# Preparation and characterization of copper thin films using

# electrochemical deposition

Thair.KH. Salih<sup>1</sup>, Hamed.H. Murbat<sup>2</sup>, Sabri.J. Mohammed<sup>3</sup>

- <sup>1</sup> Samarra university
- <sup>2</sup> Baghdad university
- 3. Tikrit university

<u>thairphy@uosamarra.edu.iq</u>

\* thairphy@uosamarra.edu.iq

**Abstract:** In this research, copper films were prepared. The thickness of the prepared films increased with decreasing deposition time, acid function, and deposition current, reaching 140.6, 258.2, and 372.7 for samples ACuITO, BCuITO, and CCuITO, respectively. The results of the cyclic voltage (CV) measurements obtained indicated that the reduction voltage increased from -0.158 to -0.221 over a period of time from 5 to 15 minutes, and the oxidation voltage also increased from -0.175 to -0.227, while the oxidation current decreased from 0.147 to 0.0234 amps. The reduction current increased from -0.0256 to -0.0401. The results of current density to voltage indicated that current density increases with increasing voltage, reaching its highest value at 700 millivolts, reaching 3.7 milliamperes per square centimeter. The results of the Hall effect showed that the type of deposited films was (-RH, n-type) and the electrical conductivity of the prepared films was 7x10-3, 2.20x10-2, and 5.15x10-2 ( $\Omega$  cm)-1 for samples ACuITO, BCuITO, and CCuITO, respectively.

**Keywords:** Copper, atomic force microscopy (AFM), electrochemical deposition (ECD) Introduction:

### 1. Introduction

Electrochemical deposition (ECD) as a liquid phase deposition method to prepare thin films of semiconductors and metals on conductive substrates, due to its good ability to control the growth rate by controlling various deposition parameters and production volume, has received much attention. has attracted In addition, it is relatively easy to fabricate and the fabrication temperature is reasonably lower than many other methods. It can be deposited into complex shapes and produced on a large scale with economical and environmentally friendly processing [1], it can also be processed into a variety of materials including polymers, metals and even ceramics. Electrochemical strategies offer important advantages and unique possibilities in the development of nanomaterials and nanostructures. On the other hand, with ECD, solar cell efficiency is generally lower compared to a method that requires a more expensive gas-phase device. However, this is offset by lower operating costs. The ECD mechanism mainly involves the interaction between the ions supplied by the electrolyte solution and the surface of the working electrode (substrate). An applied external potential/current can control deposition. Therefore, electrical energy is used to cause a chemical change. Figure 1(a) shows the ECD technique using a three-electrode cell and voltage regulator/galvanostat, with a working electrode as the cathode, a counter electrode as the anode, and a reference electrode. Various types of reference electrodes have been previously reported, such as mercury/mercury chloride, silver/silver chloride, hydrogen/palladium, etc.



**Copyright:** © 2024 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). electrode (the electrode deposition area is  $1 \times 1$  cm as shown in Figure 1.1(b)), and the other electrode was copper. The current resulting from the electrochemical reaction in the working electrode is balanced by the current flowing in the opposite direction in the counter electrode. The reference electrode provides a constant potential to the working electrode. Conversely, the counter electrode changes the ionic conductivity in the electrolyte to electronic conductivity through an electrochemical reaction.

#### 2. Materials and Methods

The Materials and Methods should be described with sufficient details to allow others to replicate and build on the published results. Please note that the publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

Research manuscripts reporting large datasets that are deposited in a publicly available database should specify where the data have been deposited and provide the relevant accession numbers. If the accession numbers have not yet been obtained at the time of submission, please state that they will be provided during review. They must be provided prior to publication.

Interventionary studies involving animals or humans, and other studies that require ethical approval, must list the authority that provided approval and the corresponding ethical approval code.



Figure 1 (a) Schematic of an electrochemical cell consisting of three electrodes. (b) A mask placed on the base for thin film deposition.

However, the disadvantages of electrochemical deposition include the low quality of deposited films and sometimes long-term instability. Also, this technology requires a conductive substrate and is expensive. Most thin films prepared by ECD are amorphous at room temperature. We can classify ECD techniques based on the specific externally applied current or potential on the substrate into three different deposition classes: at a constant voltage (constant voltage), at a constant current density (galvanostatic), and using periodic pulse potentials ( two or two) three-phase bias). In the case of pulsed deposition, potential values and duration of each voltage step

play an important role in controlling the properties of deposition layers. The structural, morphological and optical properties of the fabricated films strongly depend on ECD parameters such as electrolyte concentration, base, solution pH, temperature, applied current density/potential, etc. 2-3]. Below we explain some parameters:

· Concentration of the electrolyte solution

The electrolyte solution acts as a source of ionic species. Reactions occur and these ionic species tend to precipitate on the substrate by applying a current or potential to the thin film developing system. By adjusting different concentrations of chemicals, we have different concentrations of ionic species available, and as a result, the properties of the produced films are affected, especially in terms of composition.

