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Electrodeposition of Cu_2O and Cu thin films in the presence of sodium acetate as a supporting electrolyte for photovoltaic energy

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***Abstract*— The electrodeposition of cuprous oxide (Cu_2O) and copper (Cu) thin films at 50 °C on the ITO/glass substrates from cupric acetate aqueous solution was studied. The electrodeposition mechanism was investigated by cyclic voltammetry. The X-ray diffraction (XRD) analysis shows that Cu_2O films has a cubic structure and the preferred growth measurements indicated that the films deposited at pH = 6.2 has n-type electrical conductivity.**

***Keywords*— Electrodeposition, copper, thin film, cuprous oxide, photovoltaic solar cells.**

I. INTRODUCTION

The quest and need for clean and economical energy source have increased interest in the development of solar applications. In particular, direct conversion of solar energy to electrical energy and chemical energy using semiconductor photoelectrodes has attracted attention for many decades. Among the various metal oxide materials for solar energy application, a promising material is cuprous oxide (Cu_2O), one of the oldest known semiconductors [1]. It is an interesting and nontoxic semiconducting material with a band gap of 2 eV at room temperature suitable for solar cell application and high absorption coefficient.

In the recent past Copper (Cu) thin films are used for various applications particularly preparation of ternary I-III-VI_2 semiconductors and fabrication of interconnections in semiconductor industry. Cuprous oxide and Cu thin films are prepared by various methods like reactive sputtering, vacuum evaporation, chemical and thermal oxidation [2] and electrodeposition [3-11].

Among the various deposition techniques available for the preparation of cuprous oxide and Copper thin films, method of electrodeposition is an attractive technique because of its simplicity and the possibility in making large area thin films [12]. It has been reported previously that good quality Cu_2O films can be electrodeposited using an acetate bath [13-14].

In the present work, we report on the preparation of Cu_2O and Cu thin films on ITO/glass substrates by cathodic electrodeposition in aqueous solution. Electrodeposition thin films were characterized using X-ray diffraction (XRD), photo-current.

II. EXPERIMENTAL

II. 1. ITO/glass electrode pre-treatment

Optically transparent indium tin-oxide (ITO, 12 Ω/□) coated glass plate was used as the substrate. Prior to deposition, it was ultrasonically rinsed in acetone, ethanol and distilled water first, and then etched in the diluted hydrochloric acid (5-6%) for 15 s, and finally rinsed in distilled water [15, 16].

II. 2. Preparation of Cu_2O and Cu thin films

Electrodeposition of Cu_2O and Cu thin films on ITO/glass substrates was studied using a three electrode electrochemical cell containing an aqueous solution of sodium acetate and cupric acetate at pH = 6.2 (pH was adjusted by adding diluted CH_3COOH). Cupric acetate was used as Cu^{2+} source while

sodium acetate was added as supporting electrolyte in the growth of Cu_2O thin films.

The counter electrode was a platinum wire of 1 mm diameter and reference electrode was saturated calomel electrode (SCE). Electrolytic solutions were prepared with distilled water and reagent grade chemicals. Temperature of bath was maintained to 50 °C and the electrolyte continuously stirred using a magnetic stirrer. Electrodeposition was carried out under Potentiostatic mode using Princeton Applied Research Model 273 A Potentiostat/ Galvanostat, coupled to a personal computer with power suite software for data acquisition and potential control. The experimental device for the electrodeposition of thin films is shown in Fig. 1.

