

Effect of pH on Conductivity of Electrodeposited Cuprous Oxide Thin Films

Abdelhamid El-Shaer¹, Abeer Ramadan Abdelwahed¹, M. M. Mosaad¹ AbdElraouf Tawfik², and Dalal Hemada²

¹Physics Department, Faculty of Science, KafrelSheikh University, 33516 KafrelSheikh, Egypt

²Physics Department, Faculty of Science, Tanta University

E-mail: elshaer@sci.kfs.edu.eg

Abstract: Cuprous oxide (Cu₂O) thin films were electrodeposited on fluorine-doped tin oxide (FTO) conducting glass substrates via potentiostatic deposition using cupric acetate bath. The pH of the electrolyte was varied from 5.2 to 6.4 by carefully addition of 0.08M acetic acid. The effect of pH on the morphologies, crystalline, optical quality and conductivity of Cu₂O thin films was investigated. Uniform and adherent films of thickness of 0.7μm could be deposited potentiostatically. The dendritic morphology was observed for electrodeposited n-Cu₂O and by increasing the pH this morphology disappear. Small grains appeared at pH 5.2 and pH 5.4 and by increasing the pH (5.7-6.4) these grains disappeared. At low pH (5.2-5.4), the composition of the electrodeposited Cu₂O films were found to be a mixture of metallic Cu and Cu₂O, while by increasing the pH to 5.7 pure Cu₂O films were obtained. From both SEM and XRD we found that these spherical grains are metallic Cu. Photocurrent measurements indicated that Cu₂O films deposited at pH lower than 6.2 has n-type conductivity where films deposited at higher pH had p-type conductivity. [Abdelhamid El-Shaer, Abeer Ramadan Abdelwahed, M. M. Mosaad AbdElraouf Tawfik, and Dalal Hemada. **Effect of pH on Conductivity of Electrodeposited Cuprous Oxide Thin Films.** *Nat Sci* 2015;13(3):49-53]. (ISSN: 1545-0740). <http://www.sciencepub.net/nature>. 1

Keywords: Thin film, cuprous oxide, electrodeposition, anodic current.

1. Introduction:

Metal oxides nanomaterial like copper oxide have shown massive significance in the fields of solar energy converting devices [1-7], optoelectronics, catalysis [8,9], and gas sensors [10], due to their unique physical, optical and electrical properties. Cuprous oxide (Cu₂O) is a promising low-cost and non-toxic material satisfying the environmental and economic requirements needed for large-scale applications due to both its appropriate band-gap ($E_g = 1.9-2.2$ eV) and relatively high light absorption coefficient in visible region [11]. As a semiconductor, Cu₂O has been studied since early fifties and found that it is a p-type semiconductor due to the presence of Cu vacancies in the crystal lattice, owing to an acceptor level at 0.4 eV above the valance band [12]. However, it has been reported that n-type conductivity in electrodeposited cuprous oxide thin films is due to the presence of a donor level at 0.38 eV below the conduction band, originated from O vacancies [13]. It was observed that by controlling the pH value of the of electrolyte deposition bath, density of both O and Cu vacancies which are responsible for donor and acceptor levels in Cu₂O respectively, can be controlled. Thereby it was possible to deposit either n-type or p-type Cu₂O thin films. If we can reduce the amount of oxygen incorporated into the film, we should able to reduce copper vacancies and increase oxygen vacancies. In this way, electrochemically deposited cuprous oxide may become n-type. Control of oxygen incorporation should be reachable by

controlling bath pH. However, the effects of pH value on the crystal growth of Cu₂O in cupric acetate system during electrodeposition process have rarely been studied in detail. Various methods have been developed for the synthesis of different Cu₂O micro- and nano-structures, such as gas phase deposition techniques [14], electrodeposition [15–20] and wet chemistry methods [21,22]. Among them, electrochemical deposition has shown the advantage to control the crystallization engineering of Cu₂O and it presents a simple, gentle and economical method for preparation of large area films with the advantage of allowing controlled and patterned crystal growth. It offers the advantages of low temperature synthesis, low cost, and high purity. In addition, the structure and composition of the electrochemical deposited films can be controlled because the driving force for the reaction is precisely known. In this work, the effect of pH on the crystal structure, morphology and optical properties of Cu₂O films and conductivity type is investigated, based on this, a series of Cu₂O films were electrodeposited using cupric acetate solutions with bath pH ranging from pH 5.2 to pH 6.4.

