

UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY Escuela de Ciencias Físicas y Nanotecnología

TÍTULO: Manufacture of thin film memcapacitor aluminum oxide nanopores filled with copper oxide by electrochemical self-organizing template

Trabajo de integración curricular presentado como requisito

para la obtención del título de Ingeniero en nanotecnología

Autor:

Richard Santiago Zapata Gavilanes

Tutor: Ph.D Gema Gonzales Ph.D Henrry Osorio

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Dra. GONZALEZ VAZQUEZ, GEMA , Ph.D. Tutor



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Resumen

El presente proyecto muestra la fabricación de una película delgada con una densidad aproximada de $1.1x10^{15}$ de memcapacitors por m². El material modificado está compuesto por nano-poros de óxido de aluminio (AO) y dopado con alambres de nano-óxido de cobre (wCuOx). El material de partida para hacer el electrodo fue aluminio y mediante anodización electroquímica se obtuvo una membrana porosa de óxido de aluminio (AAO). A continuación, se utilizó AAO como sustrato para depositar wCuOx dentro de los poros para formar un material AOO / CuO. La caracterización morfológica de las películas obtenidas se realizó con un microscopio de fuerza atómica, microscopía electrónica de barrido y espectroscopía de rayos X de energía dispersiva. Y para caracterizar las propiedades eléctricas se utilizó voltamperometría cíclica y espectroscopía de impedancia electroquímica. Los resultados experimentales obtenidos mostraron un tamaño de poro de 50-200 nm con una profundidad de 40 um. La voltamperometría cíclica mostró el bucle de histéresis de conmutación resistiva característico de un condensador de memoria que muestra la variación de resistencia que va de 0 a 22,5 k Ω . La espectroscopia de impedancia electroquímica mostró un valor de capacitancia de 1,14X 10^{-5} F para la alúmina y 6,82X 10^{-6} F para el material AOO / CuO.

Palabras clave: Memcapacitor; Oxido de aluminio; Nanoporos; Nano alambres; Conmutación resistiva; Impedancia electroquímica

Abstract

The present project shows the manufacture of a thin film with a density approximate of $1.1x10^{15}$ of memcapacitors per m². The modified material is composed of nano-pores aluminum oxide (AO) and doped with nano-copper oxide wires (wCuOx). The starting material to make the electrode was aluminum and using electrochemical anodization an porous aluminum oxide membrane (AAO) was obtained. Next, AAO was used as a substrate to deposit wCuOx inside the pores to form a AOO/CuO material. The morphological characterization of the films obtained was done with an atomic force microscope, scanning electron microscopy and Energy Dispersive X-Ray Spectroscopy. And to characterize the electrical properties, cyclic voltammetry and electrochemical impedance spectroscopy were used. The experimental results obtained showed a pore size of 50-200 nm with a depth of 40 um. The cyclic voltammetry showed the characteristic resistive switching hysteresis loop of a memcapacitor showing the resistance variation ranging from 0 to 22.5 k Ω . The electrochemical impedance spectroscopy showed a capacitance value of $1.14X10^{-5}$ F for the alumina and $6.82X10^{-6}$ F for AOO/CuO material.

Keywords: Memcapacitor; Aluminum oxide; Nano pores; Nano wires; Resistive switching; Electrochemical impedance

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Chapter 1

Introduction

The accelerated technological development has been based on the miniaturization of siliconbased chips by depositing semiconductor material forming tracks with a few tens of nanometers away.(1) Currently, our society faces the challenge of creating new architectures and rediscovering materials and methods. Since the physical limits of the material will be reached very soon, it is therefore necessary to create new structures based on the manipulation of conductive molecules to manufacture new devices. The development of nano devices based on methods with high degree of manipulation looking for the use of unconventional techniques could be an opportunity to establish the foundations of the emerging technology of the future.

The fabrication of the porous structure is based on electrochemical deposition reactions. The method used is anodization in an acid medium changing the redox potential of the aluminum to form an oxide layer. The porous structure will serve as a mold to vary parameters of growth and material deposited in them. The phenomenon of self-assembly gives the system a high degree of ordering by forming nanoscale architectures and can reach micrometers. The growth variables of the system depend on the current, the potential and the concentration of metal salts. There are some experimental challenges that should be considered as the functionalization of pores. Also an important variable is the deposition of colloidal nano particle in the pores. The use of electrochemical techniques allows the manufacture of AAO membranes that have a high degree of ordering, and serve as a template to manufacture hierarchical heterogeneous structures(2). These self-assembled pore structures have served to develop photocatalysts(3), batteries (4), fuel cells(5), supercapacitors(6), and plasmonic devices (7). In addition, porous membranes serve as support material or form part of the structure of electronic devices such as resistive random-access memory (RRAM). RRAMs are a type of non-volatile memory resulting from the evolution of solid state devices that promise efficiency, energy saving and high speed. Currently, we can enjoy the benefits of magnetic random-access memory (MRAM) used in flash memory device(8). This emerging technology has been strengthened by the interest of developing multilayer artificial neural networks (ANN) and which, together with the development of powerful algorithms for artificial intelligence (AI), promise to be an attractive and exciting field of study(9–11).

In general RRAM are made up of units or cells called memristors that consist of two electors with an insulator that allows the growth of filament or a bridge between 10-20 nm long between oxygen vacancies(12). Depending on the polarisation of the oxygen vacancy configuration and the interaction with current, a more specific denomination can be given and classified as memcapacitor, memristor and meminductor(13). The methods for manufacturing small-scale memristors for academic purposes consist of the chemical or physical deposition of materials on the electrode and through the use of techniques such as lithography, laser ablation, physical vapor deposition, spattering, can generate nanometric architectures. The techniques mentioned above require vacuum conditions and are generally expensive. And therefore it has not facilitated large-scale fabrication and testing of memristors. It also allows the use of unconventional carbon-derived materials such as graphene and carbon nanotubes to be electrically deposited(14–16).

The anodination technique is typically described as the use of the electrolyte that reacts and attacks the metal anode in the electrolytic cell(17). Where interaction of the electric field with the surface of the metal allows to direct the anions of the solution carrying out a chemical reaction. This fact suggests an attractive way to manufacture nano dots, nanoparticles, nanowires, nano tubes and nanodevices(18). The use of electrochemical techniques provide molecular scaffolding to assemble various types of nanostructures on a large scale(19; 20). The versatility of the technique allows to create in situ nanometric arrays with high aspect ratios to be used in technological applications due to their high quality of thin films(21). However, the construction of memristors using electrochemical techniques represents a minority and few examples are manufactured (22; 23).

The thin film memristor works by forming a filament that grows randomly between the insulator going towards the counter electrode(24–26). The application of an electric field as part of the synthesis of the film enhances the growth of the filament in the memristor limited by the pore walls and anchored to a crystalline substrate. The ease of manufacturing 1D wire inside the pores and together with the possibility of tuning the diameter of the pores provides an opportunity to improve resistive switching compared to other techniques. One of the strategies to improve and control the performance of a memristor is an electrode that encapsulates and isolates the interior of the memristor. Copper has been one of the most used materials and serves as a top electrode allowing the study of electrochemical metallization, being the mechanism that explains the non-volatility of memory in these devices. In addition, the use of copper wires improves conductivity and in turn heat dissipation (27; 28).

There are some systems made of aluminum or titanium by others methods and uses its derivatives to build prototypes with resistive switching as the following example attributed to the morphology by a sputtering process and followed by one-step anodination and covered with TiN (29). Another prototype starts from anodination-oxidized metallic titanium with fluoridic acid by manufacturing a top Au electrode by sputtering(30). Also starts from aluminum deposited by chemical vapor deposition (CVD) by rhenium disulfide in a sulfidation reaction of ammonium perrhenate in a nitrogen reducing atmosphere and where the aluminum substrate serves as a catalyst (31). An alternative to build a memristor on a silicon substrate with a layer of silicon oxide by thermal treatment and by stoichiometric deposition of $Ge_2Sb_2Te_5$ on TiN using a standard lithography process (32). Resistive switching can also be obtained by fabricating a titanium oxide based crossbar architecture by lithography for a functional core (33). A prototype flexifle based on an aluminum electrode and a titanium oxide gel shows stability between charges with a symmetric curve (34). And used the focused ion beam on silicon nitrate. The templades builed with 150-400-nm diameter but 500-nm depth(35). The examples mentioned above are viable but somewhat difficult examples to build since the synthesis conditions make large-scale manufacturing difficult. Conventional techniques are limited by the scale, electrical consumption, and reproducibility of stable systems. Therefore, the use of electrochemical techniques is feasible due to the ease of implementation and manufacturing costs.

The interaction of the electric field and the packaging of the aluminum substrate enable the formation of the hole array template. Since the intrinsic properties of the crystalline arrangement of aluminum this process is carried out naturally with the assistance of an electric field. In the case of aluminum, this chemical reaction allows obtaining aluminum oxide, formed nanometric channels in the crystallized aluminum and in the analogue way, when using metallic amounts dissolved in the electrolyte, it is deposited inside the pores forming nano wires. The chemical treatments independent of the electric field allow modulating the pore and deposited material size, providing control parameters for a successful manufacturing. These parameters are temperature, electrolyte concentration and reaction time based on a deposition model. These parameters support an efficient, practical and low-cost method than traditional techniques for the synthesis of porous membranes.

The work presented below shows synthesis method optimized by three steps of electrochemical anodination using aluminum foil as starting material. Through a heat treatment, aluminum is transformed in crystallized aluminum sheets that will use for electrodeposition, the copper wires were made by forming arrays inserted in aluminum oxide obtaining a thin film CuO / AAO memcapacitor.

1.1 Problem Statement

The AAO have been manufactured and used in technological applications serving as support for their properties, electrical, high porosity and versatility. However, despite the efforts to obtain a reliable and low-cost method of obtaining this material, it has not been possible to extend its use. Due to the inherent difficulty of manufacturing a material with a large aspect radius with traditional methods for merely academic purposes under highly controlled conditions and not very scalable for industrial purposes. Based on processes and procedures widely reported in academia, this thesis project consists of designing and developing a synthesis method to obtain a porous material in sheets and using electrochemical techniques that can easily be scalable to develop nanostructured materials and nanodevices.

1.2 General Objective

To develop a nano-structured material with a self-assembled hierarchical architecture starting from an aluminum substrate and through the use of electrochemical techniques to manufacture a material that responds to electrical stimuli (memcapacitor) emulating traditional processes.