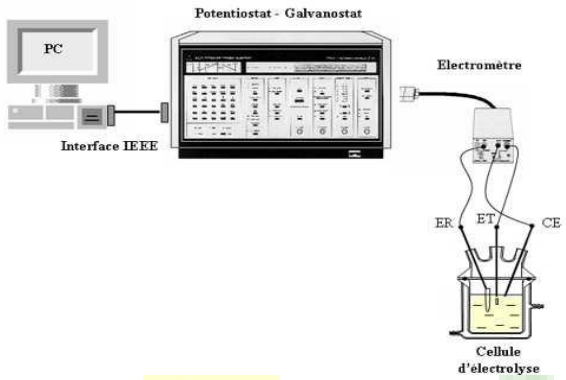

Fig. 1 Experimental device

II. 3. Characterization

The crystallographic structure of the films was determined by X-ray diffraction (XRD) using a RIGAKU RAD-2R diffractometer with Cu Kα radiation. The photo-current characterization was studied using *Current-Voltage* technique. Photocurrent characterization is carried out in a custom-built system (Fig. 2), which includes a light source, an illumination switch and three-electrodes: the counter electrode is platinum, the reference electrode is SCE and a working electrode is ITO/glass immersed in an electrochemical cell containing an electrolyte of 0.1 M sodium acetate ($CH_3COONa.3H_2O$). A 100W tungsten/halogen lamp is used to provide broad spectrum light, the working electrode is as-deposited cuprous oxide film facing the light source. The photo-current characterization will be realized by cyclic voltammetry, once, in the dark and the next time under illumination.

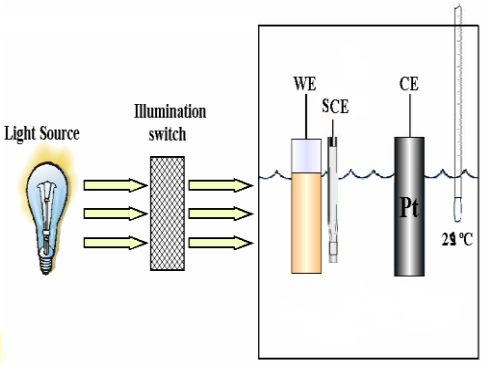

Fig. 2 Arrangement of photocurrent Characterization system

III. Results and Discussion

III. 1. Electrochemical studies

Fig. 3 shows the cyclic voltammogram of ITO-coated glass for the solution containing 0.01M cupric acetate and 0.1M sodium acetate (pH = 6.2). The sweep is measured at a scan rate of 50 mV s^{-1} over the potential range from 1 to –2 V. From these curve, we can observe two cathodic peaks at –0.5 V vs. SCE and –1 V vs. SCE due to the presence of cupric ions in the electrolyte. First cathodic peak at –0.5 V vs. SCE attributes to the formation of Cu_2O on the substrate according to the following reaction.

$$2Cu^{2+} + H_2O + 2e^- \Longrightarrow Cu_2O + 2H^+$$

Second cathodic peak at –1 V vs. SCE attributes to the formation of Cu on the substrate according to the following reaction.

$$Cu^{2+} + 2e^- \Longrightarrow Cu$$

Similar cathodic peaks have been observed by Wijesundera et al [12].

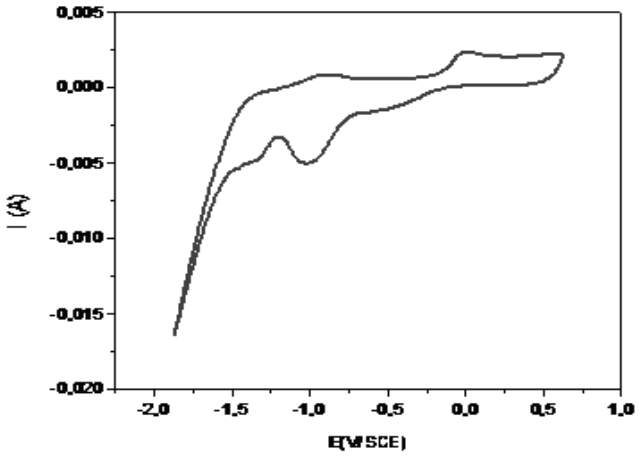

Fig. 3 Cyclic voltammogram of ITO-coated glass for the solution containing 0.01M cupric acetate and 0.1M sodium acetate (pH = 6.2), Scan rate 50 mV s^{-1}.

III. 2. X-ray diffraction analysis

Fig. 4 represents the X-ray diffraction spectra of the films deposited on ITO-coated glass substrate at pH = 6.2. This fig show five peaks at 2θ values of 21.30°, 30.30°, 50.60° and 60,30° corresponding to the reflections from (110), (111), (200) and (220) atomic plans of Cu_2O in addition to the ITO peak and three additional peaks at 2θ values of 37.25°, 45.25° corresponding to the reflections from (111), (200) atomic plans of Cu.