2. Material and Methods:

Cu₂O thin films were electrodeposited using a three-electrode setup consisting of platinum wire as a counter electrode, Ag/AgCl as a reference electrode, while FTO-coated glass substrate was employed as a working electrode. Prior to the film deposition substrates were cleaned by successive sonication in

acetone, isopropanol and finally DI water for 10 minutes, respectively and then dried in oven at 105°C for at least 30 min.

Films were deposited using electrolyte consist of 0.1M sodium acetate and 0.02M cupric acetate. Different pH values of the electrolyte were obtained (5.2 to 6.4) by a carefully addition of 0.08M acetic acid to the deposition electrolyte. The temperature of the electrolyte was maintained at 60 °C. Electrodeposition was carried out under a potentiostatic condition of -150 mV vs. Ag/AgCl for 30minutes using Bio-LogicSb-50 potentiostat. After deposition the film was good cleaned by distilled water and dried with air flow. The morphology of the deposited films was characterized by JEOL JSM 651 OLV scanning electron microscopy (SEM). Crystal structures and phase compositions of the films were confirmed by X-ray diffraction analysis using XRD-6000 Shimadzu diffractometer using Cu K α radiation (40Kv, 30 mA). Optical studies were carried out by recording the optical absorption spectra of the films using JASCO V630 spectrophotometer. Photocurrent measurements were carried out using a home-built system, which includes a light source, an illumination switch, three-electrode cell and a controlling system. A 100W tungsten lamp is used to provide broad spectrum light. The illumination switch is actually a manually controlled light chopper with certain time intervals (5 sec), while the potentiostat is used to control the applied potential and scan rate.

3. Results and Discussion:

SEM images of Cu₂O films (the thickness of which are approximately 0.7 μ m according to Faraday's law of electrolysis) electrodeposited at applied potential -0.15 V (vs. Ag/AgCl) for 30 min in solution containing 0.02 M copper acetate and 0.1 M sodium acetate at pH from 5.20 to 6.40 modulated with acetic acid are shown in Fig. 1 (a-f). It is clear from Fig 1 (a), that the lateral crystal growth is faster than vertical growth and there are small spherical grains on the sample surface. It was shown that the branches grown on the substrate are significantly longer than the branches grown out of the substrate, which indicates faster lateral growth than vertical growth. This was mainly because the FTO substrate is much more conductive than the nucleated semiconductor Cu₂O, resulting in growth on the conductive substrate faster than the growth out of the substrate. By increasing the solution pH from 5.2 Fig. 1 (a) to 5.4 Fig. 1 (b), the nucleation density increased and this leads to a decrease in the lateral crystal growth and the small spherical grains still existed.

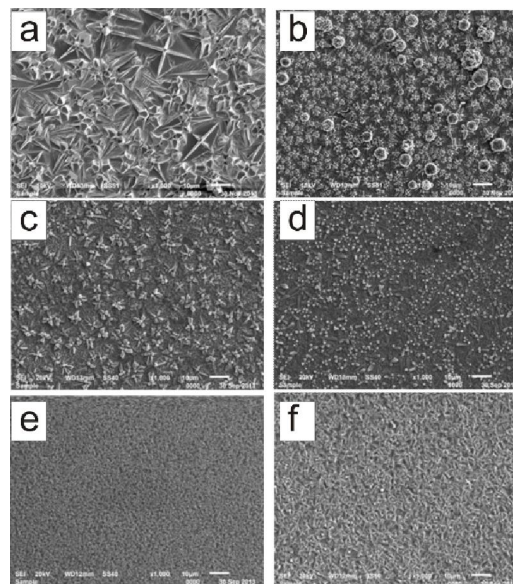


Fig.1: SEM photographs of n-Cu₂O films deposited at bath pH 5.2 (a), 5.4 (b), 5.7 (c), 6 (d), 6.2 (e), and 6.4 (f).

