SYNTHESIS AND CHARACTERIZATION OF ELECTRODEPOSITED Cu_2O THIN FILMS AT DIFFERENT pH ON FTO GLASS IN LACTATE MEDIUM

A.H.M.N.N. Bandara, V.P.S. Perera, G.K.R. Senadeera and K.N.D. Bandara
Department of Physics, Faculty of Natural Sciences, The Open University of Sri Lanka
Email: doneranji@gmail.com , vpper@ou.ac.lk , gksen@ou.ac.lk , knban@ou.ac.lk

ABSTRACT

In this study, nanostructured cuprous oxide thin films were synthesized by electrochemical deposition on FTO substrates in lactate bath (~60 °C) with different pH conditions. The investigations were focused on structural and surface morphological features of the film and their influence on electrical and wetting characteristics. SEM images exhibited micro-structured grain distribution with grain shapes diverted from compact, pallet to cubic nature with increasing pH of the bath and promising high sensitive films prepared at pH 10 and 10.5. Evidence in support of the explanation of these measurements was further verified by the contact angle measurements which revealed an increment from 73° to 103° with increasing pH indicating a reduction in wetting nature. According to the capacitance-voltage and spectral response analysis, the *p*-type conductive behaviour of Cu_2O resulted in pH 8.5-11 of the electrodeposition bath. Under stable atmospheric conditions, *p*-Cu_2O films electrodeposited at pH 10.5 exhibited the highest flat band potential of 2.64 eV and high conductivity due to enrich acceptor density of 6.61×10^{18} per cm^3.

KEYWORDS : cuprous oxide (Cu_2O), electrochemical deposition (ECD), lactate bath, surface morphology**,** fluorine doped tin oxide (FTO)

SYNTHESIS AND CHARACTERIZATION OF ELECTRODEPOSITED Cu_2O THIN FILMS AT DIFFERENT pH ON FTO GLASS IN LACTATE MEDIUM

INTRODUCTION

Cuprous oxide (Cu_2O) is a direct band gap semiconducting metal oxide that is environmentally benign and naturally abundant as a base material. Due to its advantageous characteristics of light absorption in visible regions, solar energy generation has attracted much attention in various applications as well as in studies on its material properties. Moreover, with ease and low fabrication cost, low processing temperature, higher deposition rates and controlled crystallization of large area thin films mark Cu_2O as a potential candidate for low-cost gas sensors, photoelectrochemical cells and catalytic applications. Past research works have shown the influence of crystal size of many semiconducting metal oxides such as Cu_2O being micro structured/nanostructured and crystal orientation could alter electronic properties, surface energies, physical and chemical properties that would open up new paths to surface engineering and novel applications (Jayatissa, 2009; Barreca, 2009; Shishiyanu, 2005; Siripala W. &., 1989). Further, it was also revealed that by changing deposition parameters or by introducing doping materials, it is possible to vary the film conductivity to *n* or *p*-type with high stability in air (Bandara A. H., 2022; Bandara K. N., 2017; Bandara K. N., 2018).

Currently, the synthesis of Cu_2O with different microstructures on different substrates have been carried out using various techniques such as thermal oxidation of copper sheets at 200°C and 1050°C (Musa, 1998), chemical vapour deposition on Alumina slides at 300°C (Barreca, 2009) and Magnetron DC sputtering on glass substrate at 693K (Dolai, 2017) etc. Among them, electrochemical deposition of Cu_2O has attracted much attention due to the advantage of controlled crystal growth under different deposition parameters as well as the low fabrication cost. Among these parameters, the supporting electrolyte and its concentration and pH, deposited substrate, potential/current density, deposition temperature and duration are crucial parameters that affect the surface morphology, roughness and wettability of Cu_2O films (Ehl, 1954). The fundamental surface structure and morphology of semiconductor metal oxide films such as Cu_2O defer according to their type of conductivity thereby changing the surface energy of the film.

However, using a copper sulphate solution in lactate medium, the influence of electrolyte bath pH on the Cu_2O crystal growth and surface characteristics have been rarely studied under low temperatures. This paper reports the success of using the electrodeposition technique to deposit Cu_2O thin films on FTO substrates at different pH values and conducted a detailed structural, morphological and wettability investigation of those Cu_2O films. In addition to that, the electrical characteristics of the above films were investigated by means of Mott-Schottky analysis.

