Electrochemical Synthesis of p-Cu_2O Thin Films on ITO-coated glass substrates for Photovoltaic Solar Cells

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Abstract— **Cuprous oxide (Cu_2O) thin films have been prepared on ITO-coated glass substrates by electrodeposition technique from an aqueous solution containing copper acetate and sodium thiosulfate. Electrochemical kinetics of Cu_2O films were investigated by cyclic voltammetry. The obtained films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV/Vis spectroscopy and electrical measurements. The X-ray diffraction results indicated that the synthesized Cu_2O thin films had a good crystalline of deposited Cu_2O thin films with a pure cubic structure. Morphological study showed a better compactness structure composed of pyramid shape. Optical band gap was found to be 2.103 eV. Electrical properties of Cu_2O films showed a p-type semiconductor with low electrical resistivity of 100 Ω cm, carrier concentration of 3.62×10^{15} $cm^{-3}$and mobility of 17.24 cm^2 $V^{-1}s^{-1}$.**

Keywords—**Thin film, semiconductor, Cu_2O, electrodeposition, solar cells.**

I. INTRODUCTION

Cuprous oxide (Cu_2O) film is one of the most important members of metal oxide semiconductor because of its suitable band gap and high absorption coefficient in the visible region. In addition with good optical and electrical properties the material has several advantages such as availability and abundance of the starting materials, non-toxic nature and low production cost [1]. These films have been used in the potential application areas such as gaz sensors [2], solar cells application [3], photocatalysis [4], thin film homo-junction solar cells [5], photoelectrodes for solar water splitting [6,7] and working electrode in the application of photoelectrochemical solar cell (PESC) [8].

Electrodeposition technique is one of the most several methods are usually used to prepare Cu_2O thin films. It presents many advantages such as simplicity, low equipment cost, the possibility of preparing large area thin films and the control of the film thickness [6, 9]. Cu_2O films are usually electrodeposited from copper precursor solutions, such as copper nitrate, copper sulfate and copper acetate. Many researchers have used various additives in electrolytic bath in order to improve the quality of the deposited films such as uniformity, adhesion and crystallinity [1, 6, 9].

In this work, we report the preparation of Cu_2O thin films by electrodeposition technique in a solution of copper acetate and sodium thiosulfate at pH 11. Electrodeposited of Cu_2O thin films were investigated X-ray diffraction (XRD), scanning electron microscopy (SEM), optical spectroscopy, and electrical measurements.

II. EXPERIMENTAL DETAILS

A. Reagents

All chemical reagents used in the present work were of analytical grade. Copper acetate monohydrate ($Cu(C_2H_3O_2)_2.H_2O$, 98%, Sigma Aldrich) was used as copper source. Sodium acetate trihydrate ($CH_3COONa.3H_2O$, 99%, Sigma Aldrich) and sodium sulfate (Na_2SO_4, 99%, Sigma Aldrich) were used as a supporting electrolyte. However, sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$, 99.5%, Sigma Aldrich) was used as an additive. All the aqueous solutions were prepared using distilled water.

B. *Preparation and characterization techniques of Cu_2O thin films*

Electrodeposition of Cu_2O thin films was carried out using a three electrode electrochemical cell with a platinum (Pt) wire as a counter electrode, indium tin oxide (ITO)-coated glass (8-10 Ω/square, Sigma Aldrich) substrate was used as working electrode. A saturated calomel electrode (SCE) was used in all experiments as a reference electrode. Before the deposition, the substrates were cleaned ultrasonically in acetone, ethanol and then rinsed in distilled water. Cuprous oxide thin films were electrodeposited in an aqueous solution of 0.01 M $Cu(C_2H_3O_2)_2.H_2O$, 0.1 M $CH_3COONa.3H_2O$ and 1.2 mM $Na_2S_2O_3.5H_2O$ at 60 °C. pH solution was adjusted to 11 using potassium hydroxide (KOH). Sodium thiosulfate is used to stabilize Cu^{2+} ions in the solution [10-12].