As the bath pH increased to 5.7 the spherical grains disappeared Fig. 1 (c). By reaching bath pH of 6 the nucleation density increased and the lateral growth became smaller Fig 1 (d). However, we can say that the dendritic morphology is dominant for Cu₂O samples electrodeposited at bath pH ranging from 5.2 to 6.0. The n-type Cu₂O films exhibit typical dendritic branching growth behavior caused by acetate buffer, which is also a morphology characteristic of n-type Cu₂O layers grown with the electrochemical method [23]. At solution pH greater than 6 the nucleation density became maximum and the morphology of samples changed as the dendritic morphology disappeared and the samples became more compacted Fig.1 (e, f). The nucleation density is affected by changing the deposition over potential (η) which is the difference between the applied potential, and reduction potential of Cu²⁺ to Cu⁺, a decrease of η would result in a decrease in the nucleation density.

$$\eta = |E_{appl} - E_{red}|(1)$$

For cathodic deposition as the applied potential shifts more negative η increase and hence nucleation density increased. Since all samples were deposited at fixed negative applied potential of -0.15V (vs. Ag/AgCl), we can attribute the change of samples morphology and nucleation density to another parameter which is solution pH. When bath pH increased the nucleation density of the electrodeposited Cu₂O samples increased, and hence the lateral crystal growth decrease. These results show that different dendritic morphologies of Cu₂O crystals can be formed with the change of pH values of the electrolyte.

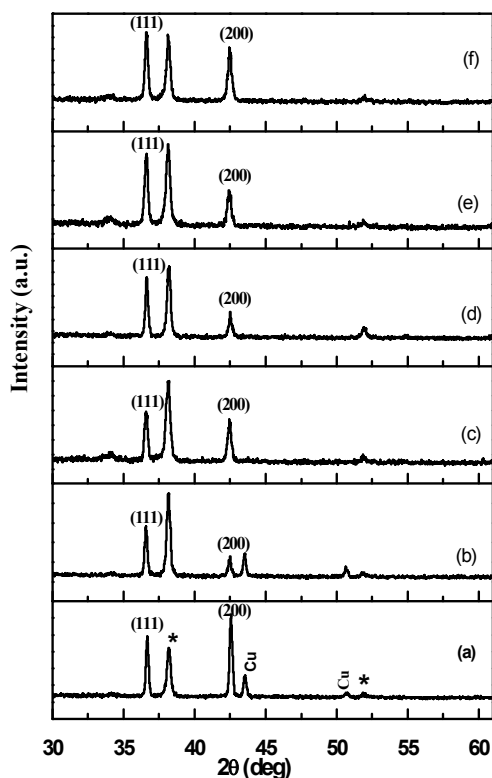


Fig.2: XRD pattern of electrodeposited Cu_2O films in electrolyte containing 0.02M copper acetate and 0.1 M sodium acetate at different bath pH (a) 5.2, (b) 5.4, (c) 5.7, (d) 6, (e) 6.2, and (f) 6.4. (* refers to FTO substrates).

XRD pattern of cuprous oxide thin films electrodeposited on FTO substrate at -0.15 V (vs. Ag/AgCl) at bath pH from 5.2 to 6.4 is shown in Fig. 2. These measurements indicated that all samples are polycrystalline and the crystallographic phase of the films is cubic as it is clear from the well-defined peaks in Fig. 2. At the bath pH of 5.2 and 5.4, besides the characteristic peaks of the FTO glass substrate, and the characteristic diffraction peaks of the Cu_2O thin film another two peaks are observed. These two diffraction peaks are related to (111) and (200) planes of metallic copper (Fig. 2 (a),(b)). As the pH increased from 5.7 (Fig. 2 (c)) to 6.4 (Fig. 2 (f)) the diffraction peaks of metallic copper disappear and there are only the diffraction peaks of Cu_2O and FTO substrate, which mean that pure n- Cu_2O can be obtained through electrodeposition at pH higher than 5.4 where no metallic copper was observed. In correlating SEM and XRD results, we can say that XRD results are in good agreement with the SEM results where some spherical grains appear at low solution pH. We observed before in SEM results some spherical grains started to appear

at bath pH 5.2 and 5.4 which is the same time when Cu metallic characteristic peak appear in XRD chart.

