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Study Of The Mechanical Properties of Cu Thin Films Deposited on SnO₂

By:

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Before the jury composed of:

Khaled MILOUDI	President	MAA	University of El-Oued
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SUJET DE LE MEMOIRE

Etude Des Propriétés Mécanique des Couches De Cu Déposée Sur SnO_2

Par:

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Abstract

The objective of this work is to study, on a tin oxide substrates , the effect of annealing treatment on electrodeposited copper. Both the microstructure and surface morphology (texture) of the coating were investigated. This deposit is obtained from baths of sulfated electroplating Watts. The copper coating is deposited at a temperature of 50 °C. The characterization has been carried out by X-ray diffraction, scanning electron microscopy, microhardness measurements, and FTIR. Vickers microhardness was used to characterize the mechanical properties of the electrodeposited Cu. The results showed the effects of the annealing treatment on the copper, the surface morphology, and the hardness of the deposited layer. However, there was not an effect of annealing treatment on texture of the layers.

Keywords: SnO₂; Copper; annealing; electrodeposition; hardness; XRD.

ملخص

الهدف من هذا العمل هو دراسة تأثير معالجة التلدين على النحاس المترسب كهربائيا على ركائز أكسيد القصدير. تم فحص كل من البنية المجهرية والتشكل السطحي (نسيج) للطلاء. يتم الحصول على هذه الرواسب من حمامات الواط المطلي بالكهرباء. يتم ترسيب طلاء النحاس عند درجة حرارة 50 درجة مئوية. تم إجراء التوصيف عن طريق حيود الأشعة السينية والمسح المجهر الإلكتروني وقياسات الصلابة الدقيقة والاشعة تحت الحمراء. تم استخدام صلابة فيكرز الدقيقة لتوصيف الخواص الميكانيكية لوحدة الترسيب الكهربائية. أوضحت النتائج تأثير معالجة التلدين على النحاس وتشكل السطح وصلابة الطبقة المترسبة. ومع ذلك، لم يكن هناك تأثير لمعاملة التلدين على نسيج الطبقات.

الكلمات المفتاحية: أكسيد القصدير؛ نحاس؛ التلدين؛ ترسيب كهربائي؛ صلابة؛ حيود الأشعة السينية.

First thanks to ***ALLAH*** for his grace
and for this help to let me completing
Our memory.

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DEDICATION

To my Life and

Sweet heart

My Daughter

“MARAM “

Gherbi Aicha

DEDICATION

*To All my family
Especially
my husband & my
dear children*

MESTAFAOUI Nafissa

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INTRODUCTION

Chapter 1

INTRODUCTION

According to general experience in materials science, metals can exhibit qualities that the parent metal cannot obtain. This is especially true for electrodeposited metals. Some important properties of the material, such as hardness, ductility, and tensile strength, may be enhanced. At the same time, it can also obtain some characteristics that the base material does not have, such as high permeability, other magnetoelectric characteristics, and amorphous structure. In some cases, metal coatings may be more suitable for subsequent electroplating and conversion chemical treatments [1].

Compared with metallurgical processes, certain metals may be easier to obtain by electrodeposition. This is especially true for metals that vary greatly in melting temperature or cannot be mixed in a liquid state. These metals can usually be co-deposited from solution (for example, metals Ag, Ni, Co, Cu, and Cd). Considering that some metals cannot be deposited from aqueous solutions (Ti, V, W, Nb, Zr, etc.), they can be deposited from their salt melts. Recently, the process of depositing metals and alloys from molten salts at room temperature has been researched and developed (Al-Cu, Al-Co, Al-Ni alloys are deposited from AlCl_3 -Me Et Im Cl melts). In the last century, the rapid growth of modern industry's demand for materials with special qualities has aroused interest in alloy electrodeposition, especially in corrosion protection and modern electronics industries. [1].

Historically, alloy plating is actually as old as pure metal plating because the plating of brass and bronze was performed by De Ruolz [2] in 1842 shortly after the discovery of the first cyanide bath. Interestingly, these baths are similar to the baths used today, and are based on the use of Cu, Sn and Zn complexes with cyanide.

From 1842 to the end of the 19th century, more than 180 alloys involving 40 elements have been deposited [3]. Brenner's work [4] provides an excellent review of achievements before 1962, and from a practical point of view, it is recommended to consider Bondar, Grimina and Pavlov (Pavlov)'s work [5], which contains recipes and references for the following: More than 1,100 baths for alloy deposition.

Although the first batch of alloys [2] were deposited in 1842, it was actually the first attempt to use scientific methods to electrodeposit the alloys, discussing the role of cathode potential in the deposition of brass, but with Spitzer [6] The work in 1905 came quite late. In 1914, Schloctter [7] made a more comprehensive attempt, but by understanding some fields such as electrochemical thermodynamics and kinetics and complex measurement, a better understanding of the alloy deposition process in order to obtain a clear scientific basis, waiting Second half of the nineteenth century.

Goals and objectives

Finding a new and highly efficient nano-material or crystalline thin film technologies that promise a bright future for photovoltaic energy is the main objective of this work.

The various semiconductor materials used are SnO_2 , TiO_2 , and ZnO . However, Tin oxide (SnO_2) is a favorite semiconductor among researchers for the possibility of utilizing it in different applications like gas sensors, light emitting diodes, lasers, thin film transistors, solar cells and photo catalytic degradation [8,9]. Besides, SnO_2 is a unique material that can be synthesized in several nanostructures with extraordinary physical properties by using appropriate physical or chemical techniques [10,11]. Thus, the special characteristics of SnO_2 motivated us to work on it. Further, though the thin film form of SnO_2 can be obtained by several fabrication techniques (sputtering, thermal evaporation, sol-gel, spray pyrolysis, laser ablation, etc.), we picked spray pyrolysis since it offers numerous advantages: simple exploratory setup, reproducibility, cost and time effective [12].

The final purpose of our present work is to utilise prepared thin films of copper by electrodeposition before and after annealing treatment on substrates of tin oxide.

In this work, we discuss the importance annealing treatment for the deposition of Cu thin films by electrodeposition, on their structural, morphological, optical and photocatalytic characteristics. X-ray diffraction, UV-Vis absorption, FT-IR spectroscopy, mechanical proprieties by Vickers hardness testing and scanning electron microscopy (SEM), were used for physical and chemical characterizations.

This memory is organized as follows:

- The first chapter “**Introduction**”: we present general introduction about this work.
- The second chapter “**Background and Literature Review**”: we present a bibliographic search exclusively directed to the study of the properties (structural, of SnO₂ and Cu in all its forms and some applications.
- The third chapter “**Characterization Of Cu Thin Films Prepared By Electro-deposition On Substrates Of SnO₂** we present firstly the description utilize the prepared thin films of copper before and after annealing treatment. Secondly for this, we have characterized the microstructure and optics of our layers by different techniques: scanning electron microscopy (SEM), and X-ray diffraction (DRX) to obtain information on the directions of crystallographic growth, a spectrophotometer (UV-Visible) to obtain information on the absorbance of the deposited layers, and Micro-hardness of ours layers.
- The fourth chapter “**Conclusion and Future Works**”: we present general conclusion about this work.

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Chapter 2 Background and Literature

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Chapter 2 Background and Literature Review

This chapter presents the fundamental physical properties of Transparent Conducting Oxides materials with their applications, tin dioxide and copper characteristics.

2 TCO_s

Transparent conducting oxides (TCO) constitute a unique class of materials, which combine two physical properties together; high optical transparency and high electrical conductivity. Studies of transparent and conducting semiconducting oxide films have attracted the attention of many research workers due to their wide range of applications. Such as solar cells and gas sensors [1].