## Preparation of copper thin films

Copper films were prepared on bases of tin oxide doped with indimium using an electrochemical cell as shown in the diagram shown in Figure (2) and as follows:

1- The paint system consists of the following main parts:

- Pure copper electrode (from the German company Merck, purity 99.99).
- An electrode made of indimium tin oxide (ITO) (Sikma Company, high purity) deposited on glass bases.
- Power supply type (potentiostat/galvanostat HA-301) with a range of (0-30 volts)
- Glass coating cell, as shown in Figure (3).

2- The plating solution consists of adding 0.005 M aqueous copper sulphate CuSO<sub>4</sub>.  $5H_2O$ , 25 mM sodium sulphate CH<sub>3</sub>CooNa, and 2 ml sodium lactate (59%) to 100 ml of aqueous solution as a pH buffer [5,6]. Experiments were conducted for three groups under the same conditions of fixed concentrations, temperature R.T, and voltage of 10 volts, and the current passing through the three prepared groups was as follows:

□ For the first group, the exposure time was 1 minute and the passing current was 0.08 amperes.

 $\Box$  For the second group, the exposure time was 0.5 minutes and the passing current was 0.07 amperes.

 $\Box$  For the third group, the exposure time was 0.25 minutes and the passing current was 0.06 amperes.

That is, the current was decreasing with time, as the current depends on the residence time in the electrolyte solution (paint solution). As shown in Table 1.



Figure (2) represents a diagram of a bipolar electrochemical cel Table 1 shows the deposition variables and thickness of the prepared films

Thickness of	Acid function	Time	Deposition	Supply	sample name
the prepared	PH	deposition	current	voltage	
film		Minute		volt	
nm					
140.6	4.1	1	0.08	10	ACuITO
258.2	3.2	0.5	0.07	10	BCuITO
372.7	2.5	0.25	0.06	10	CCuITO

#### **Thickness Measurements**

There are several methods to measure the thickness of thin films, including the Fizeaume method, which was used to measure the thickness of thin copper films. Figure (3) shows the system diagram for this method, as this system measures the thickness of films deposited on a glass base. The system consists of a (He-Ne laser) with a power of 1000 milliwatts and a wavelength of 632.8 nanometers. A beam expander has also been used to expand the width of the laser beam. The samples are placed on a stand at an angle of 300 degrees to the path of the laser beam, where the beam reflects off the surface of the thin film and falls on the beam (screen) placed at a distance of 1.5 meters, where diffraction fringes appear on the screen. The distance between one hem and another is measured and the thickness is calculated based on the following equation:





Figure 4Comparison of cyclic voltage test (CV) scheme for copper deposited on ITO glass substrate at (5, 10 and 15) min from 0.3125 M CuSO4.

ITEM	E red.	Eox.	OCP	Oxide	Reduction
	(V)	(V)	(V)	current	current
				(Amp)	(Amp)

5 min.	-0.158	-0.175	-0.197	0.0147	-0.0256
10 min.	-0.219	-0.209	-0.162	0.0214	-0.0312
15 min.	-0.221	-0.223	-0.092	0.0234	-0.0401

#### 3. Results



 Figure 5 shows X-ray diffraction diagrams for copper films prepared by chemical deposition method.

• Figure 5 shows the X-ray diffraction diagram of samples prepared from copper films deposited on bases of tin oxide doped with indimium ITO at deposition times (1, 0.5, and 0.25) minutes and pH (4.1, 3.2, 2.5). Among the results of Cubic, as for the SnO peaks at 2θ (35.2 and 36.7),

which correspond to levels (102) and (200), and the phase was hexagonal, according to reference (98-016-2148), as for the InSnO peaks, they were at the corners (20.95, 59.85), which correspond to Levels (1-11) and (125) and the phase is rhombic, according to the reference (98-018-1283)]. This indicates that nanocopper films have been successfully prepared [7,8]. Table 3 shows the values of crystal size, density of dislocations, and crystal stress, in addition to the width of the peaks, noting that these values were calculated from equations (2-2, 2-3, and 2-4).