1.3 Specific Objectives

To use a widely accepted commercial material such as aluminum and develop a heat treatment to obtain a viable substrate.

To modify crystallized aluminum using electrochemical and self-assembly organizing techniques, reducing the difficulty of manufacture and making a reliable and reproducible process.

To characterize the films obtained using electrical and electrochemical techniques, obtaining a model that verifies the manufactured structure. Using electron microscopic and quantitative analysis techniques, to verify the morphology and composition of the manufactured material.

Chapter 2

Theoretical background

2.1 Thermoelectric properties of aluminum

Aluminum is the third most abundant element in the earth's crust. (36) Typically, this metal is used as an alloy due to its high corrosion resistance and low density in structural or cladding uses and high purity 99.999 % aluminum in electrical applications. The electrical properties can be modulated with the addition of species that dopen the structure and together with a heat treatment the crystallinity of the metal is reconstituted. (37)

Currently there are several alternatives to obtain it, depending on the quantity and quality desired. Aluminum can be synthesized by chemically reducing aluminum chloride with potassium hydroxide. At first as Hans Christian Oersted did in 1825, this process was certainly costly and it was not until Karl Josef Bayer's developments in the production of aluminum in 1888 that the process is profitable using electrolytic refining. Aluminum has a crystalline face center cubic (FCC) structure in Figure 2.1. This type of structure has a coordination number of 12 and makes it more compact than other configurations. The lattice parameter a is $4.0414x10^{-10}$ m and the closest distance between two atoms is $2.863x10^{-10}$ m. The atomic radius is $1.43x10^{-10}$ m for aluminum, which is attributed to its metallic bond which corresponds to the superposition of outer electron shells. Although

this metal has defects in its crystalline structure such as point defects with a value of $9.4x10^4$ number of defects. A direct effect of vacancies is the change in resistivity that stops aluminum at 3.4 micro ohms percent. Another defect caused by plastic deformations of the aluminum is the dislocations in response to applying a shear stress triggered the occurrence dislocations as edge, screw and the conjunction of the two resulting in a poly crystalline structure of aluminum (see Figure 2.1 a and b). Slip occurs in the densest planes as in the case of aluminum with an FCC structure and a $\{111\}$ type slip plane where the small squares represent the unit cells of the aluminum that accumulate formed the poly crystalline structure of the metal. Aluminum is a good conductor of electricity compared to copper, which is 65 % similar with a value of $3.5x10^7 \frac{S}{m}$ (38), although it depends largely on the impurities that electrical properties change dramatically. Aluminum is also a good conductor of characteristic heat of metals, which for aluminum is 237 $\frac{W}{mK}$ (39) where the vibrations of the lattices cause the phonons to propagate and cause the loss of energy between the collision of atoms comparing the conductivity of aluminum versus copper, which is 401 $\frac{W}{mK}(40)$ and 30 $\frac{W}{mK}$ (41) of aluminum oxide. In general, the stability of aluminum for electric applications occurs at temperatures above 4 K until reaching 933 K in its point melting giving a regular range to be able to use this material in applications. Also, the properties of the metal apparently remain constant at room temperature but due to the plasticity of the metal, defects in the network arise and to remedy this effect it is necessary to give an appropriate heat treatment.



Figure 2.1: Crystalline structure of aluminum. FCC unit cell: Schematic representation of an aluminum unit cell composed of three layers in a sequence A (bottom), B (middle), C (top). FCC stacking: Schematic representation of the composite stacking sequence with three stacked layers(ABCABC...). They are based on sheets of spheres arranged at the vertices of a triangular mosaic and the sheets are stacked on top of each other. a) Schematic representation of a crystal where the unit cells can be observed during dispersed crystal growth. b) Schematic representation of a crystal formed with grain boundaries and phase boundaries.

Cold rolling is a traditional technique for obtaining steel and aluminum sheets. During roll deformation, microstructures are generated where the grains forms a characteristic polycrystalline state that in turn could be modified with a parallel hot rolling process that changes the size of the crystalline structure (see Figure 2.2 A). Due to controlled dislocations the above techniques modulate grain size and boundaries. Since one of the factors to obtain nano pores is to have a crystalline smooth surface and due at the initial conditions of aluminum in sheets, it is in a polycrystalline state. The superficial defects can be reduced by the use of an annealing, reheating or recrystallization that consists of providing the best conditions for temperature and crystallization time where high temperatures cause the density of dislocations are effectively diminished (37) as we can see in Figure 2.2 B which shows schematically how the heat treatment reduces the grain limits. The thermal energy supplied in the process is translated into kinetic energy that provides sufficient energy to the aluminum atoms in the domains of the structure, resulting in a new orientation in the crystal. Due to the high chemical reactivity of aluminum with atmospheric oxygen, this causes the formation of an oxide layer that covers the rest of the metal, but due to the characteristic staking of the metal, pores are formed that connect the metal with the environment. Therefore, the compact annealing process under vacuum or in an inert argon atmosphere prevents surface corrosion. Where the development of this technique involves a series of steps such as mechanical polishing, electrochemical polishing and heat treatment to eliminate the remaining surface defects. There are few contemporary studies on the use of this technique for technological applications in aluminum foil (42). Routine vacuum annealing and comparison with argon atmosphere show 30-40 % less fatigue improvement in mechanical properties compared to vacuum annealing treatment (43). The effect on the grain boundaries by sublimition shows an increase in microhardness resulting from the impregnation of the gas on the surface and the uniform diffusion. Although this thermal process does not significantly influence the ductility and electrical resistance of the material.



Figure 2.2: Representation of the rolling and annealing process. A)Schematic representation of cold rolling to obtain aluminum sheets. During roll deformation, microstructures are generated resulting in a polycrystalline material. B)Schematic representation of heat treatment in an inert atmosphere which reduces the grain limits in polycrystalline material.

The annealing process reduces defects that give rise to microcraks, which are local deformations caused by the diffusion of gases that interact and extend to the surface, which for processes such as electrodeposition, electropolishing, favor the formation of nano architectures. Finally, the use of argon annealing in the treatment of metallic titanium and aluminum favors the redistribution of the grain boundaries, forming a uniform thin surface.

2.2 Field assisted mechanism

2.2.1 Self assemble

Self assembly (SA) is a potential tool to manipulate or direct molecules and build complex structures by forming clousters, porous networks, and arrays wires. The development of hybrid materials manufactured with nanoparticles and assisted by an external agent such as a magnetic or electric field generates self-assembled structures. The versatility of these self-assembly techniques could aid the development of integrating functional molecules into hold tracks using bottom-up and top-down techniques. Since the one-by-one manipulation of individual molecules in the present would consume excessive time and resources to manufacture molecular electronic devices, limiting mass manufacturing, therefore it is necessary to develop new and efficient techniques that facilitate the miniaturization and assembly of electronic devices.

SA is the way nature organizes matter from an atomic level to planetary scales forming clusters of galaxies. Self-assembly in nanotechnology consists of the spontaneous formation of structures made up of discrete parts that interact with each other through inter- and intra-molecular forces, maintaining a defined pattern. The SA systems study is divided into two main categories: static self-assembly (SSA) and dynamic self-assembly. This basic distinction refers to the dissipation of energy and the balance of states of the system, therefore static systems are managed under the action of an external agent until the structure is built(44). These structures are characterized by consuming energy to obtain the defined structure that remains stable under specific conditions and therefore does not dissipate energy. In contrast, dynamic structures require an energy supply to form the structures since upon cessation of the energy source these structures collapse into inconsistent sub-states.

In addition, the SA can be more specifically classified into co-assembly, hierarchical selfassembly, and directed self-assembly. This classification relates the way that discrete components associate and form structures. Co-assembly structures are those that are founded by the interaction of two or more constituent blocks and that without specific assembly of these, the structure does not occur. In the same way, hierarchical self-assembly structures are those that are organized in simple blocks by the sum of constituent units, but due to continuous interaction, multiple scale lengths originate. Finally, directed self-assembly structures are those that are driven under the direct action of external forces resulting in the self-assembled structure(45). The latter type of assembly is typical of hybrid bottom-up-meets-top-down approaches such as lithography that generate a pattern by UV light action along with the dispersion of colloids on a substrate.

Hybrid self-assembly processes involve the interaction of colloidal particles on a substrate in conjunction with physical-chemical conditions to make three-dimensional patterns. The temple self assemble consists of the crystallization of colloidal materials on a substrate through the direct action of an external force, be it of an electrical, magnetic, physical, chemical or photoelectric nature that supports an inter facial reaction and allows the material to be embedded in the work area(46). The use of a direct field in the fabrication of structures is one of the most feasible strategies since it allows modulating the dynamic behavior of the species providing a switched on/off(47). The temporal dependence of the deposition process is directly controlled by the electric field or magnetic field and thermodynamic conditions such as temperature, pressure as well as chemical factors such as concentration, solvent, reaction rate, hydrophobicity, hydrophilicity and physical factors such as charge, polarity, capillarity, Van der Waals forces, forces of attraction and repulsion, Brownian movement, phenomena of convection and agitation among others (44). The sum of the factors mentioned above provides principles for the manipulation and generation of oriented patterns allowing to control the shape, quantity and type of deposited material, and giving long range order control.

The main requirements for the self-assembly of structures in a template are the mobility of the species that supports the collision between them and irreversibly fixes the colloidal material on the smooth surface. Due to the complexity of the self-assembly system and the dependence on thermodynamic factors, the process becomes a competition between the interaction of the system itself and the influence of an external force. This means that necessarily a single force is the one that actively influences and directs the process. A clear example is the use of an electric field that in principle maintains an established direction between the electrodes(48). The correct choice of electrolyte and additives positively influence the deposition of colloidal material on the electrodes. Furthermore, the use of a direct field is a wise move and a potential opportunity to manipulate the self-assembly process. Where the direct effect of the assisted field governs anisotropy in the interactions of nanoparticles when they are confined to a surface(49). An implicit benefit of using direct field is the generation of a uniform template under the action of the electric field allowing to manufacture large areas of modified material with an excellent long range order.

Traditional dynamic self-assembly processes such as Langmuir – Blodgett, dip-coating, surface chemical reactions are used industrially and academically for the purpose of creating self-assembled materials(50), but due to little or no control offered by these techniques, it is an arduous task to obtain a homogeneous surface. One tactic to obtain self-assembled structures is through the use of AAO where the pores present an intrinsic homogeneity to the anodizing process facilitated by the electric field and at the same time allow the intrusion of colloidal materials and nanoparticles.