TCOs have been known for nearly a century. Indeed, the first TCO film, cadmium oxide, was synthesized and characterized as early as 1907 [2]. The first TCO patents for undoped and doped tin oxide (SnO₂) films were filed respectively in 1931 and 1942. Such films were employed as aircraft windshield deicers in World War II. The following decades saw the development of In₂O₃ and ZnO-based TCO_s. It included indium-tin oxide (ITO) and the first Al-doped ZnO films, which was reported in the same year (1971) as the first ZnO-based varistor. Since that time, there has been steady improvement in the deposition and properties of SnO₂, In₂O₃, and ZnO-based films [1].

Transparent conductive oxides, such as Sn-doped In₂O₃ (indium-doped tin oxide, ITO), Al-doped ZnO (AZO), Sb-doped SnO₂ (ATO) and F-doped SnO₂ (FTO), have unique characteristics of combining optics. Transparent in visible light region with metallic conductivity (colorless state) [3].

TCO is a semiconductor with a wide band energy gap (≥ 3 eV) that provides optical transparency. It also has quasi-free electrons in its wide conduction band characteristics; free electrons give metallic conductivity. These are either from defects in the material or from extrinsic dopants introduced into the electron donor center below the edge of the conduction band.

In the past thirty to forty years, the main doped TCO has been based on tin oxide (SnO₂), indium oxide (In₂O₃) and zinc oxide (ZnO) [4].

2.1 Applications of TCOs

Due to its light-emitting properties, TCO film has been widely used as a transparent conductive film material in various fields, such as solar cells, flat panel displays, smart windows, touch screens, [5] optoelectronic devices, hot mirrors, liquid crystal displays (LCD), Organic Light Emitting Diode (OLED) and Gas Sensor [6], ... etc. (Fig.2.1).



Fig.2 .1 Some applications of TCOs [4].

2.2 Thin layers

A thin film is a layer of material with a thickness ranging from an atomic layer to a few microns. They are ubiquitous in the modern world and can be found in multiple applications such as mirrors, cutting tools [15], glasses, microelectronics, window glass, and solar cells [16]. It is of great significance for a wide variety of industrial applications that can meet the very wide range of requirements for specific industrial or scientific applications.

Although thin film technology has made significant progress. However, some important applications are wear-resistant, corrosion-resistant and anti-corrosion coatings; the choice of a specific thin film deposition technique can be based on a variety of considerations.

Thin films of many different materials can be deposited for many applications; therefore, there is no general guideline on what the most suitable deposition technique should be. Several criteria must be considered when selecting the appropriate deposition technique for a specific application [15].

Generally, when it is necessary to enhance or change the characteristics of an object's surface (usually called a substrate) by adding or changing its function in some way, a film is used.

It is clear that the current activity around thin films technologies is likely to continue seeing more innovation in the near future as showing in the Fig. 2. 4:

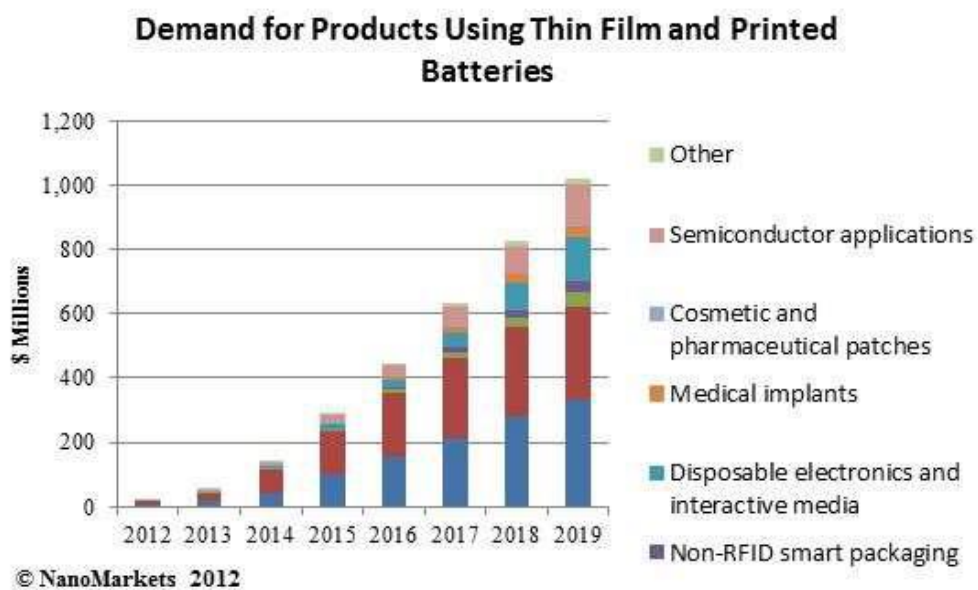


Fig.2.4 The demand for products using thin films and printed batteries[4].

2.2.1 Thin film deposition

Thin films can be deposited by a variety of methods, such as forming a liquid, for example using electrochemistry, or from steam. Vapor deposition methods are roughly divided into two categories, chemical vapor deposition (CVD) and physical vapor deposition (PVD), although hybrid processes are not unheard of. The difference

between PVD and CVD processes is how to promote material transfer and film deposition. In CVD, the deposited materials are transported as components of gaseous compounds, which are driven to react on the substrate, usually by heating the substrate at high temperatures, leaving a thin film of the required materials and reactive gases. The film characteristic closely related to the deposition conditions is the internal stress of the film. It is also very important for other film properties, such as hardness, electrical properties and film adhesion. A common cause of film stress is the difference in shrinkage between the film and the substrate causing the film to stretch or compress when it cools after being deposited at high temperatures [17]. The PVD process can be carried out at lower deposition temperatures and without corrosive products [18]. It is high wear resistance, low frictional coefficient; great variety of coatings can be producing and no toxic reaction products but deposition rates are typically lower [19].

- Physical Vapor Deposition (PVD)
- Pulsed Laser Deposition (PLD)
- Ion Beam Assisted Deposition
- Chemical Vapor Deposition (CVD)
- Sol-gel technique
- Pyrolysis spray technique (PS)
- Electrodeposition
- Chemical bath

2.3 Tin dioxide (SnO_2)

2.3.1 Definition

Tin dioxide is an inorganic compound with the chemical formula SnO_2 . It mainly exists in the mineral cassiterite and crystallizes into a tetragonal structure. It is a colorless, amphoteric and diamagnetic solid. This is generally considered to be an oxygen-deficient n-type semiconductor.

It is insoluble in water, but soluble in alkali and acid.

Tin dioxide is purified by reducing metals and burning tin in the air. [7]

2.3.2 Crystalline Structure

SnO_2 has the tetragonal structure it is means

($a = b = 4.738 \text{ \AA}$ and $c = 3.186 \text{ \AA}$).

The cell contains six atoms, four oxygen atoms,

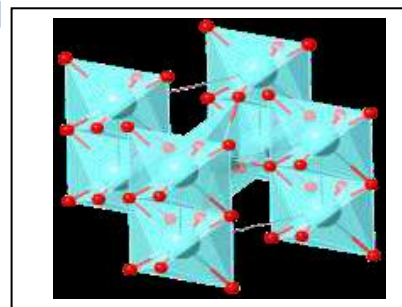


Fig.2.2 Geometry of tin dioxide [5].

and two of tin atoms. In this system each oxygen atom is surrounded by three of the tin atoms and each tin atom is surrounded by six oxygen atoms [8] (Fig.2.2).

2.3.3 Phases of tin oxide

When deposited at temperatures below 350 °C, tin dioxide films are amorphous.

It is from this that the crystallization temperature of the film begins. Thin tin oxide films prepared by various synthesis techniques are usually non-stoichiometric and exhibit metastable phases such as SnO and Sn₃O₄. The SnO phase appears at a deposition temperature of 400 °C and disappears at a temperature of 500 °C. This phase is divided into SnO₂ and Sn at an annealing temperature of 450 °C. This indicates that the film needs to be annealed at 500 °C to obtain a good stoichiometric SnO₂ [8].

