

SYNTHESIS OF Cu₂O VIA ELECTRODEPOSITION WITH VARYING DEPOSITION TIMES

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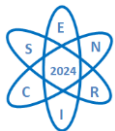
ABSTRACT

This study explores the synthesis of Cu₂O thin films via electrodeposition with varying deposition times, aiming to investigate how such parameter impacts the morphology, crystallinity, and optical properties of the films. The films were characterized using grazing incidence X-ray diffraction (GIXRD), UV-Vis spectroscopy and scanning electron microscopy (SEM). GIXRD results confirmed the presence of the Cu₂O phase, with increased deposition times leading to enhanced crystallinity. UV-Vis analysis revealed bandgap values ranging between 1.91 eV and 2.05 eV, depending on the deposition time. The SEM images showed the evolution of the film morphology from small granular particles at 60 seconds to large cubic structures above 1000 seconds. The findings demonstrate that while longer deposition times promote crystal growth, they can also result in particle aggregation. Relating the results to performance could aid in utilizing the Cu₂O films as photoelectrode materials for water splitting applications and hydrogen production, which will be the subject of future studies.

1. INTRODUCTION

Copper (I) oxide (Cu₂O) is a semiconductor material that has attracted considerable interest due to its diverse range of applications in fields such as photocatalysis [1–3], energy storage [4,5], photovoltaics [6–8], and gas sensing [9]. With a direct band gap of approximately 2.0 to 2.2 eV [10–12], Cu₂O is especially promising for renewable energy technologies, such as photoelectrochemical (PEC) water splitting and hydrogen production, given its ability to absorb visible light. Furthermore, Cu₂O is abundant, non-toxic, and cost-effective, making it an attractive alternative to more expensive materials like titanium dioxide or metal sulfides in several industrial processes [13–15]. However, the performance of Cu₂O-based devices is highly dependent on its structural, morphological, and electrochemical properties, which are in turn influenced by the synthesis method and parameters used during fabrication [11, 15–19].

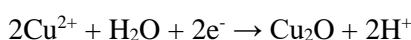
Among various synthesis methods, electrodeposition has gained popularity due to its simplicity, scalability, and ability to precisely control the material's properties by adjusting parameters such as potential, electrolyte composition, and deposition time. Electrodeposition is a versatile technique that offers several advantages over chemical and physical deposition methods, including low cost, high control over film thickness, and the possibility of tuning the material's properties by varying the deposition conditions [9, 18, 20–22]. Notably, one critical factor that directly affects the quality and performance of Cu₂O thin films is the electrodeposition time. By controlling the deposition time, one can influence the thickness, grain size, and crystal



orientation of the Cu_2O layer, which in turn impacts its electronic and catalytic properties [21, 23].

In the context of Cu_2O synthesis, the effect of varying deposition times has been the subject of numerous investigations [24], tailoring the material's microstructure and surface characteristics. Shorter deposition times typically result in thinner films with smaller grain sizes, which may be beneficial for certain applications, such as gas sensing, where increased surface area is desired. In contrast, longer deposition times tend to produce thicker films with larger grains, potentially enhancing charge carrier transport and reducing recombination losses, which is advantageous for photovoltaic and PEC applications [24, 25]. Moreover, the duration of electrodeposition can influence the stoichiometry of the Cu_2O layer, as well as the formation of secondary phases, such as copper (II) oxide (CuO), particularly in longer deposition processes where the electrolyte composition may change over time.

While previous studies have reported on the influence of electrodeposition conditions on Cu_2O synthesis [19–22,26], there remains a need for studies of how deposition time alone affects the overall properties of the material, with the aim of optimizing their performance for applications in energy conversion and storage devices. Electrodeposition is an electrochemical process in which a metal or compound is deposited onto a conductive substrate by reducing metal ions in a solution. In the case of Cu_2O , the process typically involves the reduction of cupric ions (Cu^{2+}) to copper(I) oxide (Cu_2O) in an alkaline electrolyte. The overall reaction [27] can be expressed as:

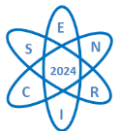


During electrodeposition, the deposition potential is carefully controlled to ensure that Cu_2O , rather than metallic copper or CuO , is formed. The selection of the deposition potential, along with other parameters such as electrolyte composition and pH, can greatly affect the nucleation and growth mechanisms of Cu_2O [11, 19]. However, deposition time remains one of the most critical factors influencing film thickness, morphology, and crystallinity [24, 25].

