Substrate Effect on the Structural and Morphological Variations of Electrodeposited Cuprous Oxide Thin films in Acetate Bath

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1. ABSTRACT

Cuprous oxide thin films were electrodeposited in acetate bath (~60 °C) using FTO, ITO, Ti and Cu as substrates to investigate their influence on surface morphology and wetting nature of the films. At the beginning of this study the effect of pH value of the electrodeposition bath on the conductivity type of Cu_2O films was investigated and identified that n-Cu_2O results in the pH range of 5.7-6.5 that confirmed by spectral response and capacitance-voltage measurements. In addition, XRD and SEM measurements were employed in characterization and observed to have unique properties such as network-like and tetrahedron morphologies of Cu_2O films on different substrates. Evidence in support of the explanation of these measurements was further elucidated by the observation of contact angle mesurements and their wetting nature. In comparison, all the experimental results directed toward the idea that substrates do have a major effect for optimization of interface properties of Cu_2O films to yield a better response in many applications of different fields.
Keywords : Cuprous oxide (Cu_2O), electrochemicaldeposition, Acetate bath, substrates, surface morphology.

2. INTRODUCTION

Among the semiconducting metal oxides available, cuprous oxide (Cu_2O) has been specially selected for most of the research work due to its advantageous characteristics including non-toxicity and the natural abundance of the base material. Currently, synthesis of Cu_2O with different microstructures is done by various techniques such as thermal oxidation, chemical vapor deposition, electrodeposition, sputtering, and anodic oxidation. Coupled with the ease and low cost of fabrication, electrodeposited Cu_2O thin films are highly suitable candidate for potential applications such as low-cost gas sensors, solar cell, photo- electrochemical cells and catalytic applications [1-6]. It also has several advantages over others, such as low processing temperature, higher deposition rates, and the ability to control the crystallization and engineering of large area of Cu_2O films. Specially, by changing deposition bath parameters and introducing doping materials, it has the ability to vary the conductivity type between n-type and p-type with high stability in air [7]. Substrate's influence in electrodeposition is one of the crucial parameters, affected on quality of surface morphology, roughness and wettability of Cu_2O films [8]. In this paper, we report the effect of electrodeposition technique in forming Cu_2O films on different substrates and have conducted a detailed structural, morphological and wettability investigation of Cu_2O films.

3. EXPERIMENTAL DETAILS

Titanium (Ti) plates, fluorine-doped tin oxide (FTO) pre-deposited glass substrates, ITO coated glass substrates and thin Cu plates were used as the substrates for electrodeposition of n-Cu_2O thin films. Prior to the deposition, the Ti substrates were cleaned with detergent, dilute nitric acid (HNO_3), acetone and finally rinsed with distilled water. The ITO and FTO glass substrates were cleaned in an acetone bath and sonicated with distilled water. The Cu substrate (99.999%) was carefully polished with 1500, 2000 and 2500 sandpapers respectively and rinsed with acetone and finally with distilled water. During the electrodeposition, an area of ~ 1×1 cm^2 of the substrate was dipped in the electrolyte solution.

3.1 Fabrication of n-Cu_2O Thin Films

The electrochemical deposition of n-Cu_2O was conducted in an aqueous electrolyte solution consisting of a mixture of 0.1 M sodium acetate (Sigma–Aldrich, purity - 99.0%) and 0.01 M cupric acetate (Sigma–Aldrich, purity - 99.0%). The deposition bath was brought to the required pH levels by adding diluted NaOH or HCl, while limiting the pH range within 5.7-6.5 [12] to minimize precipitation during electrodeposition. In this study, pH 6 is used to deposit the films for characterization. Deposition time was varied as required while the temperature of the electrolyte maintained at 60°C with continuous stirring.
The n-Cu_2O thin films were potentiostatically electrodeposited in an acetate bath at -200 mV versus the reference electrode in a three-electrode electrochemical cell (with an Ag/AgCl electrode as the reference electrode and platinum plate as the counter electrode) for 60 min durations [12]. Selection of the potentiostatic condition and deposition time period depends on the substrates' characteristics as well. This procedure was carried out separately for FTO, ITO, Ti and Cu substrates acting as working electrodes. After deposition, films were thoroughly cleaned with distilled water and allowed to dry in air.