The tin dioxide film is an n-type semiconductor with high transparency and very good conductivity; the film has chemical inertness, mechanical strength and high temperature resistance. Due to its low resistivity and high transmittance, SnO₂ is one of the most important transparent conductive oxide materials, which is very attractive from a scientific and technological point of view due to its interesting properties. Many workers try to improve the physical properties of tin oxide films by doping different dopants such as antimony, fluorine and titanium in the films. There are many applications for depositing these films, such as gas sensors, transparent electrodes, solar cells, and liquid crystal displays [9].

The high transparency of tin oxide semiconductors, coupled with its mechanical hardness, adhesion and good environmental stability, have opened up many application areas for them. Many techniques can be used to produce tin oxide films, such as evaporation, sputtering, pulsed laser ablation, and spray pyrolysis. Among these techniques, the spray pyrolysis deposition method is particularly attractive due to its simplicity. It is fast, cheap, low vacuum, suitable for mass production. In addition, this technology will allow developing countries to apply this technology in their own way [10].

It is well known that proper doping can improve the conductivity of tin oxide films; this enhancement function has not been fully explained. Recently, some reports indicate that structure plays a major role in this behavior.

2.4 Copper oxide

Copper has two oxidation states: +1 and +2, and some trivalent compounds have also been reported under special circumstances. The results show that the survival time of this trivalent copper does not exceed a few seconds. Therefore, cuprous oxide (Cu_2O) and copper oxide (CuO) are two stable forms of copper oxide. However, only the copper oxide (CuO) phase has been reported as a gas-sensitive material and exhibits many interesting properties.

2.4.1 Definition

The mineral form of copper oxide is called "tenorite". Pure copper oxide is a black solid with a density of 6.32 g/cm^3 and is insoluble in water. It melts above 1134°C , and there is some oxygen loss. Table 2.1 recombines some physical and chemical properties of copper oxide[11] .

Table 2.1 Different properties of CuO .

Cupric Oxide “ CuO ”	
Chemical names	Copper (II) oxide Cupric oxide Copper monoxide Copper oxide (CuO)
Mineral	tenorite
Molecular Formula	CuO
Appearance	Black powder
Solubility in water	Insoluble
Molecular Mass	79.55 g/mol
Density	$\rho = 6.32 \text{ g/cm}^3$
Relative permittivity	12
Melting point	1134°C
Boiling point	2000°C

2.4.2 Crystalline Structure

The black CuO belongs to the monoclinic system and has the crystallographic space group of the C2/c unit cell. The crystallographic properties of CuO are listed in Table 2.2 [12]. The copper atoms coordinate with four coplanar oxygen atoms located at the corners of the rectangular parallelogram, and they form a chain by sharing the edges. The oxygen atom coordinates with four copper atoms located at the corners of the twisted tetrahedron.

The chain passes through the structure in the directions $[110]$ and $[1\bar{1}0]$. The two types of chains alternate in the $[001]$ direction, and each type is stacked in the $[010]$ direction with an interval of approximately 2.7 angstroms between the chains. [13, 14]. Figure 2.3 shows the crystal structure of CuO.

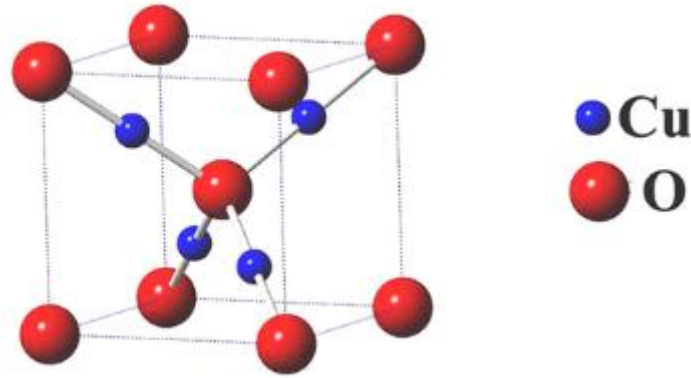


Fig. 2. 3 Crystal structure of CuO shown by four unit cells. The small blue and the big red spheres denote Cu and O atoms respectively [6].

Table 2.2 Crystallographic properties of CuO.[10]

CuO	
Unit Cell	Monoclinic
	$a = 4.6837 \text{ \AA}$
	$b = 3.4226 \text{ \AA}$
	$c = 5.1288 \text{ \AA}$
	$\beta = 99.54^\circ$
Shortest interatomic distance	$\alpha = \gamma = 99.54^\circ$
	Cu-O 1.95 $\text{\AA}$
	O-O 2.62 $\text{\AA}$
	Cu-Cu 2.90 $\text{\AA}$
Cell volume	81.08 $\text{\AA}^3$
Cell content	4 [CuO]

2.4.3 Applications of Cu_xO

Due to its abundant ingredients in nature, low production cost, good thermal stability and electrochemical performance, CuO is a promising material for various applications. This combination of characteristics makes CuO thin films an important

candidate for a variety of applications, namely: high-temperature superconductors, solar cells, gas sensors, magnetic storage media, varistors and catalysis, antibacterial activity [11], optoelectronic chemical batteries and lithium batteries [12] .

2.4.3.1 Solar cells and light emitting diodes

Cu_xO thin films are possible candidates for the development of different types of optical devices, including solar cells and organic light-emitting diodes based on dye-sensitized and heterojunction structures.

The pursuit and demand for clean and economical energy has increased interest in the development of solar energy applications. Among the various metal oxide materials used in solar applications, Cu_xO is attracting more and more interest due to its 18% theoretical power conversion efficiency (PCE) and higher absorption coefficient than monocrystalline silicon. [13]

2.4.3.2 Gas sensor

Cu_xO offers great potential for the development of high-sensitivity but low-cost sensors. This includes optical, gas and biosensors. Photodetectors are important equipment that can be used in a variety of applications, including thermal imaging systems, free space communications, navigation aids, and ozone layer monitoring. [14,15] Among semiconductor materials, Cu_xO has proven to be an attractive material for the manufacture of photodetectors because of its relatively low band gap and outstanding photoelectric properties. [16]

Cu_xO also provides great possibilities for the development of semiconductor-based high-sensitivity gas sensors. The sensing properties of Cu_xO can be improved by reducing its size to nanoscale (equivalent to twice the Debye length) and adding appropriate dopants. [17] Catalytic nanoparticles such as Pd,[18] Pt,[19] Ag[20] and Au[21] adhere to the Cu_xO surface, further increasing its sensitivity, mainly due to spillover effects. [22] Cu_xO films have been shown to be highly sensitive to various gas species, including C₂H₅OH, [23,24] CO, [25] NO₂ [26] and H₂S [27]. In addition, they have also tested organic vapor sensors, including: ethanol, methanol, and acetone vapors. Table 2.3 summarizes the performance of CuO-based gas sensors manufactured by various deposition techniques and various gases.

Sensor and fabrication method	Gas detection	Operation temperature (°C)	Sensitivity y(%)	Response time (s)
electrodeposition CuO	Ethanol 2500 ppm	350	29	247
	Methanol 2500 ppm	400	15	235
	H ₂ S 100 ppm	200	80	2
Sol – Gel CuO / ZnO	H ₂ 3000 ppm	200	60	250
RF magnetron sputtering CuO-Cu _x Fe ₃ O ₄	CO 500 ppm	400	90	1260
Chemical Bath CuO	H ₂ 1000 ppm	90	16	-
	Gasoline 1000 ppm	90	28	-
	CO 1000 ppm	90	2	-
Sol – Gel CuO	H ₂ S 200 ppm	200	24	25

Table 2.3 CuO-based gas sensor performance fabricated by various deposition techniques and for various gas sensing [28-30].