As the deposition time increases, the amount of Cu_2O deposited onto the substrate also increases, leading to thicker films. Shorter deposition times may not provide sufficient time for large grain growth, resulting in smaller, more uniform grains. In contrast, extended deposition times often promote the formation of larger grains, potentially enhancing the material's charge transport properties due to fewer grain boundaries, which can act as recombination centers for charge carriers [24, 25]. Additionally, longer deposition times may lead to changes in the surface morphology, such as the formation of rougher or more porous films [25], which can be beneficial for applications requiring high surface area.

In addition to its effects on film thickness and grain size, deposition time can influence the crystallinity and phase purity of Cu_2O films. For example, longer deposition times may promote the formation of secondary phases, such as CuO , which can negatively impact the material's performance in photovoltaic or PEC devices due to its narrower band gap and poor electrical conductivity compared to Cu_2O [2, 4, 21]. Therefore, careful optimization of the deposition time is required to balance the need for sufficient film thickness with the avoidance of undesirable secondary phases.

This study investigates the synthesis of Cu_2O films via electrodeposition, focusing on the effect of varying deposition times on the material's structural, morphological, crystallinity, and optical properties. By analyzing how deposition time influences these properties, the research aims to



optimize Cu₂O film performance for energy conversion and storage applications. While previous studies have explored the influence of electrodeposition conditions on Cu₂O synthesis [19–22,26], there remains a need for an examination of how deposition time alone impacts the overall behavior of the material. The findings will provide valuable insights for improving the efficiency of Cu₂O-based devices and offer guidelines for optimizing the electrodeposition process in future research.

2. METHODOLOGY

In this work, Cu₂O films were synthesized by electrodeposition using FTO conductive glass as the working electrode, platinum as the counter electrode, and Ag/AgCl as the reference electrode. The electrodeposition solution was prepared with 0.2M CuSO₄ and 3M lactic acid in distilled water [19,20,31]. A 6M NaOH solution was used to adjust the pH to 12. During the electrodeposition process, a current density of -1.2 mA/cm² was applied, and the electrodeposition time was varied in the following intervals: 60 s, 300 s, 600 s, 1080 s, 1260 s, and 2430 s.

The crystalline nature of the samples was analyzed by Grazing Incidence X-ray Diffraction (GIXRD) using a Rigaku Ultima IV instrument with a copper tube (Cu-Kα1 = 1.5406 Å and Cu-Kα2 = 1.5416 Å) with an applied voltage of 40 kV and a current of 40 mA. Diffraction patterns were obtained using a fixed angle of 0.1°, 2θ ranging from 25° to 120°, a step size of 0.02°, and a scan speed of 0.53°/min for data acquisition.

To estimate the bandgap energy of the produced films, UV-Vis measurements were carried out. From the obtained spectrum, the material's transmittance as a function of photon energy was determined. The classic Kubelka-Munk model was then applied [32]. Using the calculated F(R) values for different photon energies, (hν×F(R))² was plotted as a function of E (Energy). By extrapolating the linear portion of this curve, the numerical value of the bandgap (E_g) for direct transitions was obtained, corresponding to the intersection of the fitted line with the x-axis.

The morphology of the films was studied using Scanning Electron Microscopy (SEM) with a Hitachi FlexSEM 1000 instrument, operating at 15 kV, with a focus ranging from 5.6 mm to 5.8 mm, a magnification of 13,000×, and a secondary electron (SE) detector.

3. RESULTS

A global analysis of the results indicates that the longer the electrodeposition time, the thicker the films become, with more crystalline material present in the sample. This can be evaluated by the increase in counts at each 2θ angle in the GIXRD, as shown in Fig. 1. However, films with more than 1000 seconds of deposition time exhibit similar count values, suggesting that increasing the deposition time beyond this point does not significantly affect the amount of crystalline material. Relating this result to the SEM images reveals that the amount of agglomeration in the film does not correspond to an increase in the crystalline material within the sample. This is reflected in the results of Table 1, which presents the crystallographic phases, bandgap, and particle sizes, and in Fig. 2, which compares the 300 s and 2430 s films at a magnification of 2,000x, showing the agglomeration growths. It is notable that particle sizes generally increase as deposition time increases, except in the film with 2430 seconds of deposition, where the sizes range from 435 nm to 490 nm, and these particles are covered by large, undefined agglomerates.