EXPERIMENTAL

Fabrication and characterization of nanostructured Cu_2O films

Synthesis of Cu_2O thin films was carried out in a three-electrode electrochemical cell with an Ag/AgCl electrode as the reference electrode and platinum counter electrode. The working electrode was a FTO glass which was carefully washed with detergent and followed by distilled water, and finally surface treated with acetone and sonicated with distilled water to improve Cu_2O film adhesion. A surface area of ~ 1×1 cm^2 of the FTO was immersed in the

electrochemical cell containing aqueous solutions of 3.5 M lactic acid (Sigma–Aldrich, purity - 99.0%) and 0.45 M cupric sulphate $CuSO_4$ (Sigma–Aldrich, purity - 99.0%). The pH of the electrolyte was maintained at different pH levels by adding NaOH pallets directly. The temperature of the electrolyte was maintained constant at 60°C with continuous stirring throughout the deposition. The Cu_2O thin films were potentiostatically electrodeposited at -450 mV versus the Ag/AgCl reference electrode (Miremadi B.K., 1994) for a 45 min duration (Bandara K. D., 2018) to obtain optimum film thickness and surface morphology. After the deposition, films were again washed with distilled water and allowed to dry in air at room temperature. There are two steps involved in the electrodeposition of Cu_2O films. Due to the solubility limitation of Cu^+ in electrolyte, precipitation of Cu_2O is followed by the reduction of Cu^{2+} ions to Cu^+ ions as depicted in equation 1 and 2.

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

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

$$2Cu^{2+} + 2OH^- + 2e^- \leftrightarrow Cu_2O + H_2O$$

Surface structure and morphologies of prepared films were characterized using scanning electron micrographs (SEM, Zeiss EVO 15 LS) and the type of conductivity was verified using spectral response measurements and Motts-Schottky plots obtained with AUTOLAB Model PGSTAT 302 potentiostat/galvanostat using three-electrode electrochemical cell containing Cu_2O deposited FTO substrate as the working electrode, platinum counter electrode and Ag/AgCl as the reference electrode in 0.1 M NaAc electrolyte. Using the sessile drop method with double distilled water drops of 5 µl, surface tension was measured via contact angle measurements. While observing the water drop with a digital microscope (2MP 1000x 8 LED USB Digital Microscope Endoscope), the angle of contact was determined using both Image J software and virtual angle meter by drawing tangents to the splines constructed at the liquid-film interface. Droplets were settled on the film surface for 5 to 10 min and obtained an average contact angle for three separate drops on each sample surface.

RESULTS AND DISCUSSION

Surface morphological variation and film adhesive nature with pH

Average contact angles of Cu_2O thin films and bare FTO, after settling at normal atmospheric condition for a ~5 to 10 min duration, are shown in Table 1. The initial surface contact angles on the bare substrates of FTO glass were measured to be about 60° with hydrophobic nature.

The initial surface free energy of FTO has decreased with the pH of the electro deposition bath of Cu_2O resulting in an increasing non-wetting surface nature.

Table 1: Average contact angle variation of electrodeposited Cu_2O thin films grown on FTO with pH

pH 8.5	pH 9	pH 9.5	pH 10	pH 10.5	pH 11
73	78	86	89	100	103
					

Scanning electron micrographs of Cu_2O thin films deposited at pH 8.5-11 range are illustrated in Fig.1 with 1 µm magnification. The contact angle measurements are supported by the micrographs that depict distinguishable crystalline variation in compact cubic structures grown with low inter planar spacing and possible (111) orientation of Cu_2O phase. A unique pallet grain distribution in pH 8.5 can be observed which has changed to trapezium shapes and then to a consistent cubic distribution starting from pH 9.5. Small cubic crystal edges pointed upward enhance the adsorption rate of gaseous species with a moderate surface area to volume ratio and surface energy. It was observed that the sharpness of the crystal edges has reduced at higher pH values (>10.5).

