Effect of deposition time on the properties of Cu_2O thin film electrodeposited on ITO substrates

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Abstract

In the last few years, the scientists have researched for sustainable, inexpensive, and efficient new materials for enhancing electrocatalytic activity and electronic energy conversion. All explored materials have provided novel and high electrical, electrochemical, magnetic and optical characteristics. Among them, cuprous oxide (Cu_2O) thin films grown by electrodeposition clearly fulfill the sustainability and the cost pre-requisites. Therefore, if they are well prepared and electrodeposited they could lead to the fabrication of highly efficient devices.

In this study, we investigate the effect of deposition time on the electrochemical, structural, morphological and optical properties of Cu_2O thin films. The Cu_2O thin films were electrochemically elaborated on ITO substrate into a reducing sulphatic bath under pH 11 by a chronoamperometric method at a potential of −0.50V versus SCE. Deposition time was varied from 1 to 10 min. The XRD analysis indicated that the synthesized Cu_2O thin films had a cubic phase with a preferred texture along (111) plane. In addition, no trace of CuO and Cu was observed. From AFM analysis, the thickness and the roughness of the thin films increase by increasing deposition time from 3 to 5 min. The surface of the deposits was become dense and compact when the deposition time increases. The optical properties of the as-deposited Cu_2O thin films revealed an optical transmission of about 75% in visible light region. The optical energy band gap was estimated from Tauc extrapolation; it was found that the band gap of Cu_2O thin films is 1.9-2.2 eV.

Keywords: Cu_2O thin film, deposition time, Electrodeposition.

Introduction

In the last few years, many researchers have been focused on development of novel, inexpensive and efficient electrode materials which have widespread applications in catalysis, chemical sensors and energy storage devices. In this respect, structured cuprous oxide (Cu_2O) thin films grown on a foreign substrate have aroused a lot of interest because of its interesting electrochemical, magnetic and optical characteristics. Cu_2O is p-type semiconductors material with a cubic crystallinity structure [1]. It has notable properties, non-toxicity, earth abundant, low-cost fabrication, direct band gap (1.9-2.2 eV) [2], and a relatively high absorption coefficient of

10^5 cm^{-1} in the visible region [3]. Cu_2O as absorber layer in solar cell can theoretically achieve a power conversion efficiency of around 20% [4].

There are many deposited techniques physics and chemical have been intensively focused on the synthesis of Cu_2O thin films, such as, thermal oxidation [5], chemical vapor deposition [6], sol-gel [7], reactive sputtering [8] and electrodeposition [9-11]. Among available techniques to develop Cu2O thin films with enhanced physicochemical proprieties, electrodeposition is popular owing of its several advantages compared to other methods. In fact, with different operating condition such as temperature, pH, current, voltage and time deposition, this method is likely to produce different kinds of with very different performances. This study reports the effect of deposition time on the electrochemical, structural, morphological and optical properties of Cu_2O thin films electrodeposited on ITO substrates.

Experimental

Cu_2O thin films were electrodeposited in an aqueous solution of 0.05 M copper sulfate ($CuSO_4$) and 0.05 M (citric acid) $C_6H_8O_7$; its pH was fixed to 11 using sodium hydroxide (NaOH). Electrochemical experiments were carried out in a conventional three-electrode cell using a VoltaLab 40 potentiostat/galvanostat controlled by a personal computer. The reference and counter electrodes were a saturated calomel electrode (SCE) and a platinum wire, respectively. The working electrode was polycrystalline indium doped tin oxide (ITO)-coated conducting glass substrates. The bath temperature was 60 °C at a potential of −0.50V versus SCE. Two samples were deposited at 3 and 5 min.

The substrates of ITO were cleaned ultrasonically in ethanol, acetone and distilletd water for 10 min. They were activated in 45% HNO_3 for 2 min and finally rinsed with distilled water prior the electrodeposition. After deposition all the samples were rinsed with water and dried with air.