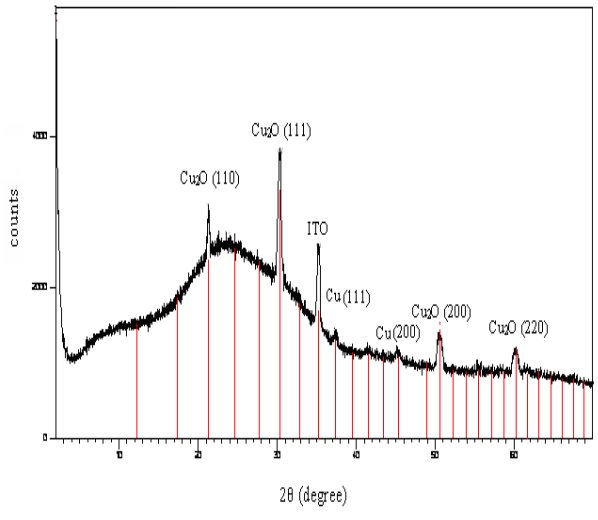

Fig. 4 X-ray diffraction spectra of the films deposited on ITO-coated glass substrate at pH = 6.2.

The intensity of the (111) diffraction is much stronger than that of other peaks, indicating that the Cu_2O film has a cubic structure.

III. 3. Photocurrent characterization

Fig. 5 Shows *Current-Voltage* characterization of cuprous oxide (Cu_2O) deposited at –0.50 V vs. SCE for the solution containing 0.1M sodium acetate ($CH_3COONa.3H_2O$), in the dark and under illumination. In the dark, we observe a low intense anodic current on the other hand, under illumination of the surface of cuprous oxide; there is appearance of a more intense anodic current in that observed in the darkness. This indicates that the cuprous oxide thin film behaves as a semiconductor of type n [17, 18].

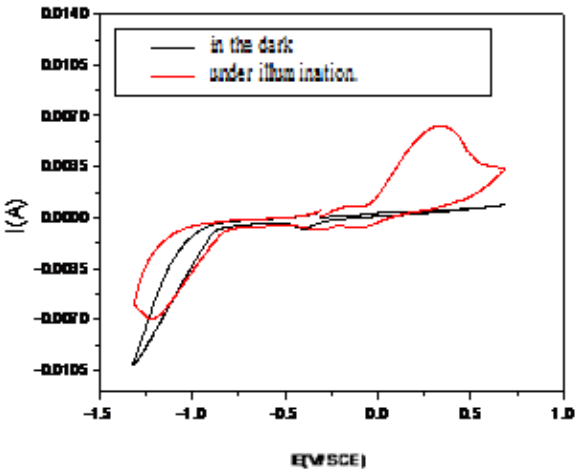

Fig. 5 *Current-Voltage* Characterization of cuprous oxide (Cu_2O) deposited at –0.50 V vs. SCE for the solution containing 0.1M sodium acetate ($CH_3COONa.3H_2O$) in the dark and under illumination.

IV. Conclusion

Electrodeposition of Cu_2O and Cu thin films can be carried out in aqueous solution containing sodium acetate and cupric acetate in a potential at –0.5 V vs. SCE and –1 V vs. SCE respectively.

The XRD measurements revealed that Cu_2O films has a cubic structure and the preferred growth orientation is the (111) direction. The photocurrent revealed that the films deposited at pH = 6.2 has n-type electrical conductivity.