3.2 Thin Film Characterization

The conductivity of deposited Cu_2O films was verified using spectral response measurements and Motts-Schottky plots. The phase of cuprous oxide and the average crystal size were monitored using the X-ray diffractrometry (XRD) (Regaku Ultima–IV) with Cu-Kα (λ=1.5418 Å) as the source of X- rays. The surface morphology studies of deposited Cu_2O thin films were observed by using a Scanning Electron Microscope (SEM) (Zeiss EVO 15 LS).
Contact angle measurements were made using the sessile drop method with double distilled water. (Parts of 5 µl) Contacting surface was observed through a digital microscope (2MP 1000x 8 LED USB Digital Microscope Endoscope) and the angle of contact was determined using both Image J software and a direct method which uses a virtual angle meter and drawing a tangent to the splines constructed at the liquid and film interface. Droplets were allowed to settle on the film surface for ~10 min before

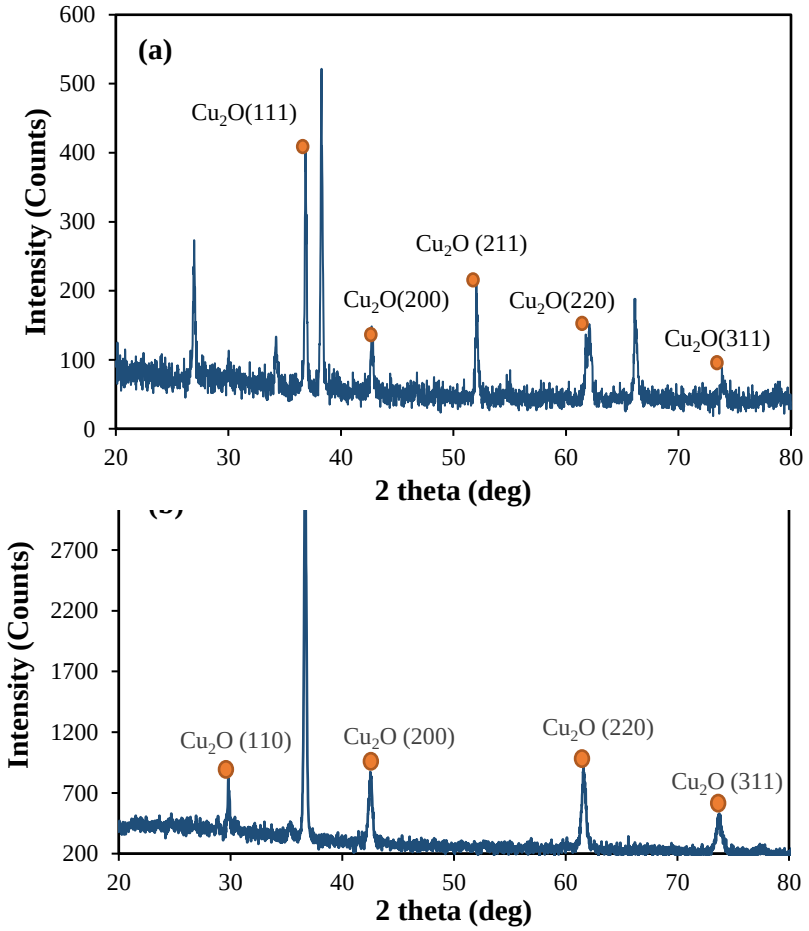
measurements and obtained an average contact angle for three separate drops on each sample surface.

4. RESULTS AND DISCUSSION

4.1 X-ray Diffraction (XRD) Measurements

The Figure 1a-d shows the XRD spectra of the n-Cu_2O (pH 6) films deposited in the acetate bath containing 0.1M sodium acetate and 0.01M cupric acetate with the deposition time of 45-60 min depending on the substrate.

It can be clearly seen in Figure 1 that the sharp peaks corresponding to crystalline planes of (110), (111), (200), (220), (311) and (222) matched well with standard Cu_2O data (JCPDS card PDF file no. 05-0667). For the n-Cu_2O thin film deposited on FTO [13-14], ITO and Ti substrates the (111) is a prominent peak; so that the crystallographic phase of the as-deposited films could be indexed to Cu_2O majorly with the cubic structure. In Figure 1(c) there are no other significant peaks observed except for the diffraction peaks of Cu_2O and Ti substrate, which means the existence of single-phase Cu_2O. For the Cu substrates there's a major presence of plane (311); which might be implying that the film is consisting of polycrystalline Cu_2O. The other significant peaks observed in each XRD spectra correspond to the diffraction peaks of the substrates.