Results and Discussion

Figure 1 shows the Cyclic voltammetry (CV) curves of ITO substrate in a solution containing 0.05 M copper sulfate and 0.05 M citric acid, while scan rate, pH and temperature, of the bath were maintained at values of 20 mV/s, 11 and 60 °C, respectively. The potential range is between -1.2 and +0.5 V vs. SCE.

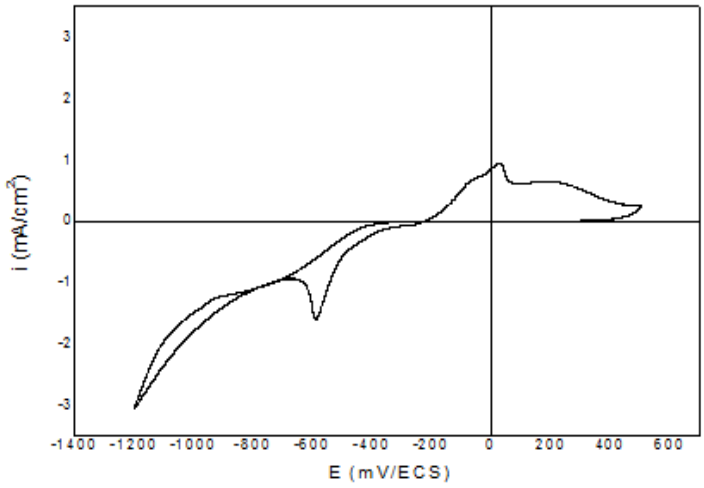

Figure 1: *Cyclic voltammogram recorded in a 0.05 M $CuSO_4$ aqueous solution with 0.05 M $C_6H_8O_7$ at 60 °C. Potential scan rate is 20 $mV.s^{-1}$.*

Two reduction reactions were observed due to the presence of Cu^{2+} ions in the electrolyte. The first reduction reaction was detected between -0.20 to -0.6 V vs. SCE which corresponds to the formation of Cu_2O by the following reactions [12]:

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

$$2Cu^+ + 2OH^- \rightarrow Cu_2O + H_2O \quad (2)$$

The second reduction reaction that occurred after -0.65 V attributes to the formation of metallic Cu by the following reaction [12]:

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

Figure 2 represents the current transient of Cu_2O thin films deposited at 0.50 V vs SCE for two deposition time 3 and 5 min.

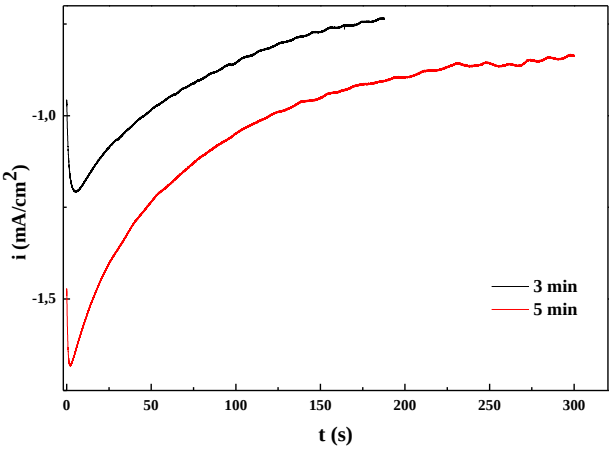

Figure 2: *Effect of deposition time on current density transient curves of Cu_2O electrodeposited on ITO at 60°C.*

The curves exhibit the same shape with three regions. In the first region, the current density increases until the current maximum, i_{max}, is reached at a time t_{max}, which is corresponding to the double-layer charging at the interface of ITO/electrolyte [13]. After the value of i_{max}, the cathodic current density began to decrease due to Cu2O thin films covers the surface. This process due to the nucleation and growth of copper oxide nuclei [13]. It can be clearly seen that the current density increases and the t_{max} become shorter with an increase in the time deposition. This could be due to that the cathodic potential resulted in the increase in electrolyte conductivity and accelerating the diffusion and the reduction of Cu^{2+} to Cu^+ for formed the cuprous oxide at the surface of ITO glass substrate. Finally, further increases to deposition time due a stabilization in the cathodic current density value due growth process of the Cu_2O thin film on the ITO substrate.