2.3 Electrophoresis

Electrophoresis is a physical chemical phenomenon in which suspended colloidal particles are driven by an external electro field to an electrode. An electrophoresis system is made up of an electrolyte and a capacitor with parallel plates subjected to a potential difference by a direct current (DC). The migration of the positive ions towards the anode is a process called cathodic electrophoteric deposition and similarly in the same anodic electrophoteric deposition phenomenon is carried out with the anions. Stern's model for suspended colloidal particles forming an anion cloud fluid covering the cation is widely used to explain the double layer of the particle. The diffuse double layer that interacts with the charged particle surface is described using zeta potential. The stability of charges in the colloidal medium depends on long-range forces such as electrostatic and van der Waals forces. Using electrophoretic deposition (EPD) as a deposition technique for traditional electroplatenig or electrolysis processes but a versatile way to create thin film, multilayer composites, functionalization of large areas, micro and nano patterned, hierarchical assemblies for nanodevices and nanoparticles.



Figure 2.3: Electrophoresis mechanism. A) Schematic representation of charged particles in a medium due to balanced charges in the medium known as the Stern model. B) Simplified schematic representation of the deposition model where the cloud of anions and the coions leave the Stern layer heading towards the electrodes by action of the electric field.

The charged particles are suspended by a cloud of anions (counterions) that balance the charge of the coions that interact on the surface. Where, the interaction of the counterions and coions occurs at the surface where the charges balance at the interface forming what is known as a double layer in the Stern model(see Figure 2.3 A). Due to the potential drop across of the charges a diffuse double layer is generated which is effectively described by a potential called a potential zeta. During the application of an external electric field the ions are precipitated out of the Stern layer causing navigation of the particles in the medium since the stability of the charges in the fluid is altered under the action of the electric field that pulls the opposite charges towards the electrodes(see Figure 2.3 B). To describe the influence of the electric field on the mobility of ions, the following term U_{eph} is defined, which is a coefficient of proportionality between the influence of the electric field and the velocity of the particle, giving the following equation $V_{eph} = U_{eph}E_{DC}$. The electrophoteric mobility effect using the Huckel equation to describe the mobility dependent on the dielectric

permitivity of the medium(ϵ) and the vacuum (ϵ_o), and the zeta potencial(ζ) within a radius less than the Debye layer length ($r \ll 1/k$) for the conterionic cloud motion described in the following equation: $U_{eph} = 2\epsilon\epsilon_o\zeta/3\eta$. On the other hand, to describe the mobility of the particles outside the Debye length of the conterion layer ($r \gg 1/k$) the Helmholtz – Smoluchowski equation is used: $U_{eph} = \epsilon\epsilon_o\zeta/\eta$. In addition, to describe the displacement of the particle in a finite time under the action of direct electric field in the electrophoresis the following equation $x_{DC} = U_{eph}E_{DC} + x_o$ is defined where x_o is the initial position of the particle. The models described above provide some basis for phenomenology, but in order to ensure experimental implementation, it is necessary to delimit the empirical conditions of the system, therefore the main parameters that influence the migration and suspension of the particles are presented below.(51)

In general, EPD occurs in two steps. First, there is the migration of the species driven by the electric field and secondly, the coagulation and deposition of the particles on the surface of the electrode. The main factor is the potential zeta that relates the electrostatic stability of the particles and chemical agents such as solvents, and various charging agents such as acids, bases or poly electrolytic species. Where the sum of attractive and repulsive forces that are directly influenced by the supplement of these chemical agents that prevent agglomeration and promote stable suspension of the particles. Another factor to consider is the size of the particles and the use of surfactants that allow the suspension and keep the medium homogeneous. Where sizes vary from nanometers giving colloidal solutions to stable suspension in aqueous microparticle media between 1 to 20um. The problem of sedimentation of the particles by the action of gravitational forces affects the final homogeneity of the surface for colloidal coating processes. In addition, another problem attributed to size is the agglomeration of the particles and the lack of active tensile agents that help to diminish the effects of electrostatic forces and van der Waals forces. Another factor inherent in the nature of the environment in which the species are dispersed. Also, it is the conductivity that relates the strength of the electric field. The direct application of the electric field between the electrodes causes the migration of ions that coexist in the electrolyte determining the conductivity of the suspension. The high conductivity of the medium reduces the mobility of the species since the amount of free ions reduces the zeta potential. In contrast, if the conductivity is low, the system becomes resistive and the suspension loses stability, generating an inhomogeneous layer. Due to the assistance of the electric field, the electrophoresis process has caught the attention of engineers and scientists, providing a useful tool to manufacture micro and nano structured materials.(51)

The EPD applications for the controlled deposition of nano material show a contrasting advance of traditional techniques such as nano lithography(52), separation of organic analytes(53), spin coating. EPD shows versatility by being able to be implemented with a wide variety of reagents and through the use of direct deposit pulses, and allowing the high speed of controlled particle deposition. Recent experiments using this technique have allowed the development of thin films, self-assembly of DRAM tracks(54), and multi functional, hybrid materials layers(55).

2.3.1 Anodic technique

The anodization of aluminum, is an efficient method to synthesize pores in an orderly manner at low cost, simple, minimum time consumption, being a possible candidate for the industrial manufacture of nano devices on a large scale. The superiority of this method over others has been studied for decades with a variety of reactions using different electrolytes of organic and inorganic nature forming porous structures in aluminum. Manufacturing conditions can be controlled and implemented in order to obtain defined synthesis routines that promote the reliable obtaining of nano-structured material. Also, the anodizing technique uses a wide variety of electrolytes such as oxalic acid(56), sulfuric acid(57), chromic acid(58), phosphoric acid(59), citric acid(60), among others. They effectively serve to make an oxide coating depending on the metal used for the substrate. Also, the parameters that can be controlled to favor the formation of pores such as the electrolyte concentration, the voltage supplied to the cell(61), effect of current density(62), temperature(63), pH(64), grain limits(65; 66), metal surface treatment(67), and purity effect of the substrate(68).

The oxidation process is typical for active metals such as aluminum and titanium generating nano pores (69). This is carried out under normal atmospheric conditions, forming an oxide layer that isolates the metal from the outside. When the oxidation reaction is carried out in a controlled manner in an aqueous medium with the help of an electrolyte and an electric current supplied by electrodes(70). The use of an aluminum electrode defines traditionally this process as anodizing with the use of an organic or inorganic electrolyte(71, 72). The anodizing process generates a porous structure due to the action of the electric field and surface oxidation. The disposition of the electrodes keeps the electric field directed perpendicularly to the surface that forms a layer a few microns thick. Depending on the quality of the metal used and the operating parameters of the electrolytic cell, a homogeneous surface of hexagonal pores can be obtained (61). However, the mechanism of the aluminum anodizing process continues to be studied. There are some approaches to better explain this physical chemical phenomenon. The chemical structure of the oxide barrier shows that it is largely composed of aluminum oxide and the remains of the electrolyte. Due to the addition of the electrolyte, the hybrid and amorphous structure of the oxide is not classified in the typical structures of aluminum oxide such as alpha aluminum, gamma alumina and corundum(73). In general, for simplicity, a general reaction that governs the formation of aluminum oxide and reaction of water is assumed, as is the following reaction (74).

$$4Al + 3H_2O \rightarrow 2Al_2O_3 + 6H^+ + 6e^-$$

Which is divided into two semi reactions like

$$4Al \rightarrow 2Al_2^{+3} + 6e^-$$
$$3H_2O \rightarrow 3O^{2-} + 6H^+$$



Figure 2.4: Formation of pore in aluminum. Three-dimensional schematic representation of the polarized surface of aluminum (left image). A) Side view of the aluminum surface under the action of the electric field. B) Side view of the formation of pores under the action of the electric field and the reaction on the metal surface. C) Continuation of the formation of aluminum oxide pores. D) Widening of the pores due to the use of acid on the surface as a reaction independent of the electric field.

The anodizing process is carried out when the electrolyte comes into contact with the electrodes, one made of aluminum and the other metal. Also the current generated between the plates generates a chemical reaction. In effect, the chemical reaction is carried out at the anode, generating a layer of aluminum oxide.

The formation of AAO involves the mobility of the ions in the solution and the surface polarization of the aluminum(Figure 2.4 A). The surface polarization due to the electric field between the plates marks a pattern that extends over the entire surface(Figure 2.4 B). The cellular structure formed by the electric field conducts a flow of ions that react at the bottom of the aluminum oxide tubes to form the characteristic honeycomb structure(Figure 2.4 C).Finally, one way to open the pores is with the use of 10% phosphoric acid in solution which reacted the aluminum oxide and in a controlled way allows the pore to expand (Figure 2.4 D).

In order to obtain AAO, different routines have been proposed that return some of the

parameters mentioned above. In general, this process can divide into three sub routines. The first refers to heat treatment along with surface cleaning of the aluminum substrate and electrochemical polishing. The annealing process reduces the grain limits and reduces the diffusion of gases in the solution and allows foal pores to form. The second routine is the use of an electrolyte and the current source since with the use of strong acids such as sulfuric acid it requires a voltage of 25 V direct current. When using mild acids such as phosphoric acid, they require a potential greater than 100 V. Weak organic acids such as oxalic can also be used where the required potential is 40 V(75; 76). Finally, the third sub-routine that involves reactions that do not depend on the electric field but rather on the use of chemical agents that treat the surface and modulate the range and quality of the pore. These chemical reactions are intended to remove in a controlled way the oxide formed (77). Numerous studies have been coupling these subroutines in order to obtain a reliable method for the manufacture of the pores. Processes called one step anodizing (78) involves the three subroutines mentioned in the previous paragraph. Another manufacturing process involves two anodizing steps(79) with the use of chemical etching, it turns out to be one of the most efficient and reproducible ways to obtain pores(80).

2.3.2 Electrochemical polish

The process of electro polishing refers to the superficial removal of a metal part through the use of an electrolyte and the passage of direct current through it. These electrolytes undergo electrolysis under the action of direct current and the result of the chemical reaction is manifested in the smoothest surface. The electropolishing process can be controlled by modulating the temperature, concentration and exposure time of the metal part in the bath.