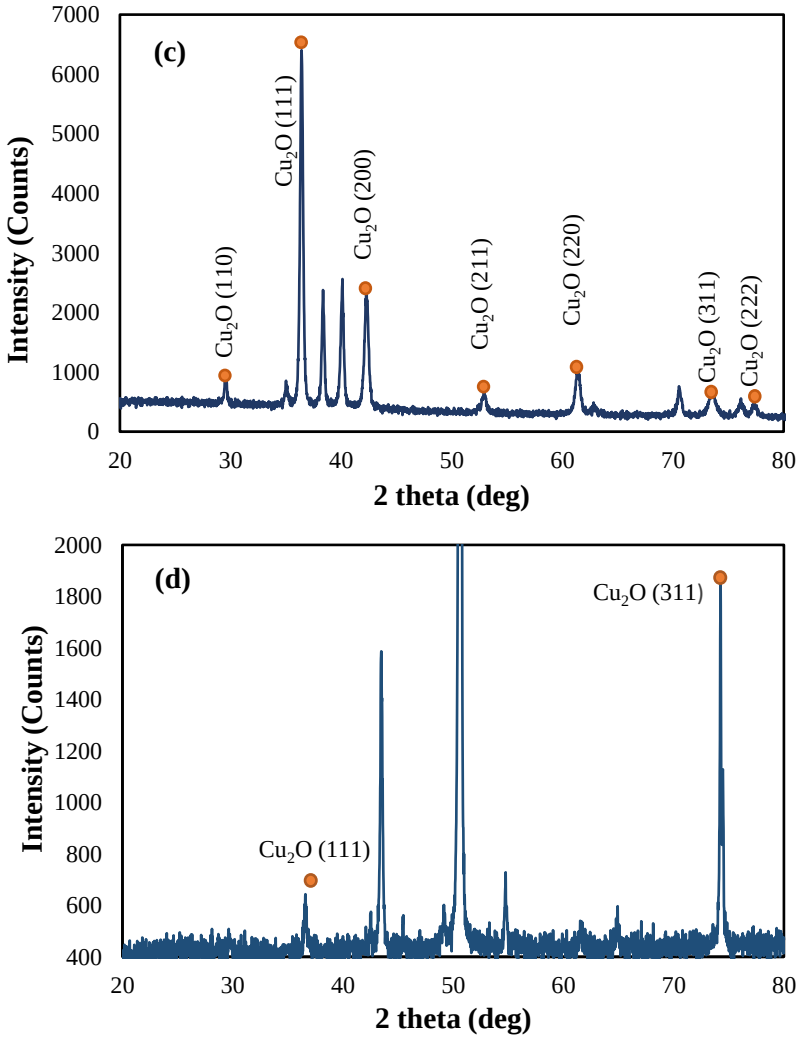


Figure 1: X-ray diffraction (XRD) spectra of *n*-Cu_2O thin films electrodeposited on (a) FTO (b) ITO (c) Ti (d) Cu substrates at pH 6 in an acetate bath.

SEM images of these *n*-Cu_2O thin films shown in the Figure 2 further confirm the polycrystalline nature depicted by the planes observed in the above figures. According to Table 1 and the XRD patterns, it is understood that the films are polycrystalline with high orientation along the (111) and (200) planes.

Table 1: XRD peak intensities of Cu_2O thin films deposited on different substrates

crystalline plane	Peak Intensity			
	FTO	ITO	Ti	Cu
110	-	822.5	992.5	-
111	714	3335	6402.5	643.333
200	539	872.5	2400	575
211	387	-	770	-
220	182	932.5	1115	540
311	459	522.5	720	1848.33
222	-	-	495	-

4.2 Surface Morphology and Compositional Analysis

The Figures 2a-d show the SEM images of n- Cu_2O thin films deposited for a duration of 45 minutes which was reported to deposit the optimum film thickness [11]. It was observed that a network like porous structure is predominant in Cu_2O film deposited on FTO and ITO substrates as shown in Figure 2(a)-(b). The film structure on FTO is inhomogeneous due to grains with slightly different peak intensities as observed in Figure 1(a). This also agrees with the availability of the prominent peak (111) as there can be seen a visible distribution of cubical shapes among the porous structure.