2.4.3.3 Photo-catalytic

Cu_xO is a promising photo-catalyst that is used in many chemical processes, such as organic contamination degradation and water splitting under visible-light irradiation owing to their small band gap and low cost.[28] Under illumination, Cu_xO produces electron/hole pairs that can generate hydroxyl radicals ([•]HO) from water. This radical is capable of mineralizing most organic molecules.[29] For water splitting applications, the majority charge carriers of the Cu_xO (holes) oxidize water to oxygen gas (O₂), while the photo-generated minority charge carriers (electrons) reduce water to hydrogen gas (H₂).[30] Significantly, the Cu_xO conduction band is more negative than the redox potential of H⁺/H₂, which allows sunlight to produce H₂ from water. [29]

2.4.3.4 Electrochromic devices

Since the 1990s, people have been studying Cu_2O electrochromic systems based on nanostructures, such as smart windows and optical displays. [31] It has been found that Cu_2O exhibits cathodic electrochromic, is transparent in the oxidized state under visible light, and is almost black when switched to the reduced state in the presence of electrolytes containing positive ions (such as H^+ , Li^+ , and Na^+). [32] Generally, it has been found that the electrochromic process corresponds to the conversion of Cu_2O (transparent) to CuO (black) in a reversible reduction oxidation process (redox). [33] So far, the best coloring efficiency obtained with Cu_2O nanostructures is as high as $37 \text{ cm}^2\text{C}^{-1}$, which is only a quarter of the best coloring efficiency made from WO_3 nonporous structures ($141.5 \text{ cm}^2\text{C}^{-1}$). [34] Unfortunately, nanostructured Cu_2O requires high coloring voltage and poor stability [32], and further research is needed to solve these important problems.

2.4.3.5 Other Applications

Nanostructured Cu_xO has also been reported for many applications other than those presented in sections 4.1 to 4.8. Of note, nanostructured CuO has been used in ceramic resistors [35] and supercapacitors. [34] Nanostructured Cu_2O has also been incorporated in memristors, [32] heterogeneous catalysis, [30] anti-fouling [31,32] and thin-film transistors. [33] Of course, there are other applications for which Cu_xO has been used, but these are beyond the scope of this research.

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Chapter 3 Characterization Of Cu Thin Films Prepared By Electro-deposition On Substrates Of SnO₂

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Chapter 3 Characterization Of Cu Thin Films Prepared By Electro-deposition On Substrates Of SnO₂

In this chapter, the conditions for the preparation of thin layers of Cu on substrate of tin oxide by electro-deposition and the annealing treatment on their physico-chemical properties are presented.

In order to obtain the desired characteristics of the developed layers, it is essential beforehand to control and optimize the deposition parameters. For this, we have characterized the microstructure, optics and mechanical properties of our layers by different techniques such as scanning electron microscopy (SEM) for the observation of the texture and the surface of the layers. X-ray diffraction (DRX), a spectrophotometer (UV-Visible) and Vickers Hardness Testing to obtain information on the directions of crystallographic growth and absorbance and micro-hardness of the deposited layers. In the follow we will represent the techniques used in this study, elaboration of the films at optimized conditions and characterization with their formulas. Then discussion of the results will be take plays in this chapter.

3.1 Electrodeposition technique

Electrochemical deposition, or electrodeposition for short, refers to a thin film growth process, which includes forming a metal coating on a substrate (substrate) through the electrochemical reduction of metal ions in the electrolyte to achieve the required electrical resistance Resistance and corrosion resistance, reduce wear and friction, improve heat resistance, and used for decoration. The analogy technique is often referred to as electroplating. In addition to producing metal coatings, it is also used in electrometallurgy for extracting metals from ore or for electroforming, in which molds are produced to form objects in the final shape. In most cases, the metal deposits obtained are crystalline. Therefore, this process can be called electro crystallization, which is a term introduced by the Russian chemist V. Kistiakovski in the early 20th century.

The electrolyte contains positive and negative ions. Therefore, it is considered an ionic conductor. In order to prepare electrolytes, in addition to different organic and ionic liquids, the required metals contained in chemical substances are currently liquefied (mostly dissolved in water) to form molten salts. These metals are currently used in specific electroplating processes. To start electrodeposition, the cathode (working electrode, W.E) is immersed in the electrolyte in the container (battery) together with the anode (counter electrode, C.E). To allow current to flow in the circuit, the two electrodes are connected to a battery or any other power source. The cathode is connected to the negative electrode of the battery, and the anode is connected to the positive electrode, reducing metal ions to metal atoms, and finally forming deposits on the surface. Figure 3 shows a schematic diagram of an electrolytic cell for electroplating or electrodepositing metal "M" from an aqueous (water) solution of metal salt "MA".

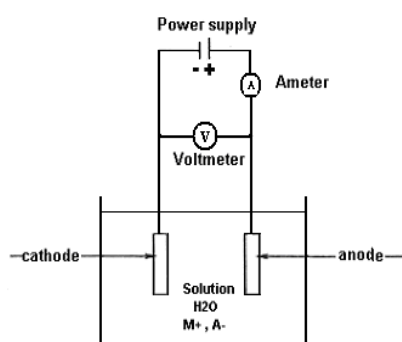
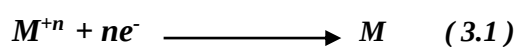


Fig 3.1 A schematic electrodeposition technique.

This type of circuit arrangement directs electrons into a bath from the power supply to the cathode. In the bath, the electric current is carried by the positively charged ions from the anode toward the negatively charged cathode. This enables the metal ions in the bath to migrate toward extra electrons that are located at or near the surface of the cathode. Finally, the metal ions are removed from the solution and are deposited on the surface of the object as a thin layer. The reaction in aqueous medium at the cathode therefore obeys equation (3.1):



where n is the number of electrons involved in the reaction.

The thickness of the electrodeposited layer on the substrate is determined by the duration of electroplating. The longer the object stays in the chemical bath, the thicker the deposited layer [1].

Recently, electrodeposition has become more and more popular and widely used by researchers in different fields. What caused this interest? The process itself seems simple. The conductive surface is immersed in an electrolyte containing the ions of the material to be deposited, and a voltage is applied to the solid/electrolyte interface to generate a charge transfer reaction and film deposition. The driving force for this process is the applied potential, and this amount can be easily and accurately controlled down to mV and time scales as short as 1ns. This feature leads to considerable control over the material formation process, its microstructure and properties. The challenge of developing an electrodeposition process today is not the synthesis of a predefined material, but a compromise between the ideal conditions for producing this material and the commercial viability of the process. Other frequently mentioned advantages of electrodeposition include high raw material utilization, low energy consumption, low material waste, low capital investment, and ease of implementation. Although the latter two are generally considered an advantage, they may be a double-edged sword, and they may actually encourage rapid experimentation, thereby putting science in the background and undermining the community to compare this technology with vacuum/gas/plasma Bulk deposition method.

New materials and processes are being developed and integrated into microelectronics manufacturing to provide new functions, such as in MEMS, lab-on-a-chip, or microfluidic devices. Polymers and biological materials are electrodeposited for biomedical applications; metal oxides and compound semiconductors are grown electrochemically for electronic or optoelectronic applications. Electrodeposition in new electrolytic media such as ionic liquids or supercritical fluids is being vigorously promoted and has achieved some success. Electrodeposition plays an important role in the development of portable and sustainable energy conversion technologies on a global scale. In addition, the principle of controlling the scale-up of the electrodeposition process is well known, which has promoted the development of large-scale manufacturing processes [2].