Cyclic voltammetry study was carried out using Princeton Applied Research Model 273 A Potentiostat/Galvanostat, coupled to a personal computer with Power Suite software for data acquisition and potential control. Thin films of cuprous oxide were electrodeposited for 30 minutes and dried in air at 100°C.

The crystalline phase of Cu_2O thin films was investigated by X-ray diffraction using a Bruker Discover D8 Diffractometer with CuK_α radiation (λ = 1.5406 Å). Scanning electron microscopy images was performed using a VEGA3 TESCAN scanning electron microscope operating at 20 kV accelerating voltage. Optical transmittance of thin films was measured by a Perkin Elmer Lambda 950 UV–vis-NIR spectrometer. Electrical properties of deposited Cu_2O films were determined by a HMS 3000 Hall measurement system at room temperature. Ag-paste was used at the corners of films to make four good contacts with probes. Thickness of the films was measured using a Dektak stylus profilometer.

III. Results and Discussion

A. *Electrochemical study*

Fig. 1 shows the cyclic voltammogram of the solutions containing 0.01 M copper acetate and 0.1 M sodium acetate and 1.2 mM sodium thiosulfate for pH 11 and at T = 60 °C . The potential sweep was ranged from 0.3 to -2.0 V with a scan rate of 50 mV s^{-1}.

From this Fig., we recorded two cathodic peaks. The first peak situated at -0.58 V, which attributed to the reduction of Cu^{2+} to Cu^{+} where water converted to hydroxide ions molecule. The hydroxide ions react with Cu^{+} in the solution to form Cu_2O film on the substrate according to the following reactions [13, 14]:

$$Cu^{2+} + e^{-} \longrightarrow Cu^{+} \quad (1)$$

$$2Cu^{+} + 2OH^{-} \longrightarrow Cu_2O + H_2O \quad (2)$$

The second cathodic peak is observed at -1.33 V which can be mainly ascribed to the deposition of metallic copper with release of hydrogen (Eq. (3, 4)).

$$Cu^{2+} + 2e^{-} \longrightarrow Cu \quad (3)$$

$$2H^{+} + 2e^{-} \longrightarrow H_2 \quad (4)$$

Similar cathodic peaks are reported in the literature [15-18], but the present cathodic peaks are shifted to negative potentials if compared with literature.

During reverse scan, an anodic peak is observed at 0.29 V corresponding to the oxidation of metallic copper [14,15], indicating the only formation of Cu_2O on ITO-coated glass substrate which is confirmed below by XRD analysis.

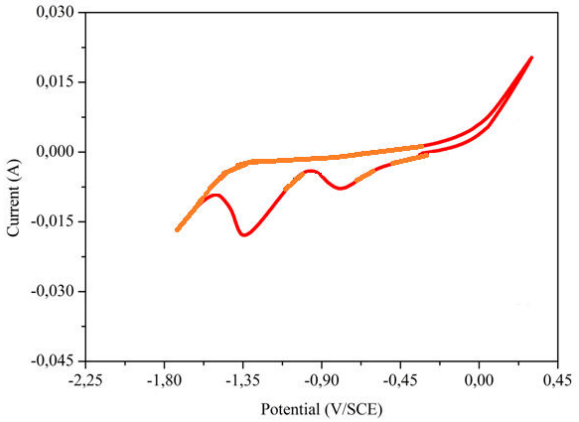

Fig.1. Cyclic voltammogram of the solution containing 0.01 M $Cu(C_2H_3O_2)_2.H_2O$ and 0.1 M $CH_3COONa.3H_2O$ at pH 11. The potential scanning rate was 50 mV/s.

