin Solid Films*, **61**, 89-98 (1979).
- [13] W. Siripala and K. Premasiri Kumar, *Semicond. Sci. Technol.*, **4**, 465-468 (1989).
- [14] F. Du, J. Liu and Z. Guo, *Mater. Res. Bull.*, **44**, 25-29 (2009).
- [15] C. Lu, L. Qi, J. Yang, X. Wang, D. Zhang, J. Xie and J. Ma, *Advanced Mater.*, **17**, 2562-2567 (2005).

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