3.1.1 The electrolysis cell

➤ Constituents of the cell

The electrolysis process consists of four parts:

- The external circuit, with power supply or battery as a source of direct current (DC), that is conveyed to the plating tank, and associated with instruments such as ammeters, voltmeters, and voltage and current regulator to regulate them at appropriate values.
- The working electrodes or cathodes (the material to be plated). The cathodes are to be immersed in the plating solution so that contact is made with the current source.
- The plating solution or solution bath.
- The counter electrodes or anodes (metal or conducting materials being plated which serves merely to complete the circuit).

The electrodeposition cell containing the plating solution or the electrolyte is usually made of plain mild steel (for alkaline solutions) or of lined steel (for acidic solutions). Steel lining could be of rubber, plastics, glass, or even lead [3].

➤ Electrolytes (Solution baths)

The solution bath serves as a source of metal to be deposited, which contains ions of that metal, hence it provides conductivity, a stabilizer to stabilize the solution, for example, against hydrolysis and to stabilize the solution pH when acts as a buffer, regulates the corporal form of the deposit and helps dissolve the anodes. Finally, modifies properties of either the solution or of the deposit,

Complex ions are formed to stabilize the cation, which becomes much more stable when complexed to some ligand or to metal atoms by coordinate bonding. The concentration of the free (equated) ion is lowered by the presence of the ligand. Complex ions are also formed to hold the equated form at suitably low concentration allowing control of the evenness of plating.

Electrolytes can be defined as substances such as acid, base, and salts, which can conduct electricity in their aqueous solution due to ionization. The ions existing in the electrolyte are responsible for the conduction that results in current or free electrons

passing through the wires. When a voltage is applied across the cell, and under the influence of the potential difference, the negatively charged ions migrate to the anode and the positively charged ions migrate to the cathode. The flowing of ions in aqueous solution of an electrolyte is called electrolysis [4].

➤ **Electrode potential**

When a metal electrode is placed in an ionic solution, ions will be exchanged between the metal and the solution. Ions from the metal enter the solution, and ions from the solution enter the metal lattice. The boundary between the two phases is called the interface. Due to an electron exchange between the electrode and the ions in solution, the interface becomes electrified and a potential difference across the metal-solution interface is generated. This potential difference is called electrode potential.

3.2 Cu thin films preparation

The goal of the present study is the deposition and characterization of Cu thin films by electrodeposition technique. Effect of annealing treatment in fabricating copper thin films. Experimental details of films preparation by this techniques and the various characterization techniques used in this thesis will be presented .In the contrary to the other deposition technique, electro-deposition has widely parameters to study. Two samples were prepared. In each sample only one parameter is varied while the rest of parameters were fixed. In our experiment, Copper coatings were electro-deposited on tin oxide substrates from an electrolytes containing copper chloride (CuCl_2), sodium chloride (NaCl), ammonium chloride (NH_4Cl), and boric acid (H_3BO_3), (see Table 3. 1). Bidstilled water was used for electrolyte preparation. The pH of the solution was adjusted by addition of the aqueous HCl or NaOH solution. Tin oxide substrates (99.9%) with dimension of 20 mm $\times$ 10 mm $\times$ 0.19 mm were used as cathode. However, the anode was a copper sheet (20 mm $\times$ 10 mm $\times$ 2 mm) of commercial purity (99.99 %). In addition, Cu coatings were deposited at fixed plating current density at 4 A/dm². The electrodeposition was carried out at (50 $\pm$ 1) °C, pH of 2.3 during 60 min. All the deposited Cu films are deposited at cleaned substrates [5]. The substrates are cleaned following these steps:

1. The glass substrate were firstly cleaned ultrasonically in methanol to remove any impurity (grease o dust) stickled in the surface of the substrate three time several and for 10 min.
2. The glass substrates were secondly cleaned ultrasonically in distilled water to remove any trace of the methanol three several times and for 10 min.
3. The cleaned glass substrates are dried with dryer.

In tables 3. 1 we have summarized the deposition parameters of all samples. The deposition system of electrodeposition used for this study is shown in figure 3. 2.

Table 3.1 Chemical compositions and working conditions of Cu electrolyte.

Compositions /(g/L)	Cu.Cl ₂	0.5
	NH ₄ Cl	0.1
	H ₃ BO ₃	0.2
	NaCl	0.05
Conditions	Current density (A/m ²)	4
	PH	2.3
	Time/ min	60
	Temperature/C°	50
	Distance (cm)	2.5
	Annealing temperature /C°	500

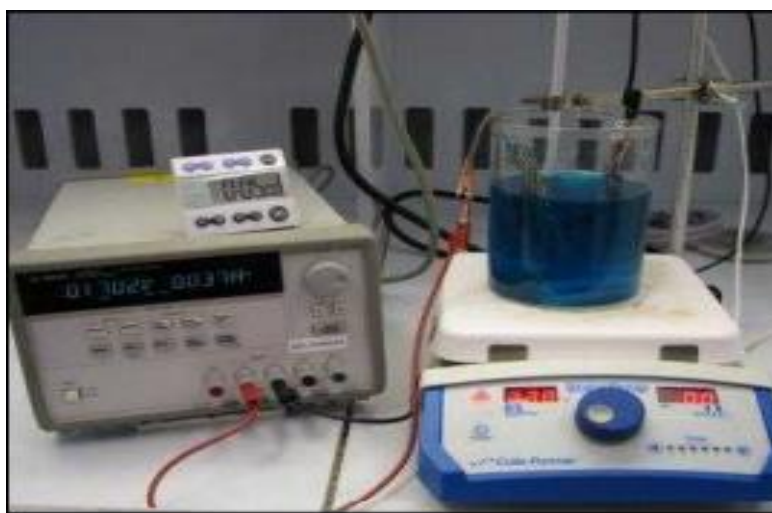


Fig 3. 2 The deposition system of Electrodeposition.

3. 3 Characterization of thin layers

Several techniques were used for the structural, morphological, optical, and mechanical characterization of the films, these techniques are described below:

3.3.1 Adhesion Test

Before any characterization of the prepared film, the adhesive strength between the film and the substrate was evaluated by applying a tape test on the deposited film.

Generally, if the film adheres to the substrate and does not peel from the substrate, the adhesion strength is considered "good."

3.3.2 Structural Characterization

➤ X-ray diffraction

The structural properties of the film were studied by X-ray diffraction (XRD), using Miniflex 600 and Cu- α radiation with a wavelength of $\lambda = 1.5418 \text{ \AA}$. The diffractometer reflection is performed at room temperature, and the 2θ value varies between 20° and 80° . The structural parameters of all deposited copper films are estimated from XRDML patterns. The crystallite size, lattice, strain, dislocation density, texture coefficient and number of crystallites are calculated by the formula given below:

The principle of this method is based on Bragg's law [6], which explains the diffraction process of electromagnetic waves on crystals

$$n\lambda = 2d \sin\theta \quad (3. 2)$$

n : is an integer called the order of reflection.

λ : the wavelength of X-rays.

d : the characteristic spacing between the crystal planes of a given specimen .

θ : the angle the incident beam and the normal to the reflecting lattice plane.

➤ The crystallites size was calculated from two formulas the Scherer's equation [7] :

$$D = k\lambda/\beta\cos\theta \quad (3. 3)$$

where β is the FWHM (full width at half maximum) of diffraction peaks, θ is the Bragg angle, λ is the wavelength of the used X rays, D is the crystallite size .

The texture coefficient (T_c) was calculated, which is defined [8,9]:

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1} \sum_n^N I_n(hkl)/I_{0n}(hkl)} \quad (3. 4)$$

where $I(hkl)$ and $I_0(hkl)$ are the measured intensity and the standard intensity of the same (hkl) plane according to the JCPDS data whereas N and n are the reflection and the diffraction peaks number, respectively

- The lattice strain is calculated from two following equation [10] :

$$\varepsilon = \beta / 4 \tan \theta \quad (3. 5)$$

$$(\beta \cos \theta) / \lambda = 1 / D + (\varepsilon \sin \theta) / \lambda \quad (3. 6)$$

where β is the FWHM (full width at half maximum) of diffraction peaks, θ is the Bragg angle, λ is the wavelength of the used X rays, D is the crystallite size and ε is the internal strain. The strain is equal to the slope of the plot of $\beta \cos (\theta) / \lambda$ vs. $\sin (\theta) / \lambda$ of different peaks.