Basically the electro polishing system can be divided into three regions where the interface is the limit between the electrolyte and electrode. This interface surrounds the active surface that will dynamically interact with the chemical agent favoring metal oxidation and dissolution. The chemical compound that must be basic or acidic in nature which must be prepared at a certain concentration and subjected to specific temperature conditions. Due to the viscosity of the electrolyte a concentration gradient of ions is formed that flow and interact with the surface. There are several theories that explain this complex phenomenon since this process is governed by several parameters and for practical purposes in the experimental implementation they have been proposed.(81)

An important parameter is the temperature to which a direct reaction between currentvoltage density is attributed with increasing temperature. The effect of temperature is explained by the diffusion coefficient and the rate limiting species. $D = D_0 exp(Q_a/RT)$, where Q_a is the activation energy, D_0 is an exponential pre factor, R the gas constant and T the absolute temperature. Also the limit of the current density of a species in the electrodeposition process is defined by $i_L = nFDC/\delta$ where F is the Faraday constant, C is the concentration of the ions in the solution, n is molar of the ion charges and δ is the is the thickness of the anodic diffusion layer. In addition, convection is a factor to consider since this influence dominates the process of gas diffusion in the solution and occurs at a certain limit in the current. In order to improve the process, δ is considered, since by decreasing the thickness of the diffusion layer by convection and agitation, the current density limit is increased. Other effects to take into account since they can hinder the final finish are metal surface treatments, choice of cathode, space between electrodes, bath age, and time of electropolishing.(82)



Figure 2.5: Diagrams electrochemical polish. A) Elmore's theory schematic representation showing the main parameters showing the oxidation and solvation process in the diffuse layer between the electrode and the electrolyte. B) Characteristic graph of I (V) in the electropolishing process. Four regions are distinguished: etching, passivating, polishing and piting. C) Schematic representation reducing the roughness of the surface by a current pulse.

Elmore's theory provides a vision of the phenomenon by proposing conditions that facilitate the modification of parameters for electropolishing. The first assumption is to consider the dispersion of ions by diffusion or convection from the anode. Therefore, from this first postulate the idea of modifying the conditions of temperature, agitation, viscosity and position of the electrode follows. On the other hand, the second assumption on the anode interface in the reaction is superficially saturated and therefore the concentration of the species depends on the supplied current density. By using the Nernst equation $i_L = nFD(C_s - C_b)/\delta$, the phenomenon can be accurately described since it involves F, the Faraday constant, D the diffusion coefficient, C_s ion concentration at the surface, C_b the ion concentration in bulk and δ as the thickness of the diffusion layer(see Figure 2.5 A). This equation describes a species diffusion gradient at the interface and is widely accepted for its linearity. In the same way, Elmore provides a model for the transport of mass in electrodeposition, correlating the movement of charged species in a viscous medium. Elmore concludes with the following ratio equation $r = t_0/i_0 t_0^{1/2} C_m AF(\pi D)^{1/2}$, where i_0 is the
supplied current, t_0 is electropolishing time, C_m the solubility of the metal, A the area of the anode, D the diffusion coefficient. The equations presented above are widely accepted as they describe the electropolishing phenomenon. Where the dependency of the supplied current forms the characteristic graph of I(V) and the different regions that are a fingerprint for the process are described by the voltage-current curve that is divided into four regions (see Figure 2.5 B). The first describes the dissolution of the surface oxide layer facilitated by the direct action of the current. While the second region refers to the formation of a passive layer that is characterized by the decrease of the current while the voltage increases. Similarly, the third region is characterized by the formation of a passive layer of anions that diffuses. Finally, the fourth region is characterized by the increase in voltage with an increasing and monotonous linear trend attributed to the formation of a diffusing surface layer. Depending on the electropolishing and graphic system it changes subtly but in essence the characteristic regions are maintained and therefore serve up as a guide to establish control parameters (82). The application of electro polishing is typical in the industry and is widely distributed because it facilitates the surface treatment of metal, resulting in a smooth surface (see Figure 2.5 C). The electropolishing process dramatically reduces the surface roughness under the direct action of an electrolyte and a direct current pulse. Typically this process is used to reduce the influence of corrosion of the steel since under the action of the current the active sites in the material are reduced, drastically reducing the formation of cracks. Another significant application is the reduction of the coefficient of metal friction since altering the surface directly with a chemical agent improves the useful life of the material (83). In general this process is widely used in the pharmaceutical, food, and biomedical applications when treating the surface to prevent the growth of bacteries.

2.3.3 Electrodeposition

The fabrication of nano-structures in one dimension is a potential tool that allows the controlled modification and production of nano devices. Specifically, the development of devices under the direct action of the electric field involves self-assembly processes, providing a high degree of homogeneity, allowing matter to be manipulated in a controlled way, achieving nano-structured materials with large-scale order. The versatility of the technique is revealed by its ease in implementation and ease of modification, obtaining hybrid structures. Based on a theoretical model, the appropriate conditions for electrodeposition are established, which provides a guide that ensures the reproducibility of the process, its execution in any medium-equipped laboratory, providing a useful tool for students, teachers, researchers and the industry to test different routines of assisted self-assembly in the manufacture of nano materials.



Figure 2.6: Schematic diagram for copper wire formation. Three-dimensional schematic representation of the nanoporous aluminum oxide surface formed by the hexagonal cell pattern (image on the left). A) Side view of the nanoporous surface. B) Side view of the formation of the copper oxide wires. C) Surface electro-polishing of the modified material to obtain a homogeneous surface.

The use of an electric field (EF) conducts the molecules and particles allowing the self-assembly of defined patterns on a gauge scale. The self-organization of structures is driven by the direct action of the assisted field allowing to control and choose the starting conditions(84; 85). For example, the Electric-field-assisted chemical vapor deposition is a one-step process where the influence of the field allows the deposition of vanadium oxide on an electrode achieving a high surface nano-structured material using an aerosol of vanadyl aceylacetanoat in a nitrogen atmosphere a reaction is achieved on a fluorine coated elec-

trode. The reaction is carried out in 20 min at a temperature of 530 °C with a field of 1500 $\frac{V}{m}(86; 87)$. Another example of deposition assisted by an electric field is in a synthesis reaction in a flame by hydrolysis of silicon tetrachoride. During ion migration at a temperature of 2400 °C under the action of a maximum field of 100 $\frac{kV}{cm}$ attributed to thermo ionic electronic emission (88). The above-mentioned examples require specific synthesis conditions such as high temperatures, gas phases, oxidative atmospheres, and strong electric fields in order to manipulate the species into a stable plasma. Due to the conditions, these gas phase systems require appropriate conditions to carry out assisted manufacturing and is also limited to the use of species that form stable aerosols to be used. In contrast, the EPD that involves the use of an electric field 80 $\frac{V}{cm}$ that assists in the direct deposition of nanoparticles in an aqueous medium at normal environmental conditions of pressure and temperature. EPD involves the migration of charged particles immersed in the solution where they are suspended. Depending on the nature of the charge that the particles acquire, these can be deposited in cationic or anodic. Colloidal solutions can be organic or inorganic in nature using acids or bases and the use of additives to stabilize the suspension with surfactants. Ion deposition takes place at the electrodes and this occurs in a dual manner at the cathode and anode. The half reactions occur on the surface of the electrodes, which corresponds to reduced and oxidized products. Using a template we can ensure that the deposition is given and fills the empty spaces in the template (see Figure 2.6) where the process begins with the use of the template and under the effect of the electric field the pores are filled as we see in Figure 2.6, going from A to B. Finally, in the process, a surface etching is finished using electro polishing to get rid of the excess material obtaining a homogeneous film see Figure 2.6 C. The EPD process involves the growth of the cast with a certain speed of formation that depends on the initial conditions and the growth time (89; 90). Therefore, in order to implement a reproducible method, a deposition model is adopted that accurately describes the linear growth of the cast. Also there are some theoretical models that describe the formation of pores and the interaction of the electric field (91-93) but due to the complexity of the process, a model is necessary that relates the real manufacturing conditions such as magnetic stirring, species concentration, supplied voltage, and reaction time.



Figure 2.7: Model setup diagram. Simplified schematic representation of the modeling constant voltage electrophoretic deposition from a stirred suspension. It is formed by two metal electrodes arranged in parallel with a space between them. The resulting arrangement is immersed in a solution under magnetic stirring contained in a glass beaker.

The following section relates the use of the "Modeling Constant Voltage Electrophoretic Deposition from a Stirred Suspension" by Gonzalez-Cuenca et all. 2000, which consists of the formation of a layer of cast or coating on one of the electrodes under the action of a constant voltage in an acoustic medium assisted by stirred suspension Figure 2.7. The EDP model considers two phases, the first is the cast and the second the suspension. The electric field formed between the plates is considered uniform and the field lines are perpendicular to the surface of the electrode and the field lines that bend at the edges of the electrodes are ignored. The well stirred suspension provides stability to the particles until they are sent to the electrodes. The following equation, $\delta = \frac{V_o\phi_{s,0}}{S\phi_c} \left[1 - exp\left(\frac{-S\mu\Delta Vt}{V_od}\right)\right]$ (94), relates the potential supplied to the cell with ΔV , $\phi_{s,0}$ suspension concentration, ϕ_c the cast packing factor, μ the mobility of a charged colloidal particle, S surface of the electrode, V_o volume of the solution and d the distance between the electrodes. In effect, the model presented above presents the time-dependent growth of cast, however, in order to use this equation for experimental purposes, only a finite time is used where the linearity of the model takes place.

The utility of the model provides controbility to make wires in the porous substrate. Due to the ease of controlling the diameter of the pores with the help of an acid, it provides one more control parameter in the template manufacturing routine that depends on the exposure time. In the same way, using the Gonzalez-Cuenca (2000) model, the amount of deposited material can be controlled in a better way, being able to manipulate the initial conditions in favor of obtaining the desired material.

2.4 Resistance random access memory

Memory devices based on resistive switching hold a promise of energy efficiency, non-volatile memory, and good performance. This new generation of memories is called resistance random access memory (RRAM) and its operation is attributed to the formation of a physical bridge through the oxygen vacancies between two electrodes by the action of electric current generating a characteristic memristive switching. The term memristive describes the resistance behavior inherent to the passage of the directed current in the dielectric that allows a flow of ions, phase change and spin transfer torque. The physical change at a nanometric scale in the material allows a characteristic switching that shows a reversible process and for practical purposes can be used for data storage.

In general, RRAMs are composed of a top and a bottom electrodes with an insulating material in the middle of the cell. The insulating material undergoes a physical-chemical change during the passage of the current that, depending on the material and the architecture in which it is assembled, has two states of resistance. The low resistance state is called as LRS/on state and for the high resistance state as HRS/off state corresponding to the conductance under the action of the current. The voltage needed for the change from HRS to LRS is called V_{set} and the return voltage between LRS to HRS state is called V_{rest} . There are two types of switching that depend on the intrinsic polarity of the system, being unipolar

and bipolar for a set and reset cycle (see Figure 2.8 C)(12; 95).