In ITO, this porous formation distributes consistently through the film than in FTO. The porosity of the film surface in ITO contains pinholes for almost 20% of its' surface area. The growth on ITO has a noticeable smooth and widely spread layer, given that less contact surface than in FTO. With the (111) planes being the most dominant state, the cubic crystal structures on Ti are compact, pinhole free and the grain sizes of crystallites are reduced. As it is evident in Figure 1(d), on Cu substrates, the Cu_2O film can be confirmed to be small polycrystalline grains.

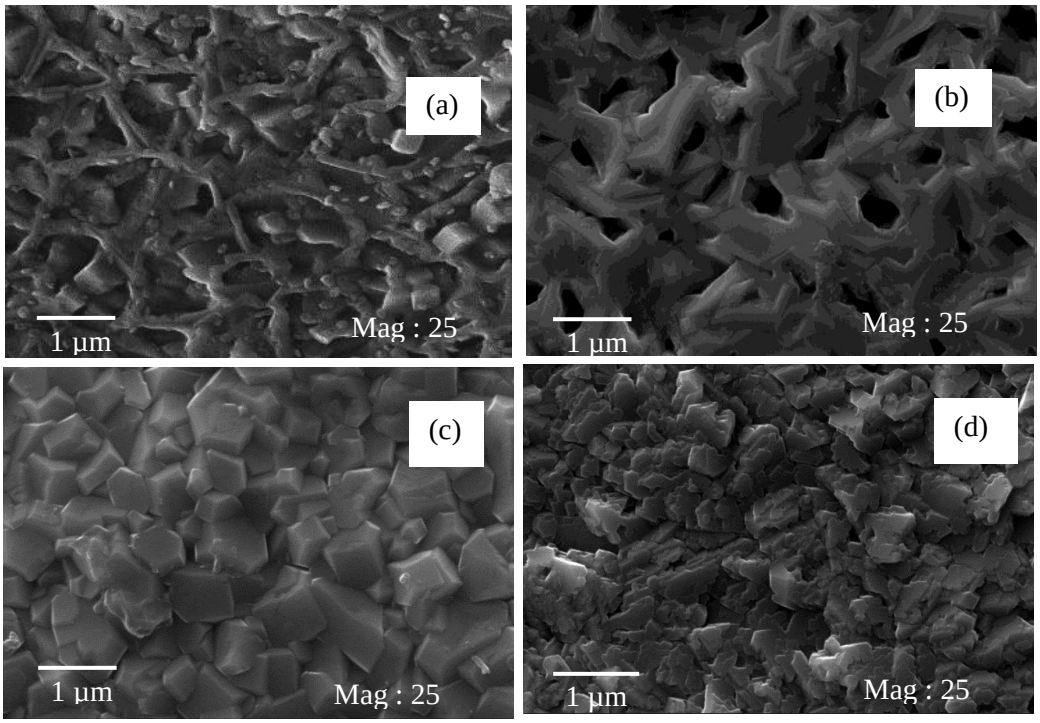


Figure 2: SEM morphological variations of electrodeposited n-Cu_2O thin films grown on (a) FTO (b) ITO (c) Ti and (d) Cu substrates at pH 6 in Acetate bath

As it can be seen in the SEM images, each substrate has unique grain distribution and visible roughness variations. This significant difference in grain size which affect the surface energy of the thin films is the reason for the differences in contact angle and surface wetting behavior observed later in Figure 3(d).

4.3 Surface Wettability through Contact Angle Measurements

Contact angle measurements was made using the sessile drop method with double distilled water for the fabricated *n*-Cu_2O thin films deposited under different deposition parameters. Figure 3 (a-d) represent the average contact angle measurements of three separate drops both left and right sides of the droplet placed on each substrate.