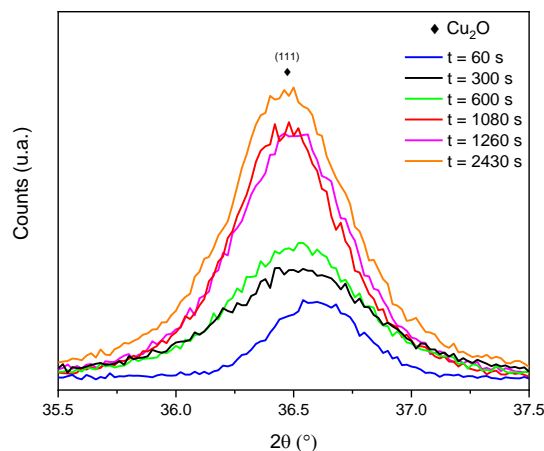


Fig. 1. GIXRD of the samples comparing the variety of the counts at the (111) plane of Cu_2O .

Tab. 1. Analysis of the films produced.

Deposition time (s)	Crystallographic Phases	Band Gap (eV)	Particle size (nm)
60	Cu_2O Cu SnO_2 (substrate)	2.05	153 – 464
300	Cu_2O	1.99	278 – 400
600	Cu_2O	1.91	228 – 386
1080	Cu_2O	2.05	600 – 847
1260	Cu_2O	1.99	435 – 806
2430	Cu_2O	2.00	419 – 490

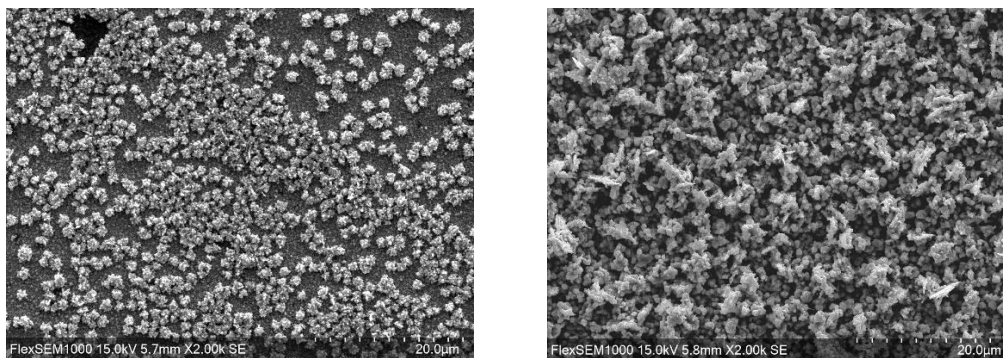


Fig. 2. SEM images, from left to right, correspond to the samples with $t = 300$ s, and $t = 2430$ s, respectively, in 2,000x magnifications.

The morphological and crystallographic properties of the Cu_2O thin films were found to vary significantly with the deposition time, as shown in the SEM and GIXRD analysis. The Fig. 3 presents the GIXRD patterns of the films. The diffraction peaks correspond to the cuprous oxide phase (Joint Committee on Powder Diffraction Standards - JCPDS File # 78-2076), with prominent reflections at 2θ values of 29.57° , 36.43° , 42.31° , 61.38° , 73.52° , and 77.38° , corresponding to the (110), (111), (200), (220), (311), and (222) crystal planes, respectively. Only the sample with 60 seconds of deposition exhibited a diffraction peak at 43.28° , attributed to metallic copper (JCPDS File # 85-1326) alongside Cu_2O . The increased deposition time influenced both the intensity and sharpness of the peaks, indicating enhanced crystallinity and grain size as the deposition time increased.