B. *XRD Analysis*

Thickness of Cu_2O films was measured by Dektak stylus profilometer and was found to be 368 nm. Fig. 2 shows the XRD pattern for a Cu_2O thin film deposited onto ITO-coated glass substrates at -0.58V and at 60 °C. From this figure, all the diffraction peaks of Cu_2O films correspond to the peaks of cubic phase of standard Cu_2O (JCPDS card no: 05-0667) [19]. X-ray diffraction patterns show that the intensity of the (311) diffraction peak is higher when compared with the other peaks (111) and (200), indicating preferential orientation along the c-axis. No impurities such as cupric oxides are found in the XRD pattern besides the substrate. The presence of several peaks in the diffraction pattern is indicative of polycrystalline nature of the film.

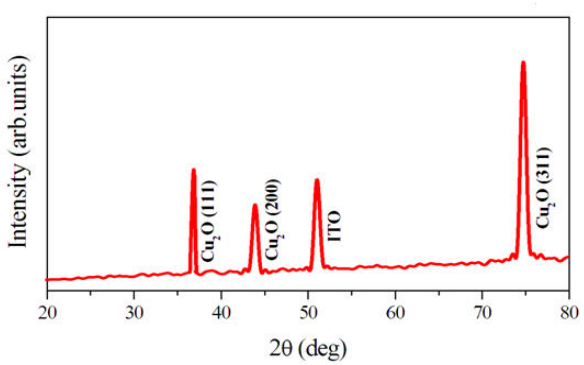

Fig. 2. X–ray diffraction of the Cu_2O thin films deposited onto ITO–coated glass substrates

The calculated value of the lattice constant parameters of Cu_2O films is 4.213 Å. which were slightly different than that of standard Cu_2O (JCPDS 05-0667, $a = b = c = 4.269$ Å) [20, 21].

The crystallite size (D) of Cu_2O thin films was calculated from the major diffraction peaks using the Scherrer's formula (Eq. (5)) [3]:

$$D = 0{,}89\lambda/\beta \cos\theta \qquad (5)$$

Where λ is the wavelength of the incident beam (1.5406 Å), β is the full width at half maximum and θ is the Bragg's angle in rad. The average crystallite size of deposited Cu_2O is found to be 28.93 nm.

C. SEM analysis

The surface morphologie of Cu_2O films deposited onto ITO–coated glass substrates obtained is shown in Fig. 3. Micrograph of deposited Cu_2O film showed a better compactness structure composed of pyramid shape. This shape is also observed when Cu_2O thin films deposited onto various substrates by different copper salt solution [22, 23], which is consistent with XRD results.

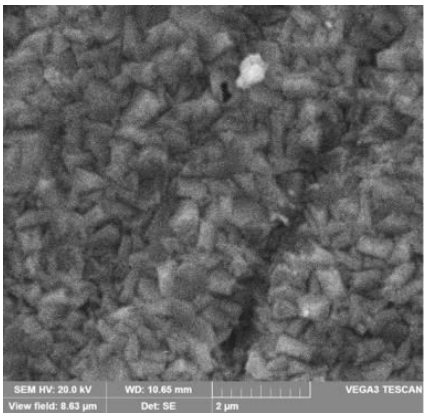

Fig. 3. SEM image of Cu_2O films deposited onto ITO–coated glass substrates

D. Optical properties

The optical transmittance spectrum of deposited Cu_2O thin films in the wavelength range from 400 to 1100 nm taken at room temperature is shown in Fig. 4. It was shown that the film present a high optical transmission (>70%) in the visible wavelength range, which confirms the good optical quality of the electrodeposited Cu_2O thin films. The absorption coefficient (α) was determined in the order of $>10^4$ cm^{-1}.