Figure 2.8: Switching mechanism bipolar. A) Schematic representation of the bipolar switching mechanism for aluminum oxide. The red lines represent the random conduction path between electrodes. B) Schematic representation of the bipolar switching mechanism for copper oxide. The red lines represent the fixed conduction path between electrodes on the surface of the wire. C) Schematic representation of bipolar switching mechanism in the characteristic graph of V(I) in cyclic voltammetry.

The cell formed by two electrodes and an insulating material under the action of the current goes from an initial pristine state to an active state where the formation of a conductive filament between the electrodes begins. This filament is attributed a redox process and nanoionic transport as seen in Figure 2.8 A and B where the red line represents the conduction between the electrodes. In principle the conduction between the aluminum oxide is random but due to the copper oxide the conduction is more stable. The apparent connection between the top and the electrode button is cataloged as LRS and under the action of a voltage V_{rest} it reaches a state HRS and similarly under the action of a V_{set} it returns to a state LRS(96). The electron transport process attributed to resistive switching depends on conduction carriers in the dielectric material and on properties of the material

such as trap level, trap spacing, trap density, relaxation time and the density of conduction states. In addition, different conduction mechanisms are attributed and among the best known we have Schottky emission, Fowler-Nordheim, Poole-Frenkel, Ohmic conduction ionic conduction (96). These mechanisms attempt to describe the complexity of the conduction of valence change resistive switching where it relates the dependence of temperature, applied electric field, voltage polarity and other factors such as construction, heat treatment, material properties, and environmental conditions in their operation. The operating ranges of the RRAMs are between ranges less than 3 V and 2 mA with an operating cycle of 10^6 set / reset reaching reading cycles between 10^{12} cycles. The architecture of RRAMs composed of two electrodes and a layer of memory material in the middle of the assembly (Metal / Insulator / Metal) provides a considerable number of fabrication options. First, the metal for the electrode bottom and top can be any but depending on availability and the manufacturing technique they are at the discretion of each researcher, such as Ag, Au, Pt, Nb, Ru, W, Mg, Al, Si, Ti, Zn, Fe, Co, Ni so on. Secondly, the insulating material can be organic or inorganic, which for the convenience of the manufacturing method results in the oxidation of the metal giving rise to binary or ternary metal oxides dependent on dopants and residues of chemical agents in the synthesis. In the same way, the storage medium can be composed of small molecules, polymers, nitrates, chalcogenides and carbon derivatives such as oxidized or reduced graphene(8; 97). However, since the phenomenology of the switching process occurs at the nanometric scale, the characterization of these materials is limited to the use of imaging, mapping, spectroscopic, in situ characterization, and electrical techniques that allow the evaluation and study of the switching mechanism (98).

The concept of memristor refers to the visualization of the pinched hysteresis loops, which is the plot between voltage and current. Recent advances have recognized the RRAMS as the fourth passive element in the circuit called the memristor. The term memristor encompasses a large amount of concepts, fundamentals and theory provided by Leon Chua in 1971 that served as an impetus for the study and implementation of unconventional computing and logic devices today(13)(99-105). Despite coupling manufacturing routines of integrated circuits (IC) strengthened by a silicon-based industry, a deep knowledge of the switching mechanism has not yet been achieved to be able to massify this new generation of technology. The difficulties inherent in scale limit the characterization, innovation and development of new prototypes. In general, it is extremely difficult to locate tiny switching in thin sheet materials since the growth of the filament is random but directed between the electrodes. The location of the reaction area is essential to be able to study and modify the parameters to obtain functional devices based on resistive switching. Bottom up manufacturing processes based on self-assembly processes to obtain RRAM are a powerful tool since they allow to obtain nano-structured materials in a simple way. The advantage of manufacturing bottom electrode and insulator layer blocks provides a basic methodology that can be exploited to be added into IC systems. The growth of complex materials assembled by the assistance of an electric field provides ease of manipulation that traditional techniques do not provide. Obtaining nano pores in aluminum by the direct action of an electric field generates a template that serves as a guide in deposition processes and due to the high degree of ordering of the material, pattern registration can be made, thus achieving crossbar architectures. Based on the specific construction of the aluminum oxide membranes, different architectures can be coupled in three dimensions, giving rise to functional stacked point arrays such as 3D horizontal stacking RRAM, $VRRAM_1$ and $VRRAM_2(106-110)$. In addition, the strengths of these assemblies are reinforced by lateral scaling, higher cell efficiency and high pillar density. The effective self-assembly technology integration process has been exploited using anodized aluminum oxide membranes. There are some examples manufactured with the use of AAO being a valid solution to generate the starting pattern for RRAM along with other modification techniques (12; 111; 112). There are also other examples of the use of AAO is the electrochemical deposition of the insulating material inside the pores and finally we have an example of bottom up fabrication by generating depositing a conformal stack by atomic-layer-deposition inside the AAO pores forming crosspoint array of vertical TiN /

TiO2 / by block copolymer self-assembly (113).

In summary, recently different approaches have been reported to integrate emerging self-assembly technology in porous materials, in devices traditionally produced by the semiconductor industry. Due to the limit in the operating range of conventional lithography techniques, it has not been possible to reach ranges less than 20 nm. Therefore, the manufacture of devices implementing self-assembly is still under development since it involves a combination of top-down and bottom-up methods for the development of devices with materials with high density properties. The combination of these techniques will allow to exploit the benefits of methodologies assisted by an electric field and the modulation of selfassembly processes in order to take advantage of the inherent assisted simplification and the reduction of manufacturing costs.

Chapter 3

Methodology

3.1 Reagents and solutions

All solutions were prepared with distilled water (DI) and ethanol (C_2H_5OH) . Commercial kitchen aluminum foil 99.99 % was used. Potassium dichromate $(K_2Cr_2O_7)$, Copper (II) sulfate pentahydrate $(CuSO_4.5H_2O)$, Phosphoric acid (H_3PO_4) , Oxalic acid $(C_2H_2O_4)$, Boric acid (H_3BO_3) , Hydrogen peroxide (H_2O_2) , Sulfuric acid (H_2SO_4) .

3.1.1 Synthesis of chromic acid

The synthesis of the acid is carried out using potassium dichromatomate, hydrogen peroxide (10 Vol) and sulfuric acid (98 %). In order to obtain a 1.8 % solution of chromic acid, Potassium dichromate of 1.12 g is used with 0.73 ml of sulfuric acid and an excess of 33 ml of hydrogen peroxide. The reaction is violent and emits gases, it is recommended to use an extractor chamber and protective equipment. Hydrogen peroxide governs the reaction and is added dropwise.

The reaction follow the equation: $K_2Cr_2O_7 + H_2O_2 + H_2SO_4 \rightarrow 2H_2CrO_4 + K_2SO_4 + 1/2O_2$

3.1.2 Reagents and amount of reagents

The amount of reagents used belong to the electrochemical process based on cell with a volume 50 ml

- Oxalic acid solution of $0.3 \text{ mol}/m^3$ for an odization process
- Boric acid 0.25 mol/ m^3 and Copper (II) sulfate pentaydrate 0.5 mol/ m^3 for eletrode-position
- Phosphoric acid of 10 wt% for opening process
- $\bullet\,$ Chronic acid 1.8 wt % and phosphoric acid 6 wt % for etching process
- Phosphoric acid 10 ml, distilled water 15 ml and ethanol 25 ml for electropolishing process

3.2 Equipment and materials



Figure 3.1: Setup home made. The equipment consists of a beaker, a heating plate with magnetic stirring, a glass sample holder, and a source of direct current.

In the first place, for the thermal process, a tube furnace is needed that reaches a temperature of 500 $^{\circ}$ C and provides a controlled atmosphere that for our purposes is argon. Second, the

equipment required to carry out the experiment is an electrochemical cell. The cell consists of a heating plate with magnetic stirring. The container is conveniently made of a beaker, being a glass resistant to sudden changes in temperature between heat and cold. The volumetric beaker is 50 ml and the electrodes are held with the help of a support and clamp holder (see Figure 3.1). The electrodes are connected to the power source with smooth clamps that prevent deterioration of the aluminum foil. The sample holder is made of acid resistant glass or plastic.

3.3 Procedure

3.3.1 Pretreatment



Figure 3.2: Temperature ramp for annealing process for aluminum foil. The thermal process is carried out in an inert argon atmosphere for a period of eight hours, reaching a maximum temperature of 450°C.

The annealing process was carried out in a quartz tube furnace. The starting material is 99.99 % commercial aluminum foil with a thickness of 1mm and an area of 0.001 m^2 . The Al foil samples were dipped with acetone and alcohol separately to avoid polar and non-polar contaminants from adhering to the surface. The samples were then placed inside the quartz tube. A temperature ramp is programmed for the process. As shown in the Figure 3.2, the degassing process takes one hour to reach 450 ° C with a slope of 0.125 °C/s. After

45 minutes of the process, the chamber is saturated with argon gas at a flow of 0.5 ml/s. The recrystallization process takes around four hours and involves a phase change where the grain boundaries of the aluminum vanish until new and larger crystals are formed. Finally, the process ends with a decrease in temperature at the rate of 0.0417 $^{\circ}$ C/s until reaching room temperature.

3.3.2 Aluminum oxide template fabrication

The aluminum foil pretreatment are immobilized on a support to be the working electrode. For the sacrificial electrode, use a piece of aluminum with a thickness of 50 mm at 99.99 % which is previously cleaned and polished. The separation between plates is 0.005 m. The reactor is kept under constant stirring 250 rpm and at constant temperature.



Figure 3.3: Schematic representation of procedure. The graphic summary shows the morphological and structural change of aluminum. The continuous process in manufacturing is outlined along with the reactions and processes. The main processes are annealing, electropolishing, chemical etching, electrodeposition and anodic process.

The electrochemical polishing process is carried out with an aqueous solution of phosphoric acid: alcohol: water at 20:50:30 Vol. The polishing solution is heated to 45° C and the voltage between the electrodes is 20 V and the working time is 120 seconds. The surface is then cleaned with deionized water until the acid residue is completely removed. The anodizing process is carried out in a 0.3 mol/ m^3 oxalic acid solution and the crystallized aluminum for 180 seconds and then it is cleaned with abundant water. As an intermediate step, the aluminum oxide surface is chemically treated by immersing it in etching solution at a temperature of 65 °C for 10 minutes and then the surface is cleaned with sufficient water. For the process, the second anodination process is carried out under the conditions mentioned above but at a temperature of 5 °C for 45 seconds and the third step at room temperature for 45 seconds. Finally, it is immersed in a 10 % phosphoric acid solution for 360 seconds and superficially cleaned with abundant deionized water.