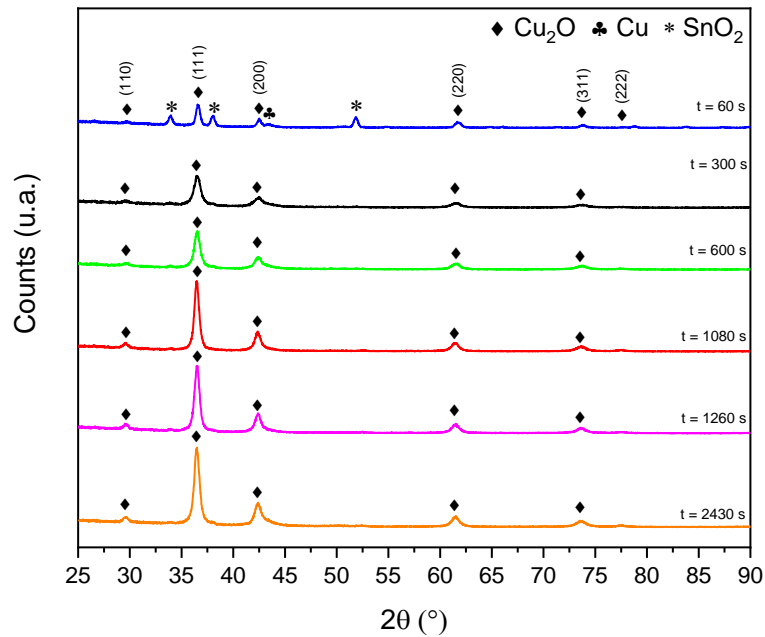
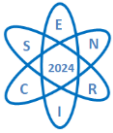


Fig. 3. X-ray diffraction patterns of the samples.

The UV-Vis results (Fig. 4) show the bandgap energy variations as a function of deposition time. The films deposited for 60 seconds and 1080 seconds exhibited a bandgap of approximately 2.05 eV, while films deposited for 300, 600, and 1260 seconds showed slightly lower bandgap values, ranging from 1.91 eV to 1.99 eV. For the longest deposition time (2430 seconds), the bandgap stabilized around 2.00 eV, near the theoretical value [10–12]. The founded values are similar to others in the literature [10,22,32,33].