- the lattice parameters were determined from XRD results using the following equation [11]:

$$1 / d_{hkl}^2 = \frac{h^2 + k^2 + l^2}{a^2} \quad (3. 7)$$

where d_{hkl} , (hkl) , (a) and (c) are the inter-planar space, Miller indices, and the lattice parameters, respectively.

- The dislocation density (ξ) is calculated using this equation [12]:

$$\xi = 1 / D^2 \quad (3.8)$$

where ξ is the dislocation density and D is the crystallite size.

➤ **Morphology of the films**

A scanning electron microscope TESCAN VEGA3 SEM microscope was used to analyze the film morphology. The estimated grain size is also used to view the profile of the sample and measure the thickness of the deposited layer through SEM images.

3.3.3 Optical properties

The optical properties of the obtained films were studied by using the Shimadzu 3101PC dual-beam spectrophotometer using ultraviolet-visible absorption spectroscopy.

3.3.4 Fourier transform infrared spectroscopy

FTIR is a technique based on the absorption of infrared radiation by the material analyzed, which is used to obtain information on the chemical bond in a material and to determine the purity and nature of the materials [\[13\]](#).

3.3.5 Mechanical properties

➤ **Vickers Hardness Testing**

Hardness is a property of a material, not a basic physical property. It is defined as the resistance to indentation, which is determined by measuring the permanent depth of the indentation.

More simply, when using a fixed force (load) and a given indenter, the smaller the indentation, the harder the material. The indentation hardness value is obtained by measuring the depth or area of the indentation using one of more than 12 different test methods. [Learn more about the basics of hardness testing here.](#)

The Vickers hardness test method, also known as the microhardness test method, is mostly used for small parts, thin sections or deep surface work.

The Vickers method is based on an optical measurement system. The microhardness test procedure ASTM E-384 specifies the light load range of the indentation made with a diamond indenter, which is measured and converted into a hardness value. It is very useful for testing on a variety of materials, but the test sample must be highly polished to measure the size of the impression. The pyramid-shaped diamond at the bottom of the square is used for the Vickers scale test. Generally, loads are very light, ranging from 10 grams to 1 kgf, although "macro" Vickers loads can reach 30 kg or more.

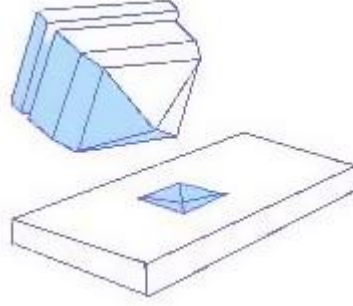


Fig 3. 3 Opposing indenter faces are set at a 136 degree angle from one another.

The micro-hardness method is used to test metals, ceramics and composite materials- almost all types of materials.

Because the test indentation in the Vickers test is very small, it is suitable for various applications: testing very thin materials (such as foil) or measuring the surface of parts, small parts or small areas, measuring individual microstructures or measuring depth through cutting Part and make a series of indentations to describe the contour of the hardness change for surface hardening.

Micro-hardness testing usually requires sectioning to provide a small enough sample to fit into the tester. In addition, sample preparation will need to make the sample surface smooth to allow regular and good measurement of the indentation shape, and to ensure that the sample can be perpendicular to the indenter.

The HV number is then determined by the ratio F/A , where F is the force applied to the diamond in kilogram force and A is the surface area of the resulting indentation in square millimeters. A can be determined by the formula.

$$A = \frac{d^2}{2 \sin(136^\circ/2)} \quad (3. 9)$$

Which, can be approximated by evaluating the sine term to give,

$$A \approx \frac{d^2}{1.8544'} \quad (3. 10)$$

Where d is the average length of the diagonal left by the indenter in millimeters. Hence, [14]

$$HV = \frac{F}{A} \approx \frac{1.8544F}{d^2} [Kgf/mm^2] \quad (3. 11)$$

Where F is in kgf and d is in millimeters.

The corresponding unit of HV is then the kilogram force per square millimeter (kgf/mm^2) or HV number. In the above equation, F could be in N and d in mm, giving

The SI unit of HV is MPa. To calculate the Vickers hardness number (VHN) using SI units, the force applied by Newton needs to be divided by 9.806 65 (standard gravity) to convert to kilogram force. This leads to the following equation:[14]

$$HV \approx 0.1891 \frac{F}{d^2} [Kgf/mm^2] \quad (3.12)$$

Where F is in N and d is in millimeters. A common error is that the above formula to calculate the HV number does not result in a number with the unit Newton per square millimeter (N/mm²), but results directly in the Vickers hardness number (usually given without units), which is in fact one kilogram-force per square millimeter (1 kgf/mm²).

3.4 Results and discussion

After the film was deposited, we used the characterization techniques mentioned in this chapter. X-ray diffraction analysis shows that we have thin layers of copper; they are crystalline and other parameters can be calculated, such as the absorbance, micro-hardness and thickness of the sample measured by UV-Vis spectroscopy.

Before performing any characterization techniques, we performed a tape test on the deposited film and confirmed that the bond strength of the pure copper film was considered "good".

3.4.1 Structural properties

The X-ray diffraction (XRD) patterns of copper to metallic thin films before and after annealed at 500 C° temperatures are illustrated in figure 3.4. The observed XRD patterns match well with cubic phase of Cu (JCPDS 00-004-0836) [15,16]. No peaks corresponding CuO or Cu₂O phases were detected in the XRD patterns. Annealing the Cu films in air at various temperatures shows an improvement in crystallinity. It is also worth we noting that peaks correspond to tin oxide are found in these spectra for sample before annealing SnO₂ (JCPDS Card 01-078-1913)

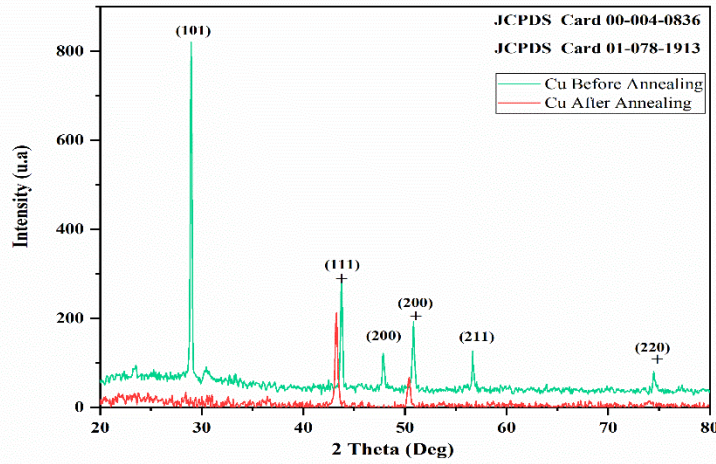


Fig 3. 4 X-ray diffraction pattern of Cu thin films.

In addition, the texture coefficient (T_C) indicates the maximum preferred orientation of the film along the diffraction plane, which means that the increase in the preferred orientation is related to the increase in the number of grains along the plane. The T_C (hkl) value is calculated from the X-ray data using the formula (Equation 3.4). Obviously, if $T_C > 1$, this means that the film growth occurs in some preferred orientation. These results confirm that the (111) plane orientation corresponding to the copper cubic structure is the preferred orientation shown in the previous section.

Table 3. 2 Peak positions, inter planar spacing d_{hkl} and lattice parameters calculated from (111) peaks.