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REFERENCES

[1] Y.Tang, Z. Chen, Z. Jia, L. Zhang, J. Li, "Electrodeposition and characterization of nanocrystalline cuprous oxide thin films on TiO_2 films," J. Mater Lett., vol. 59, pp. 434–438, 2005.
[2] T. Mahalingam, J.S.P. Chitra Khayat, J.P. Chu, H. Moon, H. J. Kwon, Y. D. Kim, "Photoelectrochemical solar cell studies on electroplated cuprous oxide thin films," J. Electron Mater., vol. 17, pp. 519–523, 2006.
[3] J. Katayama, K. Ito, M. Matsuoka, J. Tamaki, "Performance of Cu_2O/ZnO solar cell prepared by two-step electrodeposition," J. Appl. Electrochem. vol. 34, pp. 687–692, 2004.
[4] P. E. de Jongh, D. Vanmaekelbergh, J. J. Kelly, "Cu_2O: Electrodeposition and Characterization," J. Chem. Mater. vol. 11, pp. 3512–3517, 1999.
[5] S.S. Jeong, A. Mittiga, E. Salza, A. Masci, S. Passerini, "Electrodeposited ZnO/Cu_2O heterojunction solar cells," J. Electrochim. Acta. vol. 53, pp. 2226–2231, 2008.
[6] J. Cui, U. J. Gibson, "A Simple Two-Step Electrodeposition of Cu_2O/ZnO Nanopillar Solar Cells," J. Phys. Chem. vol. 114, pp. 6408–6412, 2010.
[7] K. Santra, P. Chatterjee, S.P. Sen Gupta, "Powder profile studies in electrodeposited cuprous oxide films," J. Solar Energy Materials and Solar Cells. vol. 57, pp. 345–358, 1999.
[8] T. Mahalingam, J.S.P. Chitra, J.P. Chu, S. Velumani, P.J. Sebastian, "Structural and annealing studies of potentiostatically deposited Cu_2O thin films," J. Solar Energy Materials and Solar Cells. vol. 88, pp. 209–216, 2005.
[9] C. C. Hu, J. N. Nian, H. Teng, "Electrodeposited p-type Cu_2O as photocatalyst for H_2 evolution from water reduction in the presence of WO_3," J. Solar Energy Materials and Solar Cells. vol. 92, pp. 1071–1076, 2008.
[10] V. Georgieva, M. Ristov, "Electrodeposited cuprous oxide on indium tin oxide for solar applications," J. Solar Energy Materials and Solar Cells. vol. 73, pp. 67–73, 2002.
[11] L. Wan, Z. Wang, Z. Yang, W. Luo, Z. Li, Z. Zou, "Modulation of dendrite growth of cuprous oxide by electrodeposition," J. Crystal Growth . vol. 312, pp. 3085–3090, 2010.
[12] R.P. Wijesundera, M. Hidaka, K. Koga, M. Sakai, W. Siripala, "Growth and characterization of potentiostatically electrodeposited Cu_2O and Cu thin films," J. Thin Solid Films. vol. 500, pp. 241–246, 2006.
[13] K. Han, M. Tao, "Electrochemically deposited p–n homojunction cuprous oxide solar cells," J. Solar Energy Materials and Solar Cells. vol. 93, pp. 153–157, 2009.
[14] R.P. Wijesundera, L.D.R.D. Perera, K.D. Jayasuriya, W. Siripala, K.T.L. De Silva, A.P. Samantilleka, I.M. Dharmadasa, "Sulphidation of electrodeposited cuprous oxide thin films for photovoltaic applications," J. Solar Energy Materials and Solar Cells. vol. 61, pp. 277–286, 2000.
[15] X. Gao. F. Peng, X. Li, W. Yu, J. Qiu, "Growth of highly oriented ZnO films by the two-step electrodeposition technique," J. Matter Sci. vol. 42, pp. 9638–9644, 2007.
[16] X. Gan, X. Gao, J. Qiu, X. Li, "Growth and characterization of ZnO-SDS hybrid thin films prepared by electrochemical self-assembly method," J. Applied Surface Science. vol. 254, pp. 3839–3844, 2008.
[17] W. Siripala, L.D.R.D. Perera, K.T.L. De Silva, J. K. D. S. Jayanetti, I. M. Dharmadasa, "Study of annealing effects of cuprous oxide grown by electrodeposition technique," J. Solar Energy Materials and Solar Cells. vol. 44, pp. 251–260, 1996.
[18] G. Horowitz. A. Bourrasse, "Cellules photo-électrochimiques à électrodes semi-conductrices pour la conversion et le stockage de l'énergie solaire," Revue. Appl. Phys. vol. 15, pp. 463–476, 1980.