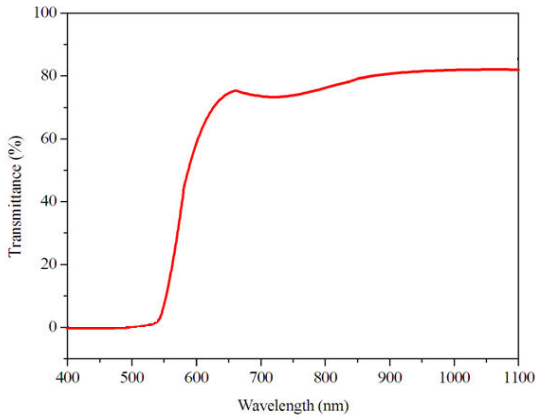

Fig. 4. Transmittance spectrum of Cu_2O thin films deposited onto ITO–coated glass substrates

Fig. 5 shows the plot of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ of Cu_2O thin films. It has been observed that the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ are linear over a wide range of photon energies indicating the direct type of transitions. The optical band gap of the films was determined using Tauc's formula (Eq. (6)) [24]:

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right) \qquad (6)$$

Where α is absorption coefficient, h is Planck's constant, ν is photon energy, A is a constant and E_g is the direct transition band gap. The optical band gap value was determined by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$, which is illustrated in Fig. 5. The band gap of Cu_2O thin films was estimated to be 2.067 eV. This value is in good agreement with the reported values of band gap of Cu_2O thin films [19, 25]. The obtained optical results make Cu_2O film as a promising semiconductor material for use in photovoltaic solar cells applications.

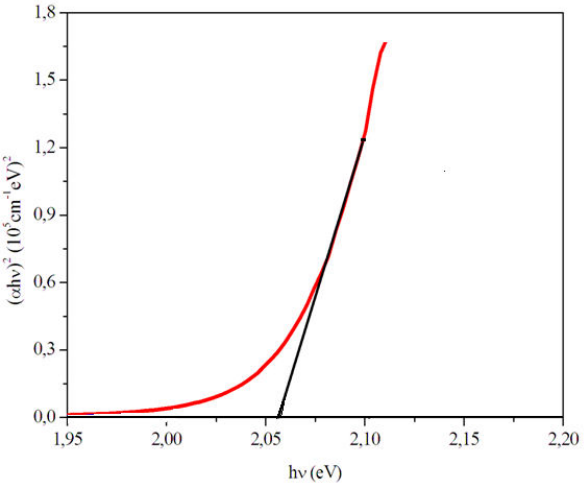

Fig. 5. Plot of $(\alpha h\nu)^2$ versus hν of Cu_2O thin films

E. Electrical properties

Electrical properties of Cu_2O films were examined by Hall Effect measurements at room temperature. Cu_2O films showed a p-type electrical conductivity with carrier concentration of 3.62×10^{15} cm^{-3}, mobility of 17.24 cm^2 $V^{-1}s^{-1}$ and a low electrical resistivity of 100 Ω cm. These values are in agreement with the results reported by others [26, 27].

IV. CONCLUSIONS

Cuprous oxide (Cu_2O) thin films have been successfully electrodeposited onto ITO-coated glass substrates from aqueous copper acetate solutions with addition of sodium thiosulfate at 60 °C. The X-ray diffraction results indicated that the synthesized Cu_2O thin films had a good crystalline of deposited Cu_2O thin films with a pure cubic structure. The surface morphology of obtained films showed a better compactness structure composed of pyramid shape. Optical properties of Cu_2O thin films revealed a high optical transmission (>70%) and high absorption coefficient ($\alpha>10^4$ cm^{-1}) in visible region. The optical band gap was estimated to be 2.067 eV. Hall Effect measurements indicated that the deposited cuprous oxide had a cathodic photocurrent indicating p-type semiconductor with carrier concentration of 3.62×10^{15} cm^{-3}, mobility of 17.24 cm^2 $V^{-1}s^{-1}$ and a low electrical resistivity of 100 Ω cm. The obtained Cu_2O thin films with suitable properties could be promising material for use in various applications such as photovoltaic solar cells.