In order to investigate the crystal lattice information and crystal size of copper films prepared under variable conditions of deposition time and acid function. Of these diffraction patterns shown in Figure 6, there were two copper peaks (98-005-3758) and two tin peaks (98-016-2148), in addition to two tin and indium oxide peaks (98-018-1283). Intensity plotted against 20. The crystal size is calculated by the Scherer equation, the crystal dislocation, which is one of the lattice parameters, and the lattice stress is calculated by the Williamson-Smallman equation, as in Table 3.

Table-3 X-ray diffraction variables for prepared copper films

Crystallographic	ACuITO	BCuITO	CCuITO
Parameters			

20	37.1	36.6	36.25
d <sub>hkl</sub>	1.9517	1.8827	1.8703
FWHM	0.3273	0.3167	0.3054
Dislocation $\delta$ (lin/m <sup>2</sup> )	1.1x10 <sup>15</sup>	9.8x10 <sup>14</sup>	9.29x10 <sup>14</sup>
Lattice strain ε (%)	0.00429	0.00409	0.004
Crystallite size D (nm)	30	31	32

We note from Table 3 that crystallinity decreased with a decrease in the deposition time and the acid function, as the crystal size increased from 30 to 32 nm. The reason can be attributed to the increase in thickness reducing the stresses on the copper atoms, in addition to the decrease in the acid function, which increased the grain size and thus increased crystallization [9]. We also note from Table 4-3 that the density of dislocations decreased from 1.1 x 1015 lin/m2 to 9.29 x 1014, while the mesh stress decreased from 0.00429% to 0.004%. The reason can be attributed to the increase in the crystalline size of the prepared films. These results are consistent with the researcher's findings (Nguyen et al., 2022) [10]).

### Atomic force microscope examinations (AFM measurement).

Figure 6 shows three-dimensional AFM images of copper films deposited electrochemically on indium-doped tin oxide bases and deposited on glass substrates. Table 4 shows the values of particle size distribution, surface roughness, and RMS for copper membranes. We notice that the particle size distribution decreases from 0.127 nanometers to 0.090 nanometers as the current, time, and acidity of the prepared membranes decrease. Figure 7 - The distribution of the granular size on the surface of the membrane (columns) is distributed, where we notice a gradient in the distribution from the highest to the smallest, with a similarity in the distribution for the three samples. Figure 9 shows a Gauss diagram of the granules on the surface of the membrane, where we notice a high homogeneity in distribution and similarity of the patterns for the three prepared samples. We also notice from Table 4 that the roughness and the average free radical increase as the deposition current, acidity, and deposition time decrease, as the roughness increased from 35.369 nanometers to 66.074 nanometers, while the average free radical increased from 44.261 nanometers to 81.236 nanometers. These results coincide with the results of the researcher (Wei et al., 2016) [11]) in the same direction.



Figure 6 Atomic force





Figure 7- Column diagram of the surface distribution of particles on the surface of the prepared membrane



Figure 8- represents the Gaussian distribution of particles on the surface of the prepared membrane

Table 4 represents the parameters of the atomic force microscope images of the prepared samples

Name of samples	Average of grain size	Roughness nm	RMS nm
	distribution nm		
ACuITO	0.127	35.569	44.261
BCulTO	0.096	52.386	67.519
CCuITO	0.0903	66.074	81.236

**SEM measurement** 

The SEM image of the electroplated copper nanoparticles is shown in Figure 9. It contains spherical shaped copper nanoparticles with significant aggregation and agglomeration in all the prepared samples. In order to produce coating with spherical shape and small particle size. This study demonstrates the feasibility of producing high-performance copper thin films using a copper sulfate solution-based copper plating solution. The SEM image at different magnifications in microns shows four images of each sample (1, 2, 10, 50) microns for each sample. The particle size of copper and the oxide formed with it for the prepared samples was (88.14, 85.66. 84.285 nm) for the samples (ACUITO, BCUITO, CCUITO), respectively. The crystal diameter distribution was analyzed by precisely extracted size measurements using ImageJ software according to the scale shown in the SEM image. Hence, the maximum number of particles lies in the range of 84.285 – 88.14 nm. According to Figure 10, it can be seen that there is almost uniform uniformity, and the shapes of the particles are between circular and agglomerated, noting that the agglomerations

are few, which indicates the quality and uniformity of the coating. These results are consistent with the researcher's findings (Mohra et al., 2016) [12]



Figure 9, electron microscope images of the prepared samples, with four images for each sample, (a) for the ACUITO sample, (b) for the BCUITO sample, (c) for the CCUITO sample.