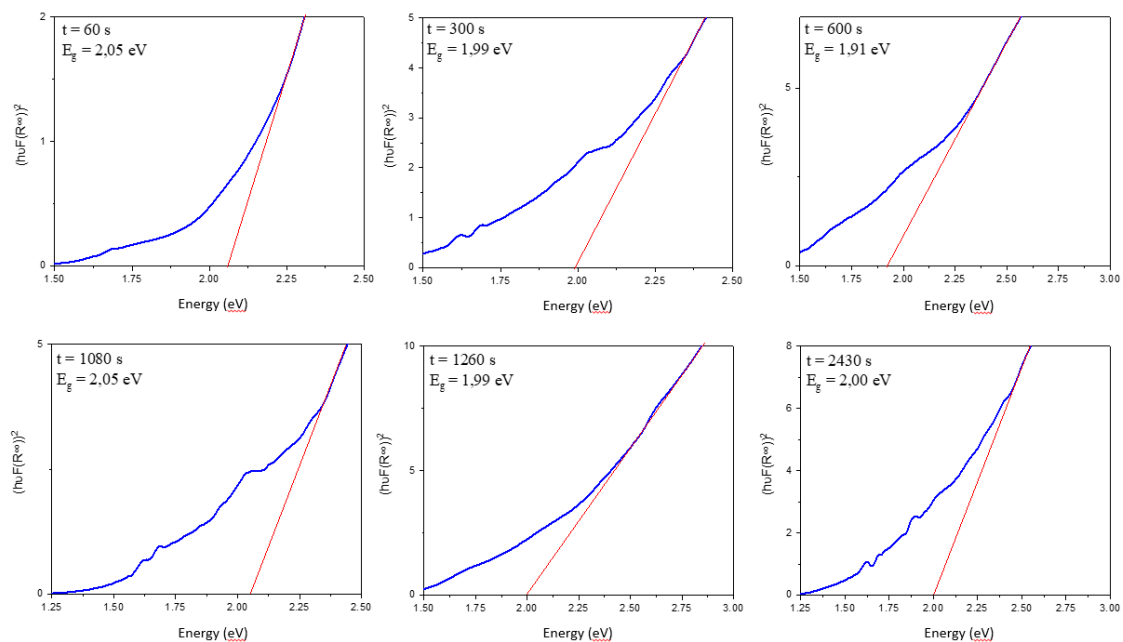


Fig. 4. UV-Vis measurements of the samples analyzed by Kubelka-Munk method

The SEM analysis (Fig. 5) further revealed the morphological evolution of the films with varying deposition times. At 60 seconds, the film displayed small, granular particles, indicative of the early stages of nucleation with particles from 153 nm to 464 nm. With increasing deposition time, the particles became larger and more faceted, transitioning from disordered granular morphology to well-defined cubic structures. The largest grains, with sizes up to 847 nm, were observed in the sample deposited for 1080 seconds. However, prolonged deposition led to increased particle aggregation and revealed a small number of particles with sizes ranging from 419 nm to 490 nm, reducing the uniformity of the film. The progression in crystal size (Tab. 1) from 60 seconds to 2430 seconds clearly indicates that longer deposition times promote crystal growth, although excessive deposition times can result in the verticalization of the agglomerations.

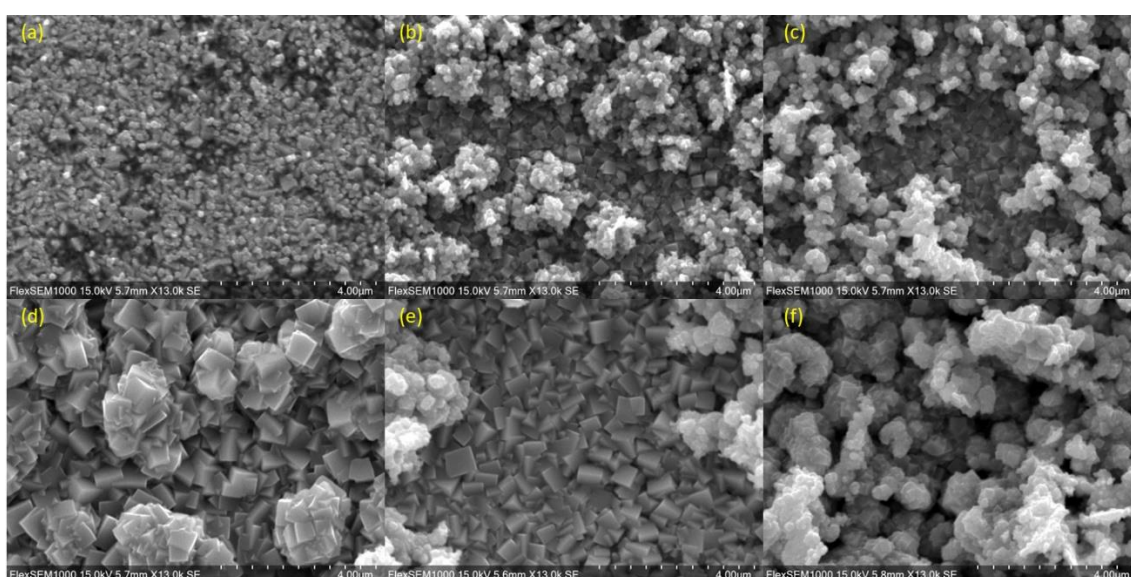


Fig. 5. SEM images of the samples synthesized with depositions times of (a) $t = 60$ s, (b) $t = 300$ s, (c) $t = 600$ s, (d) $t = 1080$ s, (e) $t = 1260$ s, and (f) $t = 2430$ s.

4. CONCLUSIONS

The effects of varying electrodeposition times on the synthesis of Cu_2O thin films were analyzed. The results demonstrated that shorter deposition times (60 seconds) led to smaller, more granular particles, while intermediate deposition times (600-1260 seconds) yielded more uniform and well-defined cubic crystals. However, prolonged deposition times (2430 seconds) resulted in the formation of large particle aggregates, which diminished the uniformity of the film. The bandgap energy, which ranged from 1.91 eV to 2.05 eV, was influenced by the morphology and thickness of the films, with more expected value (2.00 eV) observed for depositions times 300 s, 1260 s and 2430 s. Overall, this study highlights the importance of optimizing deposition time to achieve Cu_2O films with desirable structural and optical properties, making them suitable for applications in photoelectrochemical and optoelectronic devices.

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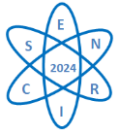
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