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REFERENCES

[1] R. Oommen, U. Rajalakshmi, Sanjeeviraja, "Characteristics of electron beam evaporated and electrodeposited Cu_2O thin films-comparative study", Int. J. Electrochem. Sci., vol.7, pp.8288-8298, 2012.

[2] P. A. Praveen Janantha, L. N. L. Perera, K. M. D. C. Jayathilaka, J. K. D. S. Jayanetti, D. P. Dissanayaka. W. P. Siripala, "Use of Cu_2O microcrystalline thin film semiconductors for gas sensing", Proc. Tech. Sess. Inst. Phys– Sri Lanka, vol. 25, pp.70-76, 2009.

[3] N. Soundaram, R. Chandramohan, S. Valanarasu, R. Thomas. A. Kathalingam, "Studies on silar deposited Cu_2O and ZnO films for solar cell application", J. Mater. Sci.-Mater. Electron., vol. 26 (7), pp. 5030-5036, 2015

[4] J. Dong, H. Xu, F. Zhang, Ch. Chen, L. Liu, G. T. Wu, "Synergistic effect over photocatalytic active Cu_2O thin films and their morphological and orientational transformation under visible light irradiation", Appl. Catal., A, vol. 470, pp. 294-302, 2014.

[5] R. P. Wijesundera, L. K. A. D. D. S. Gunawardhana, W. Siripala, "Electrodeposited Cu_2O homojunction solar cells: Fabrication of a cell of high short circuit photocurrent", Sol. Energy Mater. Sol. Cells, vol. 157, pp. 881-886, 2016.

[6] Q. Ma, J. P. Hofmann, A. Litke, E. J. M. Hensen, "Cu_2O photoelectrodes for solar water splitting: tuning photoelectrochemical performance by controlled faceting", Sol. Energy Mater. Sol. Cells, vol. 141, pp. 178-186, 2015.

[7] Zh. Zhang, P. Wang, "Highly stable copper oxide composite as an effective photocathode for water splitting via a facile electrochemical synthesis strategy", J. Mater. Chem.,vol. 22, pp.2456-2464, 2012.

[8] D. S. C. Halin, I. A. Talib, A. R. Daud, M. A. A. Hamid, "Characterizations of cuprous oxide thin films prepared by sol-gel spin coating technique with different additives for the photoelectrochemical solar cell". Int. J. Photoenergy, vol. 2014, pp. 1-6, 2014.

[9] H Rahal, R Kihal, AM Affoune, S Rahal, "Electrodeposition and characterization of Cu_2O thin films using sodium thiosulfate as an additive for photovoltaic solar cells", Chinese J. Chem.Eng., vol. 26, pp.421-427, 2018.

[10] S. S. Nikam, M. P. Suryawanshi, S. M. Bhosale, M. A. Gaikwad, P. A. Shinde, A. V. Moholkar, "Cu_2O thin films prepared using modified successive ionic layer adsorption and reaction method and their use in photoelectrochemical solar cells", J. Mater. Sci.-Mater. Electron., vol. 27 (2), pp.1897-1900, 2016.

[11] S. S. Oluyamo, Nyagba, S. Mbafan, Ojo, S. Ambrose, "Optical properties of copper (I) oxide thin films synthesized by silar technique", J. Appl. Phys, vol. 6 (3), pp. 102-105, 2014.

[12] A.T. Ravichandran, K. Dhanabalan, R. Chandramohan, A. Vasuhi, P. Parameswaran, "Optical properties of modified-silar grown copper oxide nanocrystalline thin films", Int. J. Inf. Res. Rev., vol. 1 (1) , pp. 007-011, 2014.

[13] A. El-Shaer, A. R. Abdelwahed, A. Tawfik, M. Mossad, D. Hemada, Effect of deposition parameters on electrodeposited cuprous oxide thin films, Int. J. Emerg. Technol. Adv. Eng., vol. 4 (12), pp. 595-602, 2014.