3.3.3 Copper oxide wire fabrication

The galvanostatic deposition process is carried out with the copper sulfate solution. Previously, the solution is heated to a temperature of 45 °C and a constant stirring of 250 rpm is maintained. The porous aluminum oxide substrate is connected to the negative pole of the direct current source and is subjected to a voltage of 5 V for a period of eight seconds. Finally, the remains of the copper sulfate solution are cleaned with plenty of water and the sample is stored in a container with a desiccant such as silica bag.

3.3.4 Reaction of decomposition

The following equations show the decomposition process that aluminum oxide undergoes by the action of an acid. In general the decomposition reaction results in water, aluminum ions and molecular oxygen. Experimentally this reaction is verified by the diffusion of gases in the form of bubbles when submerging the foil in the solution. Reaction decomposition (Opening)

Consider a mono protonation for acid phosphoric

$$4H_3PO_4 \to 4(H_2PO_4)^{1-} + 4H^+$$

$$Al_2O_3(s) + 4H^+(aq) \to 2Al(aq) + 2H_2O(l) + 1/2O_2(g)(7)$$

Consider the total protonation for chronic acid

$$\begin{split} & 2H_2CrO_4 \to 2(CrO_4)^{2-} + 4H^+ \\ & Al_2O_3(s) + 4H^+(aq) \to 2Al(aq) + 2H_2O(l) + 1/2O_2(g) \end{split}$$

3.3.5 Process Flow Diagram



Figure 3.4: Representation of procedure. The graphic shows the process. The main processes are annealing, electropolishing, chemical etching, electrodeposition and anodic process.

3.4 Manufacturing details

The manufacturing process involves a set of procedures and reactions in order to obtain a reliable and reproducible product. This section will detail the main intermediate steps that improve manufacturing and determine the final state of the modified material. The two main types of reactions must be distinguished: the first is the reactions dependent on the electric current and the second is those that are independent of the current and are governed by surface chemical reactions.

Reactions dependent on electric current involve all the thermodynamic factors of the electrolytic cell such as temperature, concentration of chemical reagents, agitation, and reaction time. Another factor that influences the reaction is the choice of materials that support and contain the aluminum foil since the chosen material must meet some basic requirements such as resistance to sudden changes in temperature, resistance to strong acidic media and not electrically interacting with the sample (see details in Figure 3.5 B). For convenience and to avoid errors in the method, a standard sample holder composed of glass plates was manufactured at a defined distance according to the pre-established calculations with the deposition model. On the other hand, the choice of the counter electrode or sacrificial electrode is based on the mechanical resistance of the aluminum foil and the influence of a common ion in the reaction. A detail of this electrode is that it must be mechanically and electrically polished before each procedure since the reagent residues from previous sessions can compromise the product obtained. In order to facilitate and improve the reproducibility of the method, the positions of the sample holder will be fixed as can be seen in the Figure 3.5 A. Depending on the volume of the cell and to maximize the manufacturing area, the extent to which the sample holder should be submerged should be established, leaving adequate space for magnetic stirring. For convenience, the cell material is temperature-resistant pyrex glass or borosilicate glass.



Figure 3.5: Setup home made. A) Schematic representation of the complete equipment. B) Schematic representation of sample holder with front and side view details.

On the other hand, we have the independent reactions of the current that is to say they are chemical reactions. Therefore these reactions depend specifically on the degree of purity of the reagents, reaction time and temperature. In general the reactions that govern this procedure are decomposition. To facilitate manufacturing, it is necessary to have all the solutions prepared at the optimum concentration and temperature conditions according to the volume of the work cell. The solutions required for manufacturing have a useful life time since, despite preparing and storing them correctly, they lose effectiveness as they age. An important detail is the surface cleanliness of the sheet since it absorbs reagents and can generate defects. Cleaning consists of washing with distilled water at considerable pressure without damaging the aluminum foil and also leaving the film immersed in distilled water as an intermediate step between processes.

3.5 Characterization techniques and equipment used

3.5.1 Scanning electron microscopy and Energy Dispersive X-Ray Spectroscopy

Phenom Pharos Desktop scanning electron microscopy (SEM) is a scanning electron microscope that has a light optical magnification of 20-134x and an electron optical magnification range of 200-1000000x. The resolution of the equipment is given by two detectors, one of secundary electrons at 2.5 nm and the other of back scatter detector at 4 nm that work from 3 kV to 15 kV. The equipment has several vacuum modes, being able to go from medium to high vacuum for greater resolution. In addition, the equipment has an EDS detector. Elemental analysis is the fundamental application of EDS energy scattering X-ray spectroscopy, also called EDX or XEDS. With EDS, vital composition information is added to electron microscopy images, giving you a combined morphological and chemical overview of your sample. Finally, the sample size is Up to 25 mm diameter and the sample height Up to 35 mm.

The SEM is a microscope that uses an electron beam instead of a light beam to generate a high-quality image. The microscope generates a scan of electrons that are controlled by a specific electric field through the use of reflector coils that control the electron beam. The scanning process begins with the emission of electrons by a typically tungsten cathode filament called an electron gun.(114) The generated electron beam passes through a pair of scanning coils in the column that deflects and modulates the electron beam. The vacuum conditions properly improve the quality of the images since the vacuum prevents diffraction and reflection processes of the electron beam with molecular species that make up the air.(115) The interaction of the incident beam with the sample generates many interactions, producing secondary electrons, back scattered electrons, x-rays, Auger electrons so on. Mainly, the SEM as standard equipment has secondary electron detectors that work locally on the surface of the sample in an energy range of 50 eV, providing a resolution of 1 nm.(116) On the other hand, we have the second detector of back-scattered electrons(BSE) that result from the reflection of the first electrons and propagate in an elastic scattering way. The BSE are much more energetic than the SE because the intensity of the BSE signal is strongly related to the atomic number. Characteristic x-rays are also generated which serve to measure the Energy-dispersive X-ray spectroscopy or Wavelength-dispersive X-ray spectroscopy. The use of x-rays in spectrometry is used to measure the abundance of elements in the sample by giving a map with the relative distribution of each element.(117)

3.5.2 Atomic force microscopy

The NaioAFM is the atomic force microscope with a scan range of 70 um and a scan height of 14 um. The integration of a modern flex-guided tip scanner, XYZ sampling platform, camera, active vibration isolation table and airflow protection. The sample size is 12 mm and 3.5 mm in height in addition to the sample stage positioning range 12 mm in X and Y. This equipment has a top view camera 2x1.5 mm field of view with 2 um and 5 Mpixel color CMOS optical resolution with digital zoom. Also the equipment has a side view observation 5x5 mm field of view with 1.3 Mpixel monochrome CMOS. The microscope has a 4 mm linear motor continuous or step by step approach. The equipment has several imaging modes such as static force, dynamic force, phase contrast and a spectroscopy modes such as force-distance, amplitude-distance and voltage-distance modes. The software used for the analysis of the AFM data was WsxM which is a third party. WSxM is the recognized, powerful and easy Windows application for data acquisition and processing in scanning probe microscopy (SPM) and a wide range of microscopy or spectroscopy techniques.(118)

AFM is a scanning probe microscopy technique using a cantilever which is a tip to scan over a sample surface. The approach of the cantilever on the surface causes a deflation by forces of attraction which are measured and stored allowing to measure and characterize the topography of the sample studied. The forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces. The forces between tip and sample can also be used to change the surface of the sample in a controlled way. Examples of this include atomic manipulation, scanning probe lithography and local stimulation of cells.(119) The way to measure the deflation of the cantilever is by using a laser beam that, together with a position-sensitive photo diode, determines the value resulting from the change in position, allowing the measurements to be saved in order to map the studied surface. The generation of the topography image is given by gathering all the relative position data of each point collected in the surface scan. Through the use of precise piezoelectrics, the range of motion of the cantilever is adjusting to be able to map the surface and where the raster scanning software gathers and stores the rotations and translations suffered in the scan of the image.(120) There are two main types of AFM data acquisition modes. The first is the contact mode, which consists of dragging the cantilever over the sample and over the contours to measure the deflection of the cantilever directly and thus to give a feedback penalty to keep the tip in a constant position.(121) Finally, we have the touch mode which consists of keeping the tip of the probe close enough to the sample so that the short-range forces become detectable while preventing the tip from adhering to the surface. In tapping mode, the cantilever is moved to oscillate up and down at or near its resonant frequency. This oscillation is commonly achieved with a small piezoelectric element in the cantilever bracket.(122)

3.6 Electrochemical measurement

Electrochemical studies involve cyclic voltammetry, chronoamperometry, and impedance measurements that analyze the biosensing ability of materials. Electrochemical measurement is carried out using the aluminum oxide substrate and the copper oxide modified substrate. The electrolyte used is $1 \text{ mol}/m^3$ NaOH at normal temperature and pressure conditions. The measuring instrument used was a Metrohn Autolab PGSTAT302N spectroeletrochemical station. The measurement system consists of three electrodes, one working for the modified foils with 0.025 cm^2 , the second electrode is a platinum electrode and a calomel reference electrode. The cyclic voltammograms were obtained at $100 \frac{mV}{s}$ scanning rate. Electrochemical impedance spectroscopy measurements were performed at open circuit potential in 1 mol/m³ solution of NaOH. The frequency ranges for the measurement vary from 10^{-1} to 10^5 with an amplitude of 5mV. The EIS parameters were calculated by fitting the experimental results creating an equivalent circuit. The anodic and cationic polarization curves were recorded with a scan rate of $10 \frac{mV}{s}$.