Samples	$2\theta_{(111)}$ (°)	d_{111} (Å)	a (Å)	Cell Volume (Å ³)
Before annealing	43.47	2.830	3.233	47.27
After annealing	43.33	2.724	3.230	46.27

It can be seen from the XRD spectrum that the intensity of these peaks is affected by the annealing temperature. The interplanar distance d_{hkl} value of the Cu film is calculated by the Bragg equation (Equation 3.2). The two lattice parameters (a) of the cubic phase are calculated using the (Eq. 3. 7) relationship with the help of the (111) orientation.

Table 3.2 summarizes the position of the (111) peak and the calculated value of d_{hkl} as well as the lattice parameter (a). Compared with the Cu film, it can be seen that the lattice parameter (a) related to the annealing temperature is slightly decreased.

In the following, we will explain the structural defects in our samples based on the crystallite size, micro strain and stress. The full width at half maximum (FWHM) can be used to estimate the size of crystallites grown along the c-axis. The average crystallite size D of all copper films is evaluated using Debye sheer's formula (Equation 3.2). Table 3.3 shows the change of crystallite size before and after annealing.

The crystallite size of the copper film is in the range of 54.02-40 nm. A significant change in the size of crystallites was observed in 10 years. The small reduction in crystallite size may be related to annealing treatment.

Table 3. 3 Estimation of crystallite size, micro strain, dislocation and stress of Cu thin layers.

Samples	D (nm)	$\epsilon \times 10^{-4}$	$\xi \times 10^{14}$ (line/m ²)	σ (GPa)
Before annealing	54.12	3.09	1.84	-1.086
After annealing	40.52	2.42	2.46	-1.10

The

micro stain (ϵ), which is considered as an interesting structural parameter of copper deposited thin films, is calculated using the following relation (Eq.3. 5).

The dislocation density (ξ) values of films are calculated using the expression (Eq.3. 8):

The estimation of stress was performed using the following formulae:

$$(3. 13)\sigma = \left[2C_{13} - \frac{C_{33}(C_{11}+C_{12})}{C_{13}} \right] \epsilon$$

and

$$(3. 14)\epsilon = (C_0 - C)/C_0$$

where, ϵ is strain, C_{13} (1.05×10^{11} N/m²), C_{33} (2.1×10^{11} N/m²), C_{11} (2.1×10^{11} N/m²), and C_{12} (1.2×10^{11} N/m²), are the elastic stiffness constants.

The negative values of the stress indicate the presence of compressive stress [17]. This compressive stress occurs usually if there are native defects and distortions in the lattice. It is worth to note that, Cu after annealing treatment resulted in less stress. Also, T. P. Rao et al. [18] observed a compressive stress in deposited Cu thin films.

3.4.2 Surface morphology and composition

➤ SEM analysis

The growth mechanism, particle shape and size, and morphology of the prepared samples were studied by using a scanning electron microscope (SEM). Figure 3. 5 is a low magnification SEM image of the microstructure of the Cu film after annealing. In this film, particles with regular shapes and porosity can be seen on the surface. As we all know, SEM visualization can only see crystal grains composed of more or less disordered atoms and crystallites, while in the XRD method, the range of the crystalline region of coherent diffraction X-rays is measured. This is a stricter standard and leads to a smaller grain size [19].

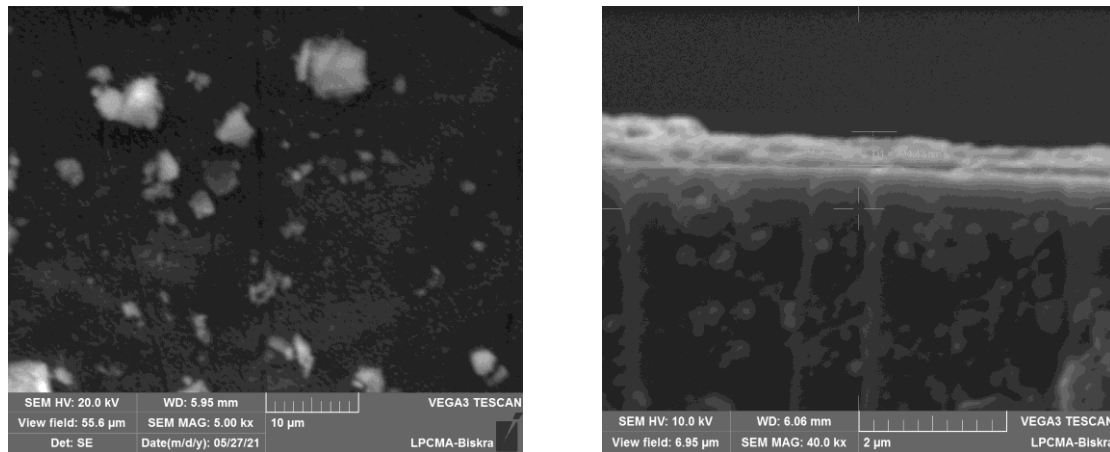


Fig 3. 5 SEM images of Cu film after annealing treatment and their cross section.

➤ Film thickness measurement using SEM

The thickness can be measured by breaking the sample and coating the non-conductive substrate with gold. The SEM micrograph of the cross section of the Cu layer was obtained at an inclination angle of 80 degrees.

The SEM image in cross section made for the copper thin layer is illustrated in figure 3. 5, from which an estimated thickness of thin film is around 434nm.

➤ EDAX analysis

The chemical composition of the Cu film is determined by energy dispersive analysis X-ray spectroscopy. Figure 3. 6 shows the EDAX spectrum of a Cu sample. The elements identified in the copper thin layer are copper and oxygen. EDAX analysis did not show the presence of other impurity peaks. This proves the purity of synthetic copper. There is a carbon peak in the EDAX of the entire sample, which may come from the air as shown in the figure.

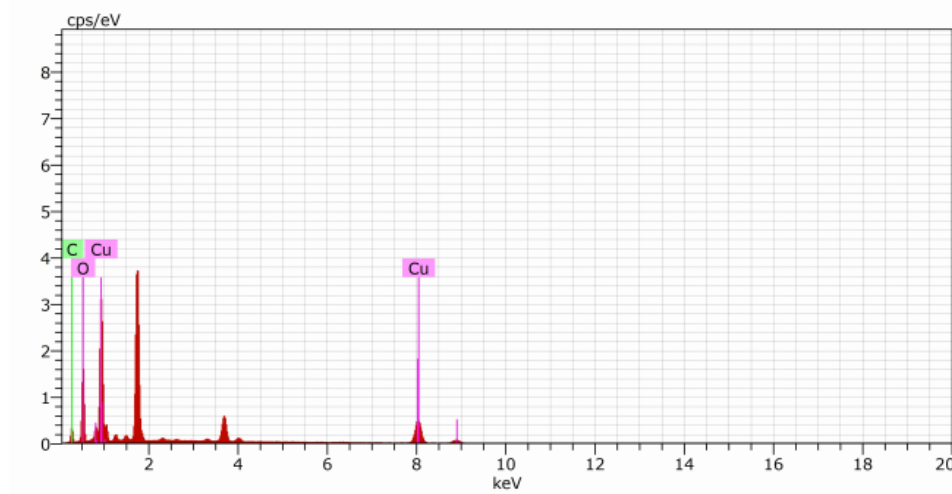


Fig 3. 6 Typical EDAX spectra for the deposited film Cu.

3.4.3 Optical properties

Ultraviolet-visible absorption spectroscopy plays a very important role in studying the optical properties of thin films [17]. The light absorption spectrum of the Cu thin film in the wavelength region of 310-900nm is shown in Figure 3. 7. These spectra show that the prepared film exhibits higher absorbance to copper film after annealing, while the absorbance to copper decreases slightly before annealing.