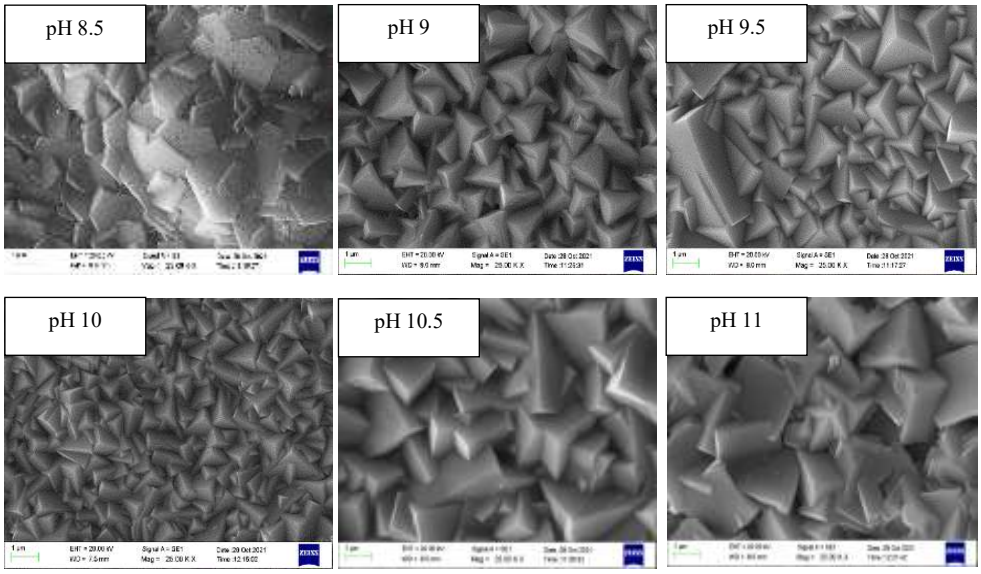

Figure 1: SEM morphological variations of electrodeposited Cu_2O thin films grown on FTO substrates using electrolytes with different pH values

pH and electrical characteristics

Semiconductor materials that perfectly abide by the Mott-Schottky plots can be characterized according to eq. 3 given below where, $C, e, \epsilon_0, \epsilon_r, N_D, A, V_{FB}, k$ and T are the space charge layer capacitance of the of the film at potential V, the electron charge (1.602×10^{-19} C), permittivity of the vacuum (8.854×10^{-12} F m^{-1}), the relative permittivity of Cu_2O *(Sawicka-Chudy, 2018)*, free carrier concentration of the semiconductor, flat band potential, Boltzmann constant and absolute temperature respectively.

$$\frac{1}{C^2} = \left(\frac{2}{e\epsilon_0\epsilon_r N_D A^2}\right)\left(V - V_{FB} - \frac{kT}{e}\right) \qquad (3)$$

The type of the conductivity can be determined by using the Mott-Schottky analysis. Fig. 2 depicts the Mott-Schottky plots observed for Cu_2O films grown with electrolytes having different pH values. As can be seen from the figure, the negative slope of the linear region confirmed that all the deposited Cu_2O films are *p*-type. The flat band potential (V_{FB}) and the free carrier concentration (N_D) (Hssi, 2020; Windisch Jr, 2000) have been calculated with the intercept and slope of equation 3, given by equations 4 and 5 respectively and estimated values are listed in Table 2. The valence band positions of all *p*-Cu_2O films deposited at different pH values are more positive than the reduction potential of H^+/H_2 (0V of NHE) (Wang, 2017). Among them, films grown at pH 10.5 showed the highest flat band value of 2.64 eV and acceptor density of 6.6104×10^{18} cm^{-3}.

$$V_{FB} = -\left(\frac{\text{intercept}}{\text{slope}} + \frac{kT}{e}\right) \quad (4)$$

$$N_D = \left(\frac{2}{e\epsilon_0\epsilon_r A^2\,(\text{slope})}\right) \quad (5)$$

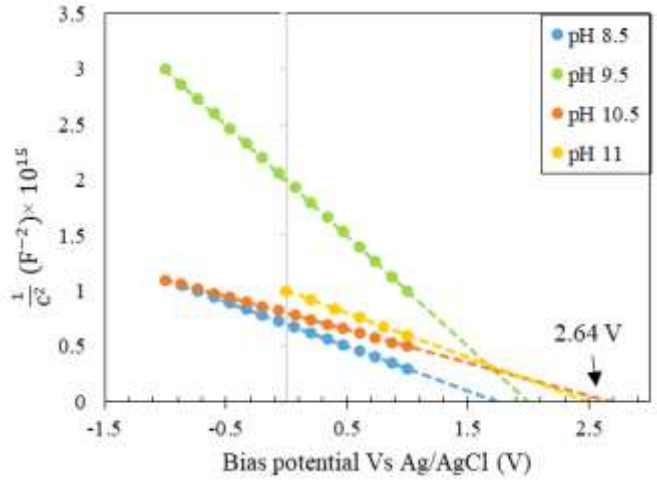

Figure 2: The linear regions of Mott-Schottky plots observed for p-Cu_2O thin films grown at pH 8.5, 9.5, 10.5 and 11 in lactate mediums on FTO