#### Conclusion:

Thin copper films were deposited under different operating conditions of deposition time, acidity, and current at constant voltage. The results indicated that the best sample was at operating conditions of deposition time of 0.25 minutes, acidity of 2.5, and deposition current of 0.06 amperes. The highest thickness we obtained in this sample was 172.2 nanometers. It showed. Results of Atomic Force Microscopy (AFM): The average particle size on the surface of the prepared films decreased from 0.172 to 0.0903 nm with a decrease in the deposition time, acid function, and deposition current, while the roughness increased from 35.569 to 66.074 nm. The electron microscopy results showed that the particle size of the prepared films decreased from 88.14 to 84.285 nm with a decrease in the deposition time, acid function, and deposition current. The shape of the particles obtained was between circular and agglomerated, with the observation that the agglomerates were few. The results of EDX scattering Targeted for preparing copper films.

#### **References** :

[1] Lee, J., & Tak, Y. (1999). Electrochemical Deposition of a Single Phase of Pure Cu2 O Films by Current Modulation Methods. *Electrochemical and Solid-State Letters*, *3*(2), 69.

[2] Keikhaei, M. (2020). Electrochemical Deposition of Copper-based Oxide Thin Films for Optoelectronics Applications.

[3] S. Cheng, Y. He, and G. Chen, Mater. Chem. Phys. 110 (2008) 449-453.

[4] Sahu, S. N., & Sanchez, C. (1992). Preparation of Fe x S y thin films by an electrodeposition technique. *Journal of Materials Science Letters*, *11*, 1540-1542.

[5]. Collins, D., Luxton, T., Kumar, N., Shah, S., Walker, V. K., & Shah, V. (2012). Assessing the impact of copper and zinc oxide nanoparticles on soil: a field study.

[6] Lam, N.H.; Le, N.; Kim, E.S.; Tamboli, M.S.; Tamboli, A.M.; Truong, N.T.N.; Jung, J.H. Powder X-ray diffraction analysis of Cu/Cu2O nanocomposites synthesized by colloidal solution method. Korean J. Chem. Eng. 2022. [CrossRef]

[7] Madusanka, L. W. P. M., Pitigala, P. K. D. D. P., Fernando, C. A. N., & Karunarathna, P. G. D. C. K. (2023). Fabrication

of Copper (I) Oxide (Cu2O) thin films on Transparent Conductive glass substrate. In *Proceedings of the Technical Sessions* (Vol. 39, pp. 46-53).

[8] Lam, N. H., Smith, R. P., Le, N., Thuy, C. T. T., Tamboli, M. S., Tamboli, A. M., ... & Jung, J. H. (2022). Evaluation of the structural deviation of Cu/Cu2O nanocomposite using the X-ray diffraction analysis methods. *Crystals*, *12*(4), 566.

[9] Wei, C., Wu, G., Yang, S., & Liu, Q. (2016). Electrochemical deposition of layered copper thin films based on the diffusion limited aggregation. *Scientific Reports*, 6(1), 34779.

[10] Mohra, D., Benhaliliba, M., Serin, M., Khelladi, M. R., Lahmar, H., & Azizi, A. (2016). The investigation of electrodeposited Cu2O/ITO layers by chronocoulometry process: effect of electrical potential. *Journal of Semiconductors*, *37*(10), 103001.

[11] Puzer, D. B., Nkrumah, I., Ampong, F. K., Paal, M., Botchway, E. A., Nkum, R. K., & Boakye, F. (2021). Copper-tinsulphide (CTS) thin films, obtained by a two-electrode electrochemical deposition of metal precursors, followed by soft annealing and sulfurization. *Chalcogenide Letters*, *18*(8).

[12] Rahman, A. S., Islam, M. A., & Shorowordi, K. M. (2015). Electrodeposition and characterization of copper oxide thin films for solar cell applications. *Procedia Engineering*, *105*, 679-685.

[13] Kremmer, K., Yezerska, O., Schreiber, G., Masimov, M., Klemm, V., Schneider, M., & Rafaja, D. (2007). Interplay between the deposition mode and microstructure in electrochemically deposited Cu thin films. *Thin Solid Films*, *515*(17), 6698-6706.

[14] Abaas, R. A., Salim, E. T., & Mahdi, R. O. (2023). A sight of view on hydrothermal synthesis of copper oxide. *Engineering* and Technology Journal, 41(4), 592-602