[14] G. Riveros, A. Garmendia, D. Ramirez, M. Tejos, P. Grez, H. Gomez, E. A. Dalchiele, Study of the electrodeposition of Cu_2O thin films from DMSO solution, J. Electrochem. Soc., vol. 160 (1), pp. D28-D33, 2013.

[15] S. Laidoudi, A. Y. Bioud, A. Azizi, G. Schmerber, J. Bartringer, S. Barre, A. Dinia, Growth and characterization of electrodeposited Cu_2O thin films, Semicond. Sci. Technol, vol. 28 (11), pp. 115005-115011, 2013.

[16] A. El-Shaer, M. T. Y. Tadros, M. A. Khalifa, Fabrication of homojunction cuprous oxide solar cell by electrodeposition method, Nat. Sci., vol. 13 (5), pp.1-9, 2015.

[17] P. Grez, F. Herrera, G. Riveros, A. Ramirez, R. Henriquez, E. Dalchiele, R. Schrebler, Morphological, structural, and photoelectrochemical characterization of n-type Cu_2O thin films obtained by electrodeposition, Phys. Status Solidi A, vol. 209 (12), pp. 2470-2475, 2012

[18] A. S. M. Hanif, F. Mohamad, R. Z. Zakaria, Cyclic voltammetry measurement for n-type Cu_2O thin film using copper acetate-based solution, J. Eng. Appl. Sci., vol.10 (19), pp. 8562-8568, 2015.

[19] P. Grez, F. Herrera, G. Riveros, A. Ramirez, R. Henriquez, E. Dalchiele, R. Schrebler, "Morphological, structural, and photoelectrochemical characterization of n-type Cu_2O thin films obtained by electrodeposition", Phys. Status Solidi A, vol. 209 (12), pp. 2470-2475, 20.12.

[20] Z. C. Orel, A. Anzlovar, G. Drazic, M. Zigon, "Cuprous oxide nanowires prepared by an additive-free polyol process", Cryst. Growth Des., vol. 7 (2), pp. 453-458, 2007.

[21] M. A. Amrani, V. V. S. S. Srikanth, N. K. Labhsetwar, A. S. Al-Fatesh, H. Shaikh, "Phoenix dactylifera mediated green synthesis of Cu_2O particles for arsenite uptake from water", Sci. Technol. Adv. Mater., vol. 17 (1), pp.760-768, 2016.

[22] Y. Yang, Y. Li, M. Pritzker, "Control of Cu_2O film morphology using potentiostatic pulsed electrodeposition", Electrochim. Acta, vol. 213, pp. 225-235, 2016.

[23] C. Wang, J. Xu, S. Shi, Y. Zhang, Z. Liu, X. Zhang, S. Yin, L. Li, "The structural, optical and photoelectrical properties of Cu_2O films electrodeposited in different pH", RSC Adv., vol. 6, pp. 4271-5140, 2015.

[24] R. Kihal, H. Rahal, AM. Affoune, M. Ghers, "Electrodeposition of SnS Thin film Solar Cells in the Presence of Sodium Citrate", J. Electro. Sc. Tech. vol. 3 (8), pp. 206-2014, 2017.

[25] A. El-Shaer, A. R. Abdelwahed, M. M. Mosaad, A. Tawfik, D. Hemada, "Effect of pH on conductivity of electrodeposited cuprous oxide thin films", Nat. Sci., vol. 13 (3), pp.1-5, 2015.

[26] Y. Abdu, A.O. Musa, T. H. Darma, "Electroless deposition and electrical characterization of n-Cu_2O LAYER. " J. Pure. Appl. Sci., vol. 5 (2), pp.1-10, 2012.

[27] T. Jiang, T. Xie, W. Yang, L. Chen, H. Fan, D. Wang, "Photoelectrochemical and photovoltaic properties of p-n Cu_2O homojunction films and their photocatalytic performance", J. Phys. Chem. C, vol. 117, pp. 4619-4624, 2013.