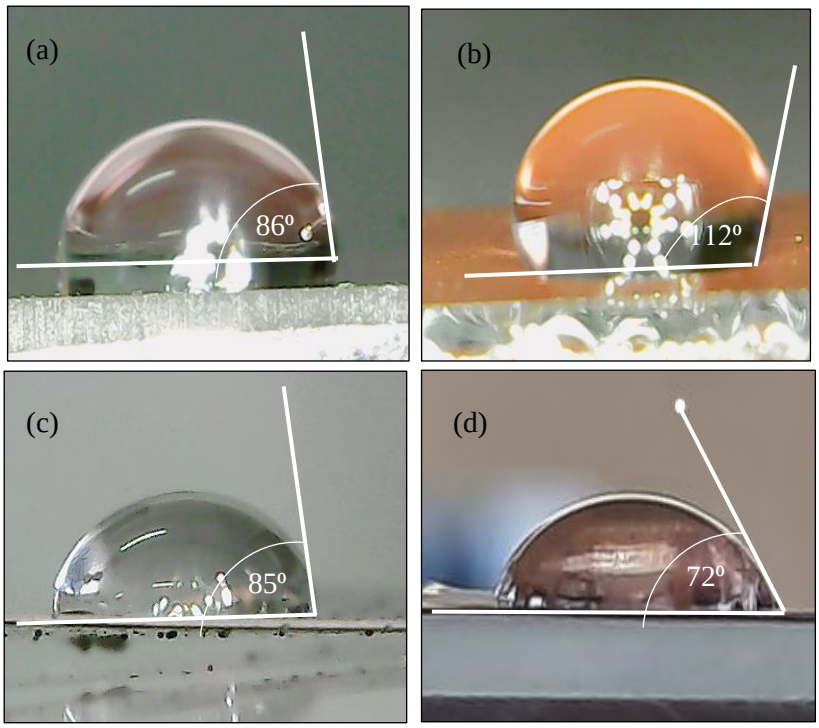


Figure 3: Average contact angle variations of electrodeposited n-Cu_2O thin films grown on FTO (b) ITO (c) Ti and (d) Cu substrates at pH 6 in Acetate bath

The average contact angles measured for *n*-Cu_2O thin films in FTO, Ti and Cu substrates have shown the probability of stable partially wetting behaviors with contact angles which abide by the findings of former studies [9].

According to Figure 3(b), with and average contact angle of 112^0, *n*-Cu_2O films deposited on ITO tends to have non-wetting nature. By measuring the wettability of each Cu_2O thin film deposited in different substrates, it could be identified that only FTO, Ti and Cu substrates have the ability to being introduced to gaseous content and retrieve its original state due to their partially wetting nature.

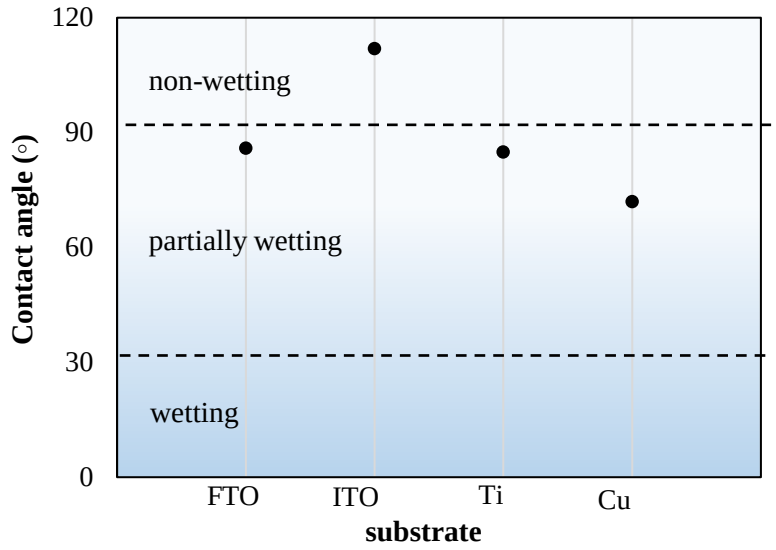


Figure 4: Wetting nature of *n*-Cu_2O thin films deposited on FTO, ITO, Ti and Cu substrates in acetate bath

5. CONCLUSION

In summary, it was revealed that, by electrodeposition, crystal morphologies of Cu_2O can be modulated in cupric acetate system on different substrates. With the variation of deposited substrate, the morphologies of Cu_2O change from compact to network-like shapes. Changing the substrate affects the grain size and the structure as well. It ultimately creates a platform for introducing gaseous content and change the behavior accordingly to its wetting nature.

The study reveals the possibility to optimize the fabrication process of Cu_2O in acetate bath depending on the substrate, which could be useful in forming the perfect combination of nano structured Cu_2O thin films for various fields such as gas sensing and solar cells.

6. REFERENECES

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