Surface morphology

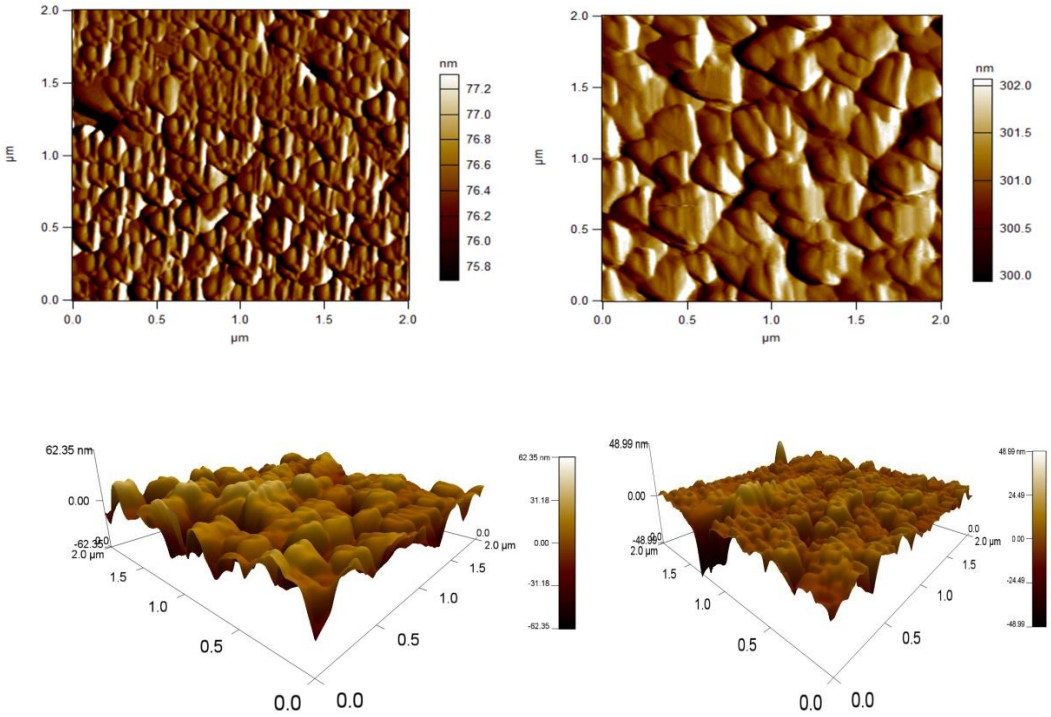

Figure 3: *2D and 3D AFM images of Cu_2O thin films deposited at different a) 3 min and b) 5 min. The bath pH is 11 and the bath temperature is 60°C.*

Structural characterization

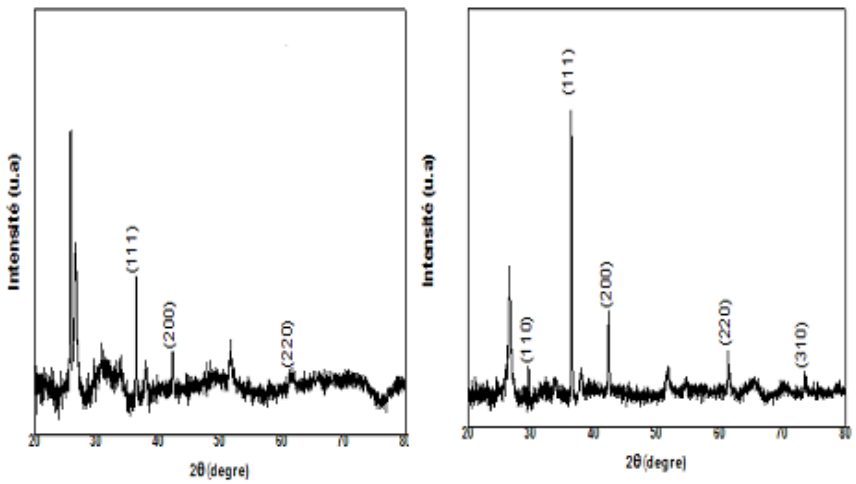

Figure 4: *XRD patterns for Cu_2O thin films electrodeposited at: a) -3 and b) 5 min. Asterisks denote diffraction peaks derived from the ITO substrate.*