Table 2: Flat band potentials and carrier densities of different pH p-Cu_2O thin films deposited on FTO

pH	Carrier concentration (N_D) (10^{18}) cm^{-3}	Flat band potential (V_{FB}) eV
8.5	4.9578	1.7759
9.5	1.9831	2.0259
10.5	6.6104	2.6408
11	4.9578	1.0259

CONCLUSION

In conclusion, by electrochemical deposition, crystal morphologies of Cu_2O can be modulated in a lactate medium by changing the pH of the electrolyte. When increasing the pH of the solution, the micro-crystal structure of Cu_2O varies from homogeneous pallets to cubic nature providing moderate surface area and surface free energy which were compared with contact angle measurements. The surface carrier concentration recorded its highest at pH 10.5 for Cu_2O thin films deposited potentiostatically at - 450 mV with respect to Ag/AgCl reference electrode at constant temperature of 60 °C.

REFERENCES

Bandara, A. H. (2022). Substrate Effect on Liquid Petroleum Gas Sensors of Cuprous Oxide Thin Films Electrodeposited in Acetate Bath. *ECS Journal of Solid State Science and Technology*, 11(10), 107002.

Bandara, K. D. (2018). *Application of Electrodeposited Nano/Micro Structured Metal Oxide Thin Films for Liquefied Petroleum Gas Sensing.* Faculty of Science, University of Colombo.

Bandara, K. N. (2017). Surface properties of sulphur based surface modified n-Cu_2O thin films for enhanced liquefied petroleum gas sensing. *Journal of Physics D: Applied Physics*, 50(48), 485304.

Barreca, D. C. (2009). Chemical vapor deposition of copper oxide films and entangled quasi-1D nanoarchitectures as innovative gas sensors. *Sensors and Actuators B: Chemical*, 141(1), 270-275.

Dolai, S. D. (2017). Cuprous oxide (Cu_2O) thin films prepared by reactive dc sputtering technique. *Vacuum*, 141, 296-306.

Ehl, R. G. (1954). Faraday's electrochemical laws and the determination of equivalent weights. *Journal of Chemical Education*, 31(5), 226.

Hssi, A. A. (2020). Optical and dielectric properties of electrochemically deposited p-Cu_2O films. *Materials Research Express*, 7(1), 016424.

Jayatissa, A. H. (2009). Methane gas sensor application of cuprous oxide synthesized by thermal oxidation. *physica status solidi (a)*, 206(2), 332-337.

Miremadi B.K., S. R. (1994). Chromium oxide gas sensors for the detection of hydrogen, oxygen and nitrogen oxide. *Sensors and Actuators B: Chemical*, 21(1), pp.1-4.

Musa, A. O. (1998). Production of cuprous oxide, a solar cell material, by thermal oxidation and a study of its physical and electrical properties. *Solar Energy Materials and Solar Cells*, 51(3-4), 305-316.

Sawicka-Chudy, P. S.-W. (2018). Numerical analysis and optimization of Cu_2O/TiO_2, CuO/TiO_2, heterojunction solar cells using SCAPS. *Journal of Physics* (pp. Vol. 1033, No. 1, p. 012002). IOP Publishing.

Shishiyanu, S. T. (2005). Sensing characteristics of tin-doped ZnO thin films as NO_2 gas sensor. *Sensors and Actuators B: Chemical*, 107(1), 379-386.

Siripala, W. &. (1989). photoelectrochemical investigation of the n-and p-type semiconducting behaviour of copper (I) oxide films. *Semiconductor science and technology*, 4(6), 465.

Wang, P. Z. (2017). The fundamental role and mechanism of reduced graphene oxide in rGO/Pt-TiO_2 nanocomposite for high performance photocatalytic water splitting. *Applied Catalysis B: Environmental*, 207, 335-346.

Windisch Jr, C. F. (2000). Mott–Schottky analysis of thin ZnO films. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 18(4), 1677-1680.