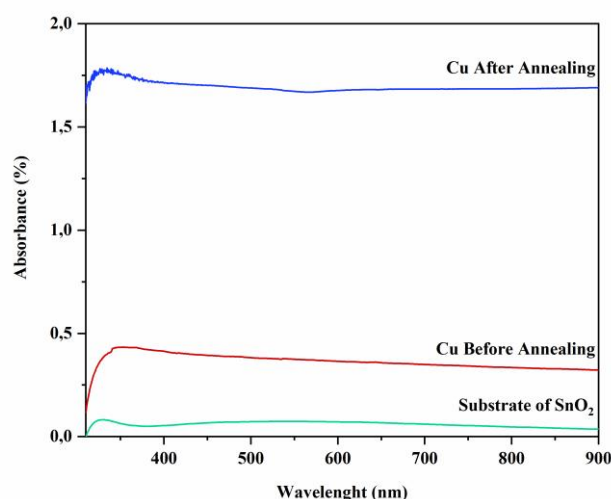


Fig 3. 7 Absorbance spectra of Cu thin films before and after annealing.

3.4.4 FTIR spectroscopy analysis

Figure 3.8 shows the FTIR spectra of Cu thin films of SnO_2 products before and after annealing temperature. The absorption bands at 500 and 618 cm^{-1} correspond to the stretching vibration of the Cu-O bond in cubic Cu [18]. It is worth noting that the absorption band of Cu-O becomes larger than the absorption band synthesized from the copper film, which indicates that the annealing treatment improves the copper thin layer. But the other absorption bands correspond to the stretching vibration of the Sn-O bond tetragonal system. SnO_2 crystals [19].

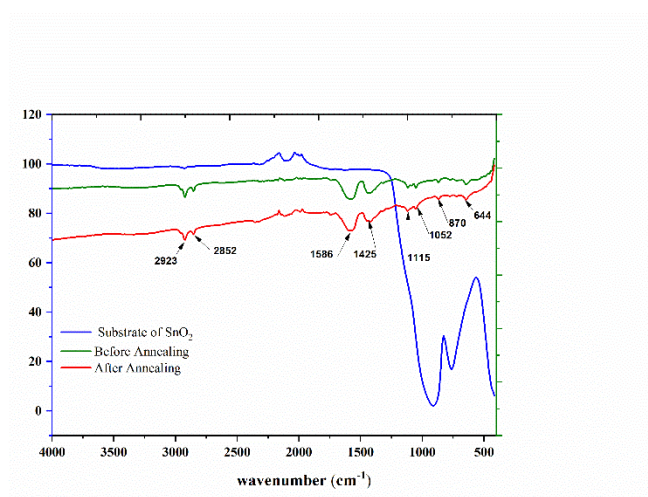


Fig 3. 8 FTIR spectra of Cu before and after annealing and SnO_2 substrate synthesized electro-deposition method.

3.4.5 Micro-hardness Measurement

Vickers micro-hardness of the coated samples is shown in figure 3. 9. The Vickers micro-hardness of composite deposit Cu-layer coating after annealing is higher than the Cu thin film coating before annealing, substrate of tin oxide, and glass. The annealing treatment in the deposit Cu-layer is one of the reasons to increase micro-hardness of the coatings. Further increase in micro-hardness of deposit Cu-thin film by the high temperature is also clearly observed.

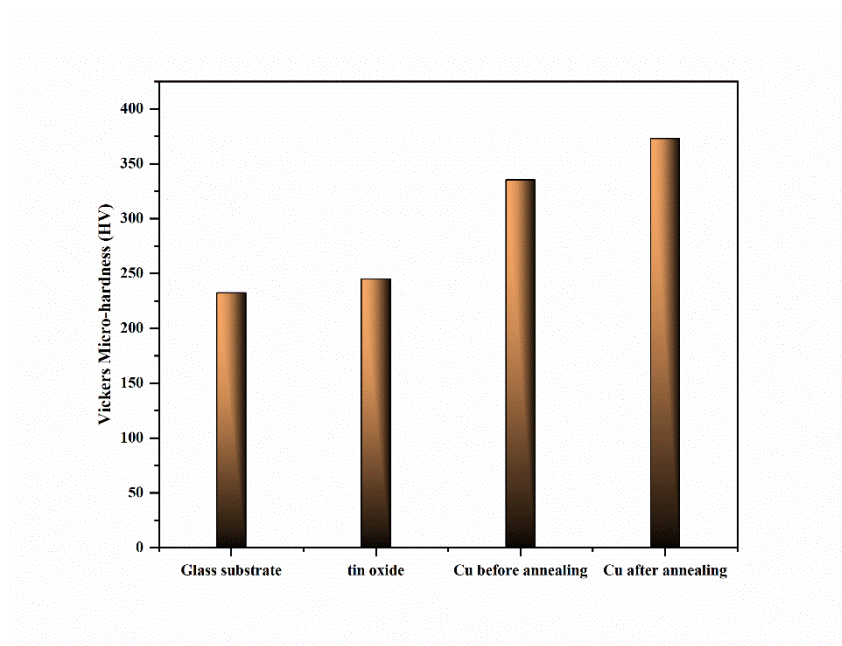


Fig 3. 9 Vickers micro-hardness of the electrodeposited Cu on substrate of tin oxide (a) glass substrate, (b) Tin oxide, (c) Cu before annealing, (d) Cu after annealing.

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General Conclusion

Chapter 4

General Conclusion

Cu thin films were deposited on substrate of tin oxide by electro-deposition. The Cu films are deposited with different deposition conditions in order to optimize these parameters for elaborate a Cu films with good quality which can be used in several applications such as: solar cells and gas sensor. The investigated parameters in this study were nature of substrate; substrate temperature. These layers have been characterized by different methods; X-ray diffraction (XRD) and scanning electron microscopy (SEM) for the observation of the microstructure, UV-visible-IR spectroscopy of optical properties and Vickers hardness testing for the study mechanical properties.

The aim of the research is to elaborate and characterized the substrates of thin films of copper on substrates of tin oxide. This study was therefore carried out in one part.

In this part of this work have been characterized the layers after and before annealing treatment at 500 C°. The films structure reveals that all deposited films crystallize in Cubic structure. The calculated texture coefficient reveals that copper thin layers have best crystallization level along preferred orientation (111). The crystallite size decreases from 54 to 40nm in the annealing temperature. The growth mechanism, shape and size of the particles as well as topography study of the prepared sample was performed by using scanning electron microscopy (SEM). Shows low-magnification SEM images of microstructure the Cu thin films after annealing treatment. In this film, grains with regular shape and porosity are visible in the surface. The thickness of thin film for t copper is around 434nm.

The chemical composition of the Cu thin film was determined by the energy dispersive analysis X-ray spectra, The elements identified in the thin layer of Cu are copper and oxygen. The EDAX analysis does not reveal the presence of the other peaks which are at the origin of the impurities. This proves the purity of the synthesized Cu. A peak of carbon is present in EDAX of the whole samples may be come from air.

The optical absorbance spectra of Cu films in the wavelength 310-900nm region are shown in figure 3. 7. These spectra show that the prepared film exhibit a high absorbance for copper thin films after annealing treatment with a little decreased for Cu before annealing. The absorption bands at 500 and 618cm⁻¹ correspond to the stretching vibration of Cu-O bond in cubic Cu [1. It is worth noting that the absorption band of Cu-O becomes greater than those obtained from

the as synthesized of copper films revealing that the annealing treatment ameliorates the copper thin layers .but other absorption bands correspond to the stretching vibration of Sn-O bond tetragonal type SnO₂ crystal.

The Vickers micro-hardness of composite deposit Cu-layer coating after annealing is higher than the Cu thin film coating before annealing, substrate of tin oxide, and glass.