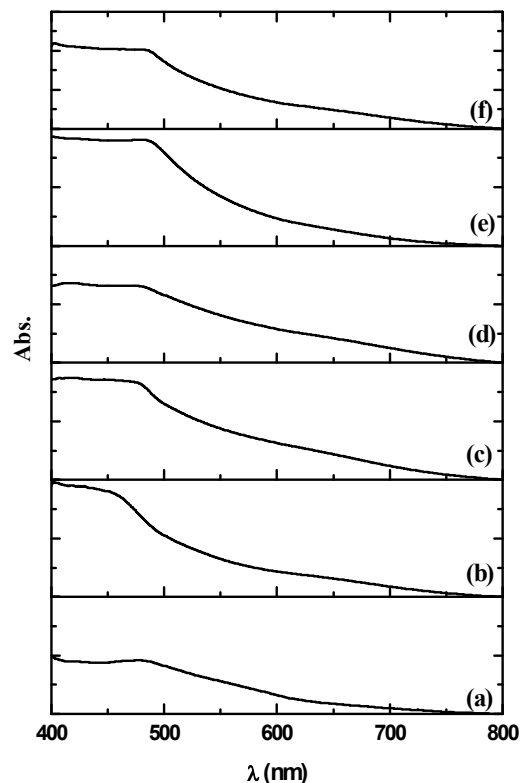


Fig.3: Absorption spectrum of n- Cu_2O films deposited at different pH 5.2 (a), 5.4 (b), 5.7 (c), 6 (d), 6.2 (e), and 6.4 (f).

From both SEM and XRD we can explain that these spherical grains are metallic copper. Optical characterization is performed with JASCO V-630 UV-Vis spectrophotometer. Absorption spectrum (200-800nm) shows that changing the deposition parameters have no effect on the optical properties of the deposited cuprous oxide thin films Fig.3 represents the absorption spectrum of the Cu_2O films deposited at applied potential -0.15 V (vs. Ag/AgCl) and different bath pH. To analysis the spectrum, the following equation is used:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (2)$$

where α is the absorption coefficient and n depends on the nature of the band gap ($n=1/3$ for indirect forbidden transition, $n=1/2$ for indirect allowed transition, $n=2/3$ for direct forbidden transition, and $n=2$ for direct allowed transition). We tried all the values and only $n=2$ give a linear relation between $(\alpha h\nu)^2$ and $h\nu$.

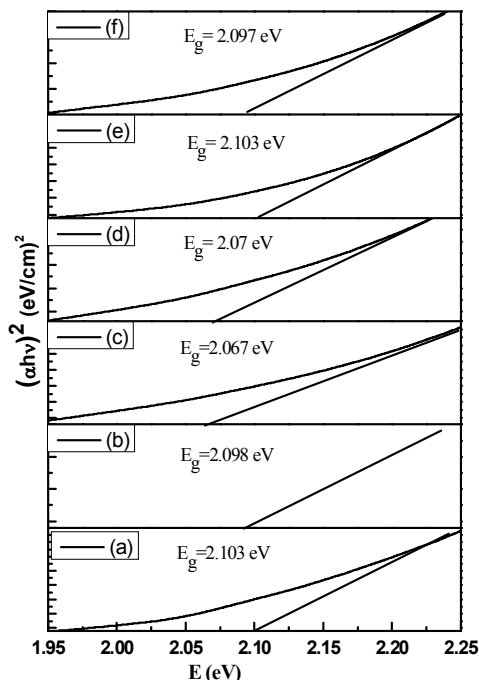


Fig.4: Dependency of energy band gap of n-Cu₂O on deposition bath pH 5.2 (a), 5.4 (b), 5.7 (c), 6 (d), 6.2 (e), and 6.4 (f).

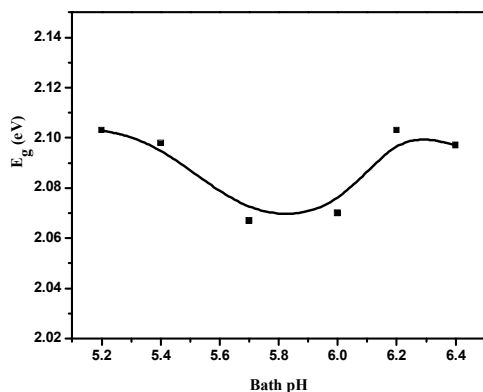


Fig.5: Relation between the bath pH and energy band gap of electrodeposited Cu₂O thin films.