3.6.1 Cyclic voltammetry

Cyclic voltammetry (CV) is a type of electrochemical measurement. When performing a cyclic voltammetry measurement, the potential of the working electrode increases linearly as a function of time. CV are carried out in a solution in a cell equipped with electrodes. The solution consists of the solvent in which the electrolyte is dissolved and the species to be studied. The standard cell employs a cell equipped with three electrodes: reference electrode, working electrode, and counter electrode. Also, the counter electrode can be of any material that conducts the current easily, does not react with the solution. The reactions that occur on the surface of the counter electrode are not important as long as the current continues to conduct through the electrode. To maintain current flow the counter electrode will often oxidize or reduce together with the solvent or electrolyte. CV can be performed using a variety of solutions where the choice of solvent for cyclic voltammetry takes into account some requirements, such as that the solvent must dissolve the analyte and high concentrations of the electrolyte and soluble. It must also be stable in the potential window of the experiment with respect to the working electrode. It must also be pure to avoid interference. The electrolyte ensures good electrical conductivity and minimizes the potential drop to register oxidation or reduction potentials respectively.(123)

3.6.2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) involves measurement of the intrinsic properties of the impedance of an electrochemical system over a range of frequencies using a sinusoidal source such as alternating current. This technique measures the impedance of a system over a range of frequencies showing the dependence of the particular frequency of materials and revealing storage properties, dielectric properties and energy dissipation. Typically, the data obtained by electrochemical impedance spectroscopy are graphically expressed in a Bode plot or a Nyquist plot.(124) In general, impedance is the opposition of an electrical system to the flow of electrical current and expressed as commonly in units of ohms. Impedance is the opposition to the flow of alternating current (AC) in a complex system made up of energy dissipation (resistance) and energy storage (capacitor) elements and a damping element (inductor).Composite materials or systems exhibit multiple phases that commonly show a universal dielectric response, so dielectric spectroscopy reveals a power law relationship between the impedance and the frequency of the applied field. EIS reveals information about the reaction mechanism of an electrochemical process and the different reaction steps will dominate at certain frequencies, and the frequency response displayed by EIS can help identify the rate limiting step.(125)

Chapter 4

Results and Discussion

4.1 Scanning electron microscopy and Atomic force microscope for porous aluminum oxide membrane

The Figure 4.1 shows a SEM image taken from the aluminum oxide template showing the porous structure synthesized by three anodization steps using oxalic acid.



Figure 4.1: Images of a the surface of typical AOO fabricated in $0.3 \text{ mol}/m^3$ oxalic acid under three steps of anodization at 40 V. A) SEM imagen and B) A comparative image of AFM with area of 5 um x 5 um and SEM technique.

This figure shows the image of a porous structure together with an AFM image of the same manufactured sample. In order to corroborate the distribution and homogeneity of the obtained nanostructures, a sampling of the template made with AFM was carried out. The surface topography of the samples was examined using the contact mode, thus determining the homogeneity of the pores. The Figure 4.2 shows the different zooms in order to have a vision of the extension of the pores and their homogeneity. The different areas studied generally have a good distribution and, as can be seen in each sub-figure A,B,C,D, it is made up of pores. The figure of SEM mentioned above reveals a pattern formed by nano-sized objects attributed to the action of the electric field on the surface, where the circular shape of the pores shows a regularity, forming the typical Moire pattern.(126).



Figure 4.2: AFM analysis for AOO fabricated in $0.3 \text{ mol}/m^3$ oxalic acid under three steps of anodization. The figure shows the different consecutive zooms going from a sample area of 20 um x 20 um up to a sample area of 2 um x 2 um. The sequence of increasing the zoom between subfigures is as follows A,B,C and D. A) Area of 20 um x 20 um B)Area of 10 um x 10 um C) Area of 5 um x 5 um D) Area of 2 um x 2 um

The physical interpretation of the Moire patterns corresponds to the interference of

the electron waves of the SEM on the nanostructured surface. Where the diffraction of coherent spherical waves in an interplanar space of the aluminum oxide resulting in a circular pattern contained in the grain boundaries with a particular orientation being characteristic of polycrystalline materials such as aluminum.(127; 128). In an analogous way, we can compare the AFM image with a 5 um x 5 um area and a section of the SEM image. This comparison allows us to better analyze the structure of the surface of the AAO sample allowing us to figure out the texture of the pores that goes up to 186.77 nm represented in the side bar of Figure 4.1 B.



Figure 4.3: AFM analysis for AOO of 2 um x 2 um fabricated in 0.3 mol/ m^3 oxalic acid under three steps of anodization. A) AFM analysis. B) The size of the pores and their diameter. C) Histogram of pore distribution. D) Three-dimensional model of pores.

The Figure 4.3 shows an image in part A of AFM of a 2 um x 2um area composed of pores with a diameter between 50 nm to 200 nm as verified in the cross section taken in Figure 4.3 B. The measurement of pores are pores diameter 119 nm, 89.1 nm, 52 nm, 208 nm

corresponding to D1, D2, D3 and D4. In the same way, making a count of the number of pores we have a value of 22 in this area and that is extrapolated to an density of $1.1x10^{15}$ nano pores per m^2 but the obtained value transformed is $1.1x10^{11}$ nano pores per cm^2 . In the same way, when comparing this density with the available literature. We have a value of $4.6x10^{10}$ nano pores per cm^2 for High-Aspect-Ratio and Highly Ordered systems(129). In addition to corroborating the value of the density obtained by Fabrication of highly ordered nanoporous alumina membranes: Probing microstructures by SAXS, FESEM and AFM, which is $7.12x10^9$ nano pores per $cm^2(130)$.

In addition, in part C of the same figure, the diameter distribution and the number of pores can be visualized. Statistical values are presented in Table 4.1. The bimodal distribution is skewed by a greater number of pores smaller than 50 nm and there is a smaller number of pores with a diameter between 75 nm and 300 nm.Based on the AFM analysis in the Table 4.1, it was possible to determine the average value of the pore radius, which is 20.33 nm. Finally, we have a three-dimensional model in part D of Figure 4.2 which shows a regular distribution formed by pores.

Radio [nm]	Number of pores
319.49	1
255.59	1
223.64	1
207.67	1
159.74	2
95.85	1
79.87	1
51.12	1
49.52	2
47.92	1
43.13	2
41.53	1
39.94	2
23.96	2
15.97	3
Total pores	22

Table 4.1: Histogram information for aluminum oxide nano pores distribution. Average pore radio is 20.33 nm obtained from AFM data in table

4.2 Scanning electron microscopy and Atomic force microscope for nano-copper oxide wires

On the other hand, we have Figure 4.4 A which is a SEM imagen of the template modified by the electrodeposition technique. The action of the electric field favors the deposition of copper oxide within the porous structure.



Figure 4.4: SEM and AFM images of a the surface of typical AOO/CuO modified by electrodeposion of copper sulfate solution under pulse galvanostatic process with 5 V. A) SEM imagen of AOO/CuO and B) A comparative image of AFM and SEM technique of AOO/CuO.

The spherical shape of these islands on the porous substrate can be seen in the image. Due to the density of the contrast, two gray tones can be differentiated, where light gray refers to copper oxide and the other refers to the aluminum substrate. The compositional contrast is due to the signal intensity generated by different areas that chemically have a defined composition and that proportionally have an average atomic number. The region with a high average atomic number will appear bright relative to regions of low atomic number. Therefore, based on the manufacture and the architecture developed, we know aluminum with an atomic number of 13 and copper with an atomic number 29 will present a compositional contrast resulting in two shades of gray. Where the light gray is attributed to the copper wires and the dark gray to the aluminum oxide template. The SEM imagen mentioned above shows the surface accumulation of copper oxide going from small clusters to 5-10um in size. In Figure 4.4 B, we have a comparison of a section of the SEM image and an AFM measurement with 5 um x 5 um which allows us to figure out the relative height of the islands that goes up to 5um in the sidebar. Next we have Figure 4.5 A which is an AFM image of a 5 um x 5 um area corresponding to copper oxide wire in the aluminum oxide pores.



Figure 4.5: AFM analysis for AOO/CuO template modified with area of 5umx5um. A) AFM analysis. B) Histogram of wire CuO distribution. C) The size of the wires and their length.

In the AFM image, we can see the scattered pores over the entire surface and small diffuse lines of the cantilever when colliding with the wires. To ratify the measurements of the wires, three cross section were taken and they are found in part C of Figure 4.5. In general, the diameters measured are 50 nm but the heights range from 50 nm, 30 nm and 35 nm corresponding to cut C_1 , C_2 and C_3 . The distribution of the wires is described in Figure 4.5 B with a number of 94 wires in an area of 25 um^2 . The unimodal distribution of the graph is accentuated in values than 10 nm of radius for the copper wires and the detail of the data is found in table 4.2.

Height [nm]	Number of wires
65	1
32	1
27	1
17	1
16	1
14	1
13	1
12	1
10	2
9.6	1
9	2
8.4	6
7.8	2
7.2	2
6.6	3
6	3
5.4	1
4.8	3
4.2	4
3.6	7
3	8
2.4	10
1.8	8
1.2	6
0.6	18
Total wires	94

Table 4.2: Histogram information for copper oxide wires distribution. Average of wire height is 5.20 nm obtained from AFM data in table.

4.3 Energy Dispersive X-Ray Spectroscopy

The chemical composition of the studied materials was qualitatively characterized using EDS. The Figure 4.6 B shows the pattern corresponding to the aluminum oxide membrane modified by the deposition of the copper oxide wires. Figure 4.6 B for site 1 shows oxygen (K line, 0532 keV) and aluminum (K line, 1.56 keV). In the same figure for site 2 it shows oxygen (K line, 0.532 keV), aluminum (K line, 1.56 keV) and copper (L line 1.096 keV and K line, 8.979 keV). The data obtained is compared using a Handbook of x ray data(131). The stoichiometric composition could not be weighted based on the EDS data due to the interaction of the beam with the heterogeneous surface, but if the quantitative composition for site 1 is estimated, there is an aluminum percentage of 81.1 % and 18.9 % oxygen (take from table 4.3). In addition, the quantitative composition of site 2 has a percentage of aluminum of 23.9 %, oxygen 72.3 % and copper 3.7 %(take from Table 4.4). In summary, chemical micro analysis of modified aluminum oxide template by copper oxide deposition has been confirmed.



Figure 4.6: Energy Dispersive X-Ray Spectroscopy for aluminum oxide membrane modified by the deposition of the copper oxide wires. A) SEM imagen with spot location for site 1 and site 2. B) X-Ray spectrum for site 1 and site 2.

Element number	Element symbol	Element name	Weight percentage concentration	Error
13	Al	Aluminium	81.1	0.1
8	0	Oxygen	18.9	0.1

Table 4.3: X-Ray Spectroscopy for site 1

Element number	Element symbol	Element name	Weight percentage concentration	Error
13	Al	Aluminium	23.9	0.0
29	Cu	Copper	72.3	0.4
8	0	Oxygen	3.7	0.7

Table 4.4: X-Ray Spectroscopy for site 2

4.3.1 Cyclic voltammetry



Figure 4.7: Cyclic voltammograms of the foils in a $1 \text{ mol}/m^3$ NaOH electrolyte. A) Cyclic voltammetry for anodic template. B) Cyclic voltammetry for modified template by copper deposition

Figure 4.7 shows the cyclic voltammograms of the immersed foils in a 1 mol/ m^3 NaOH electrolyte where part A is for the aluminum oxide sample and part B corresponds to the template modified by the deposition of copper oxide. The successive cyclic voltammetries were carried out in a potential range from -0.2 to 0.8 V with a scan rate of $10 \frac{mV}{s}$.