Optical properties

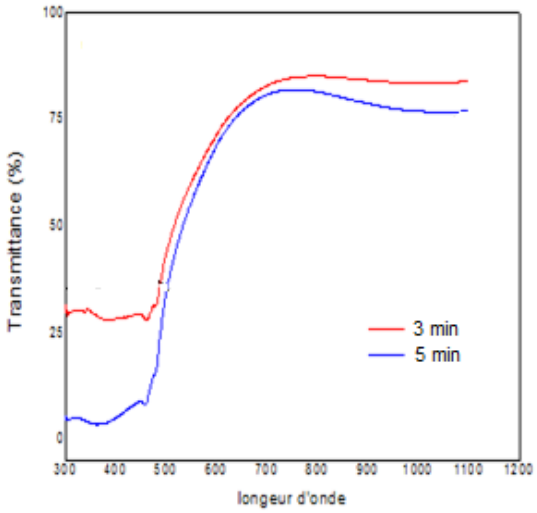

Figure 5: *UV–VIS transmittance spectra of electrodeposited Cu_2O/FTO films at tow deposition time.*

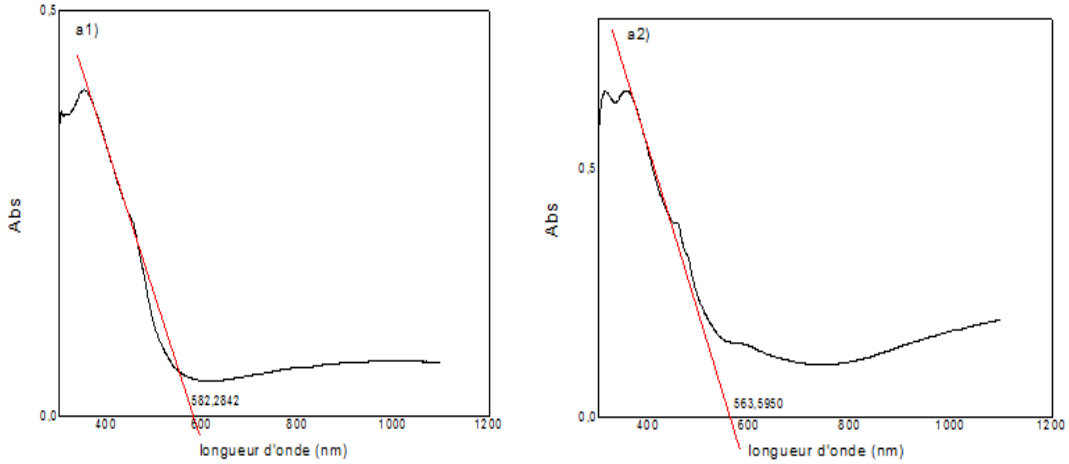

Figure 6: *Plots of $(\alpha hv)^2$ vs. (hv) for the electrodeposited Cu_2O thin films onto ITO substrates at tow deposition time.*

Conclusion

In this Work, effect of deposition time on the morphology, structural and optical properties of Cu_2O thin films on ITO surfaces from aqueous cupric sulfate bath has investigated. Cyclic voltammetry experiments were performed to elucidate the electrodic processes that occurred when potentials were applied and the optimum potential for electrodeposition were determined. The surface of the deposits was become dense and compact when the deposition time increases. The samples were characterized by XRD and the results clearly demonstrate that all the obtained film display a Cu_2O cubic structure with a strong preferential orientation of the (111) direction. In addition, no trace of CuO and Cu was observed. The optical transmission spectra in the UV-Visible domains indicate transmission values

greater than 75 % for all the deposited layer. And their calculated gap values increased from 1.9 to 2.2 eV, with increasing time.

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