The dependence of the energy band gap of Cu₂O on the bath pH is shown in Fig.4 which indicates that the deposited films have a direct band gap. The intercept of the plot with the $h\nu$ axis shows that Cu₂O has a band gap ranging from 2.067 eV to 2.1 eV (see Fig 5). These values are consistent with the reported band gap of Cu₂O. From these results we can conclude that the band gap of Cu₂O is less sensitive to the solution pH. Photocurrent measurements were performed on electrodeposited samples at 0V (vs. Ag/AgCl) to verify their conduction type. Fig 6 represents zero bias photocurrent measurements of Cu₂O samples. These results revealed anodic

photocurrent for samples deposited at bath pH of 5.2, 5.4, 5.7 and 6 (Fig 6 (a, b, c, d)), indicating n-type conductivity. For Cu₂O sample deposited at bath pH 6.2 and 6.4 we found that they produce cathodic current which mean p-type conductivity Fig 6 (e, f). Since, electrodeposition of Cu₂O involves two steps: The first step of the reaction would be the formation of Cu⁺ ions at the electrode surface due to the cathodic reaction (Eq.3) and the second step will be the formation of Cu₂O by reacting Cu⁺ with OH⁻, (Eq.4) [24].

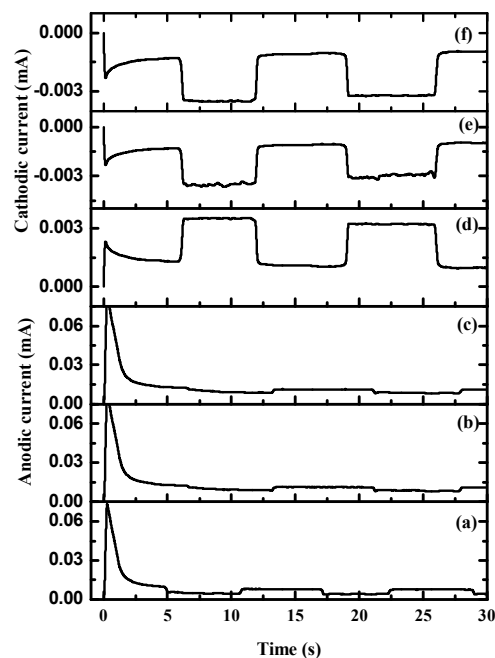
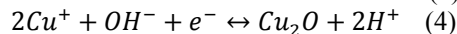


Fig. 6: Zero bias photocurrent of Cu₂O films electrodeposited in electrolyte containing 0.02M copper acetate and 0.1 M sodium acetate at different bath pH (a) 5.2, (b) 5.4, (c) 5.7, (d) 6, (e) 6.2 and (f) 6.4.

It is clearly seen that reaction (4) is highly dependent on the [OH⁻] concentration, in other words, pH of the bath. At low pH values the reaction rate is low and presence of excess Cu⁺ ions favors the formation of Cu rich or O deficient (i.e. having O vacancies) Cu₂O films. Thus high density of donors can be expected and therefore the film becomes n-type. This agrees with the result shown in Fig.6 (a-d) where at low pH values films grown are n-type. However, when the pH of the electrolyte is higher, reaction rate will be higher and insufficient Cu⁺ ion concentration might yield Cu₂O films with Cu deficiency. In other words, acceptor density will be higher and the film will be p-type. This agrees with the

result shown in Fig.6(e,f). From these results we found that pH has massive role in controlling the conductivity type of the electrodeposited Cu₂O thin films.

4. Conclusion:

In this work, we report on the electrochemical deposition of n-Cu₂O thin films on FTO substrate by cathodic reduction of cupric acetate. The applied potential was -0.15V (vs. Ag/AgCl). A systematic study of pH effect on the properties of electrodeposited Cu₂O thin films were done. It was found that the composition and crystal quality of the Cu₂O thin films is strongly dependent on pH and pH range from 5.7 to 6 is the preferable pH range for the deposition of pure and high quality n-Cu₂O thin films. The dendritic morphology was observed for electrodeposited n-Cu₂O and by increasing the pH this morphology disappear. Optical measurements indicated that the deposited Cu₂O thin films have a direct band gap (2.067eV-2.103eV) and changing pH have a weak effect on the optical properties of the prepared films. Photocurrent measurements indicated that Cu₂O films electrodeposited at pH lower than 6.20 had n-type conductivity where films deposited at higher pH had p-type conductivity. In this way, electrochemically deposited cuprous oxide may become n-type or p-type by controlling of the amount of oxygen incorporation into deposited Cu₂O by controlling bath pH.