The characteristic CV curves of AAO reflect the typical electrochemical behavior when interacting with the electrolyte. The loop is corroborated with the characteristic form of the state equation of potassium ion-channel memristor. Where the sodium ion channel in the generic voltage-controlled memristor nerve axon. In a similar way, the behavior of the generic memristor translates into a functioning similar to that of a nervous membrane.(101) The cathodic current follows an increasing exponential behavior for each manufactured system

and in each charge and discharge cycle the action of the current decreases. In general, the anodic peak (0.6 to 0.8 V) is observed but for the aluminum oxide template this value is displaced by resistive and memory effects towards more positive values but for the cathodic peak (-0.2 to 0 V) this value remains stable when returning for each cycle. In addition to the modified foil, we have that the anode peak (0.55 to 0.8 V) remains stable and does not shift. Due to the interaction of copper in the pores, the conductivity remains stable and does not fluctuate causing a hardening of the memory that leads to lower resistance ranges compared to the pristine template. A change with respect to the pristine material is the fluctuation of the cathodic peak (-0.2 to -0.1 V) in the modified foil where the return potentials move progressively in a negative direction. On the other hand, in order to detect the resistive switching electrical test was used. Cyclic voltammetry shows three consecutive bias sweeps. During these three charge and discharge cycles, the current causes a polarization causing a gradual decrease in conductivity forming the typical characteristic resistive switching of a memristor (132; 133). A gradual change in conductivity in each cycle is noticeable and can be attributed to the effect of the electric field that influences the Schottky barrier (134). However, the positive sweep bias in the device increases to 0.8 V and the formation of the negative sweep to -0.2 V. The operating range for pristine and modified material is 1 V which makes this system highly efficient. Also, the resistance increases abruptly by the formation of the conducting filament. Using the data obtained in cyclic voltammetry, the resistance is calculated over time, see Figure 4.8 A. The resistive switching $\frac{R_{off}}{R_{on}}$ ratio values for the aluminum oxide template is 2.35 and for the modified template is 1.52 all take from EIS data. When comparing the AAO and AAO / CuO curves in Figure 4.8 A, we can see that the first in their initial operating cycles are displaced by the effects of conduction in an oxidized material, but when observing the trend of the curves in the AAO / CuO system, the displacement between operating cycle curves remains fixed. The hardening in the cycles is kept stable by the presence of the copper wires that keep the current conduction stable. When comparing the curves of the third cycle of load for each system manufactured in the Figure 4.8 B we can see an improvement in the hardening of the resistive memory properties. Finally, we can see in Figure 4.8 B shows the high and low resistance values in the memristors for each sample of manufactured material. This figure shows the minimum and maximum values in which the resistive memory fluctuates and they are corroborated with the EIS in the Boge plot Figure 4.11.



Figure 4.8: A) Time dependent resistance for anodic aluminum oxide(AOO) and nanocopper oxidewire(AOO/CuO) for three consecutive cycles. B) Comparative plot of AOO template and AOO/CuO in one cycle showing the high and low resistance states.

4.3.2 Electrochemical impedance spectroscopy



Figure 4.9: Nyquist plots. The graph is made up of two curves where the blue line is for anodic aluminum oxide wire (AOO) and the orange line for copper nano-oxide (AOO/CuO). In general, the curve for each sample starts at positive resistance values until reaching negative values all dependent on the frequency.

Figure 4.9 shows the impedance of the AOO template and the sheet modified by the intrusion of copper oxide. Nyquist plots were recorded at room temperature for each sample with a variation of frequency since 100000 Hz to 0.1 Hz. The shape of the semicircle is characteristic of polycrystalline systems composed of two sections where the first part of the curve has positive resistance values until reaching a frequency of 3.9811 Hz for AAO and the same for AOO/CuO. In the same way, continuing with negative values of resistance, forming another semicircle start from a frequency of 0.31623 Hz for AAO and 3.1623 Hz for AOO/CuO. The frequency-dependent behavior forms two semicircles between positive values and the negative resistance is attributed to the change or rotation of the spins that make up the polycrystalline structure (135). The size of the loop is related to the size of the grain and the number of them. Each curve is made up of two semicircles corresponding to the internal conduction of the bulk grain (136; 137). The addition of copper in the nanopores of the film increases the current conduction between the grain boundaries, which translates into a reduction in the internal resistance of the system and can be seen in the size between the

curves (see Figure 4.10).



Figure 4.10: The equivalent electrical models for anodic aluminum oxide(AOO) and nano-copper oxide wire(AOO/CuO)

To perform data fitting and extract information regarding the capacitance and resistance of the system, equivalent electrical models were used the model Dino Klotz that allows to explain low frequency hook(138). In addition, the equivalent circuit model is included for each sample and it contains a net resistance in series together with two resistors and respective parallel capacitors for each system. The values for the equivalent electrical models are $R_1 = 3119.18 \ \Omega, \ C_1 = 1.14X10^{-5} \ F, \ R_2 = -1325.431 \ \Omega, \ C_2 = -6.20X10^{-3} \ F$ for anodic template and $R_3 = 869.25 \Omega$, $C_3 = 6.82 \times 10^{-6} F$, $R_4 = -292.11 \Omega$, $C_4 = -1.07 \times 10^{-3} F$ for copper oxide wire inside of template. An explanation for the transmission of charge carriers is when it gives rise to two states of resistance characterized by a high and a low resistance, as can be seen in the Bode plot. Where you can see the dependence of resistance and frequency. The figure shows the high and low resistance values for each sample material. The Figure 4.11 that shows how the resistance varies with frequency and that for each sample shows two values, one maximum and one minimum of resistance. The results obtained by CV and the EIS corroborate each other since the values of minimum and maximum resistance are specifically verified. On the one hand we have in the CV the dependence of the resistance and the time where the resistance values can be seen in the Figure 4.8. While in the Figure 4.11, we have the dependence of the resistance and the frequency in the Bode plot. The conjunction of the data obtained shows a concordance despite the fact that the CV technique has a temporal dependence on resistance and the EIS has a frequency dependence on a logarithmic scale.



Figure 4.11: Bode plot showing the high and low resistance states
Chapter 5

Conclusions

In this thesis project, a nano-structured material was manufactured consisting of aluminum oxide nano pores and modified by a deposition of copper oxide wires resulting in a selfassembled hierarchical structure. The thin film obtained responds electrically in characterization tests to a memristor.

The design of the material began with the recrystallization of the aluminum sheets under the action of a thermal treatment. The crystallized material was then used in electrochemical reactions using organic acids, greatly reducing waste and costs by reducing the energy gap using a source of 60 V direct current. Due to the robust experimentation in the use of these nano-structured materials, reagents can be exchanged and thus reduce production costs. In order to spread the use and application of nano-porous materials using commercial aluminum that due to an intensive manufacturing process has spread in its use around the world. The present characterization carried out shows how the doping of the material with copper generates in the consolidated copper wires a crystallinity and grain limits directed by the electric field that maintains a directionality in the spins. The electronic properties of the thin film manufactured were characterized using Cyclic voltammetry and electrochemical impedance techniques which verified characteristic switching in non-volatile memory devices. The voltammetry demonstrated the characteristic switching and the electronic properties of the manufactured material shows a 1V operating range with a scan rate of 10 $\frac{mV}{s}$. Regarding the $\frac{R_{off}}{R_{on}}$ ratio switching for the AAO it is 2.35 and for the modified material it is 1.52 which shows a hardening and improvement with respect to the starting material. The results of the electrochemical impedance were fitted to the Klotz model and showing the predominance of the electric field in the spins of the polycrystalline material and the influence of the oxide wires on the structure of the film. Equivalent circuit values for AOO are generally higher for resistors and capacitors since aluminum oxide has a high dielectric constant value. In contrast, when modifying the material and transforming it into AOO/CuO, the values for the equivalent circuit decrease since the intrusion of a more conductive material radically changes the electronic properties, decreasing the resistance and capacitance values by an order of magnitude. A joint analysis of the cyclic voltammetric and electrochemical impedance could correlate the resistance values distinguishing the maximum and minimum values for manufactured samples.

In the same way, using electron microscopic and atomic force microscopy techniques, the nanometric structure was verified. The pore size obtained is variable, and two modes can be distinguished in the distribution. The first with a high incidence in a range that goes from 15 nm to 51 nm and the second with a low incidence in size that goes from 79 nm to 319 nm. In addition, when analyzing the size of the wires on the surface of the material, there is a simple distribution with an incidence of sizes ranging from 0.6 nm to 65 nm. On the other hand, the chemical composition was characterized of the material using energy dispersive x-ray showed a definite composition for aluminum oxide, being able to establish the respective stoichiometry but for the modified material AOO/CuO the chemical analysis does not allow to establish the stoichiometry. Due to the nano topography and the incidence of the electron beam that does not allow a homogeneous scan on the surface. Based on the surface analysis carried out by the atomic force microscope, it was possible to determine the relative density of nano-structures formed by filling the pores with a value of $1.1x10^{15}$ in

nano-structured devices per square meter.

In addition, by using a González-Cuenca deposition model to favor homogeneity in the distribution of the wires on the porous surface. Where, the design and simplification of the reactor to systematize the material are based on the use of the deposition model. The selection of the sample holder avoids the auto-corrosion by action of the electrolyte and the electric field. In the same way, by using a deposition model coupled to reproducible empirical conditions, it allows morphological modulation of the material's surface, being able to embed and fill the nanometric pores of aluminum oxide.

However, despite the small advance in the simplified manufacturing of the material, it is necessary to develop prototypes and equipment based on self-assembled hierarchical structures since, due to the implicit benefits of nano materials, the existing technology can be adopted and improved.

5.1 Outlook

Due to the potential of this technology and the ease of synthesizing porous structures can be applied to massify nano-structured devices in energy applications, virus sensors, spintronic devices, catalysis, and non-volatile memories. In addition, the design and development of the material taking advantage of the intrinsic benefits of the properties of aluminum in a specific state of crystallinity that favored the formation of nano pores and the advantages in the implementation and synthesis of the material could serve as a templete for technological applications.

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