Acknowledgements This study was supported by Research Support Fund Kafr El-Sheikh University Project ID: KFSU-3-13-03.

Corresponding Author:

Dr. Abdelhamid El-Shaer
Department of physics
KafrelSheikh University
33516 KafrelSheikh, Egypt
E-mail: elshaer@sci.kfs.edu.eg

References

1. A.E. Rakhshani, Solid-State Electron 29, 7 (1986).
2. K. Akimoto, S. Ishizuka, M. Yanagita, Y. Nawa, G.K. Paul, T. Sakuri, Sol. Energy 80, 715 (2006).
3. B.P. Rai, Cu₂O solar cells: A review, Sol. Cells 25, 265 (1988).
4. A.O. Musa, T. Akomolafe, M.J. Carter, Sol. Energy Mater. Sol. Cells 51, 305 (1998).
5. L.C. Olsen, F.W. Addis, W. Miller, Sol. Cells 7, 247 (1982).
6. M Izaki, T Shinagawa, KT Mizuno, Y Ida, M Inaba, A Tasaka Journal of Physics D: Applied Physics 40, 3326 (2007).
7. Mittiga, E. Salza, F. Sarto, M. Tucci, R. Vasanthi, Appl. Phys. Lett. 88, 163502 (2006).
8. J. Ramirez-Ortiz, T. Ogura, J. Medina-Valtierra, S.E. Acosta-Ortiz, P. Bosch, J.A. De Los Reyes, V.H. Lara, Appl. Surf. Sci. 174, 177 (2001).
9. H. Yang, J. Ouyang, A. Tang, Y. Xiao, X. Li, X. Dong, Y. Yu, Mater.Res. Bull. 41, 1310 (2006).
10. S.T. Shishiyanu, T.S. Shishiyanu, O.I. Lupan, Sensors Actuators B 113, 468 (2006).
11. L. Wan, Z. Wang, Z. Yang, W. Luo, Z. Li and Z. Zou, J. Cryst. Growth 312, 3085 (2010).
12. J.Bloem, Phillips Res. Reports 13, 167 (1958).
13. R.Garuthara and W.Siripala, J. Luminescence 121, 173 (2006).
14. A.S. Reddy, G.V. Rao, S. Uthanna, P.S. Reddy, Mater. Lett. 60, 1617 (2006).
15. J.Y. Chen, P.J. Zhou, J.L. Li, S.Q. Li, Carbohydrate Polym. 67, 623 (2007).
16. L. Huang, H. Wang, Z. Wang, A. Mitra, D. Zhao, Y. Yan, Chem. Mater. 14, 876 (2002).
17. H. Luo, J. Zhang, Y. Yan, Chem.Mater. 15, 3769 (2003).
18. J.A. Switzer, C.J. Hung, L.Y. Huang, E.R. Switzer, D.R. Kammler, T.D. Golden,E.W. Bohannon, J. Am. Chem. Soc. 120, 3530 (1998).
19. T. Mahalingam, J.S.P. Chitra, S. Rajendran, M. Jayachandran, M.J. Chockalingam, J. Cryst. Growth 216, 304 (2000).
20. A.L. Daltin, A. Addad, J.P. Chopart, J. Cryst. Growth 282, 414 (2005).
21. H.L. Xu, W.Z. Wang, W. Zhu, J. Phys. Chem. B 110, 13829 (2006).
22. F. Luo, D. Wu, L. Gao, S. Lian, E. Wang, Z. Kang, Y. Lan, L. Xu, J. Cryst. Growth 285, 534 (2005).
23. Zhao, W.; Fu, W.; Yang, H.; Tian, C.; Li, M.; Li, Y.; Zhang, L.;Sui, Y.; Zhou, X.; Chen, H.; Zou, G. Cryst. Eng. Comm. 13, 2871 (2011).
24. B. Millet, C. Fiaud, C. Hinnen E. M. M. Sutter, Corrosion Science, 37, 1903 (1995).