



Treball Final de Grau

Improving electrical and thermal surface properties of polymer composite materials

Cristina León Casablanca

June 2017



**UNIVERSITAT DE
BARCELONA**

Aquesta obra esta subjecta a la llicència de:
Reconeixement–NoComercial–SenseObraDerivada



<http://creativecommons.org/licenses/by-nc-nd/3.0/es/>

*The important thing in science is not so mucho to
obtain new facts as to discover new ways of
thinking about them*

William Henry Bragg

Voldria transmetre el meu agraïment al departament de ciència de materials per oferir-me i donar suport a aquest projecte. A la Dra. Núria Llorca li agraeixo especialment el seu suport, els seus comentaris i constant acompanyament al llarg d'aquest mesos. Agrair a Ana Maria Escobar la seva experiència que ha fet possible la realització d'aquest projecte. I finalment voldria donar les gracies al Dr. Enric Bertran i al grup de Física i Enginyeria de Materials Amorfs i Nanostructures per posar-me a disposició l'equip de sputtering.

CONTENTS

SUMMARY	i
RESUM	iii
1. INTRODUCTION	1
1.1. CARBON FIBRE REINFORCED POLYMERS	2
1.1.1. EPOXI RESIN	4
1.1.2. CARBON FIBRE	4
2. OBJECTIVES	5
3. BACKGROUND AND STATE-OF-ART	7
3.1. JONING	7
3.1.1. Mechanical Fastening	8
3.1.2. Adhesive bonding	8
3.2. COATING METHODS	9
3.2.1. GASEOUS STATE	10
3.2.1.1. Physical Vapor Deposition (PVD)	10
3.2.1.2. Chemical Vapor Deposition (CVD)	15
3.2.1.3. Ion Plating	15
3.2.2. LIQUID STATE	16
3.2.2.1. Chemical Solution Deposition	17
3.2.2.2. Electrochemical Deposition	17
3.2.2.3. Sol-Gel Processing	19
3.2.3. MOLTEN AND SEMIMOLTEN STATE PROCESS	19
3.2.3.1. Laser Surface Treatments	20
3.2.3.2. Thermal Spraying	20
3.2.3.3. Welding	22
3.2.3. SOLID STATE PROCESS	23

4. ELECTRICAL AND THERMAL CONDUCTIVITY	23
4.1. ELECTRICAL CONDUCTIVITY	23
4.1.1. THE NEARLY FREE ELECTRON MODEL	24
4.1.2. ELECTRICAL CONDUCTIVITY IN METALS	25
4.1.2.1. Factors affecting electrical conductivity	26
4.1.3. ELECTRICAL CONDUCTIVITY IN INSULATORS AND SEMICONDUCTORS	28
4.2. THERMAL CONDUCTIVITY	29
4.2.1. THERMAL CONDUCTIVITY IN METALS	30
4.2.2. THERMAL CONDUCTIVITY IN NO-METALS	31
5. EXPERIMENTAL PROCEDURE	33
5.1. ADHESIVE BONDING	33
5.2. SPUTTERING	34
5.3. ELECTROCHEMICAL DEPOSITION	36
5.4. FOUR-POINT PROBES METHOD	38
6. RESULTS AND DISCUSSION	42
6.1. COATING TECHNIQUES RESULTS	42
6.2. ELECTRICAL CONDUCTIVITIES RESULTS	44
6.3. THERMAL CONDUCTIVITIES RESULTS	47
7. CONCLUSIONS	49
REFERENCES AND NOTES	51
 APPENDICES	 55
APPENDIX 1: PARAMETERS OF SPUTTERING TESTS	57

SUMMARY

The use of new composite materials has increase in the last decades due to the possibility to achieve great properties with the combination of two or more materials. A great example is carbon fibre reinforce polymers (CFRPs), which are intensively use in many applications for their good strength to weight ratio. These materials are apparently an ideal component for aircraft industrial; however, the electrical and thermal conductivity they exhibit makes it unsuitable for certain applications like lightening strike protection.

To achieve better performance on CFRPs, it is common to metallise the surface with aluminium, copper or others conductive materials. In this project two different approaches have been compared: joining, with adhesive tape, and coating, with electrochemical deposition and sputtering. The electrical conductivity of the samples, before and after the metallization, has been studied with the 4-probes method and we have studied the influence of thickness on thermal and electrical conductivity.

Keywords: CFRP, Coating methods, metallization, 4-probes method

RESUM

L'ús de nous materials compostos s'ha incrementat en les últimes dècades degut a la possibilitat d'aconseguir grans propietats amb la combinació de dos o més materials. Un gran exemple són els polímers reforçats amb fibra de carboni (CFRPs), que s'utilitzen intensivament en moltes aplicacions per la seva alta resistència i baixa densitat. Aquests materials són aparentment un component ideal per la indústria aeronàutica; Tot i això, la conductivitat elèctrica i tèrmica que exhibeixen fa que siguin inadequats per a determinades aplicacions com la protecció contra els llamps.

Per aconseguir un millor rendiment en els CFRP, es habitual que la superfície es metal·litzi amb alumini, coure o altres materials conductors. En aquest projecte dos maneres d'enfocar el problema s'han comparat: les unions, amb cinta adhesiva, i els revestiments, amb l'electrodeposició i una polvorització catòdica (sputtering). La conductivitat elèctrica de les mostres, abans i després dels experiments, ha sigut estudiada per el mètode de les 4-punts i s'ha realitzat un estudi de la influència del gruix de la pel·lícula front la conductivitat elèctrica i tèrmica.

Paraules clau: CFRP, mètodes de revestiment, metal·lització, mètode 4-punts

1. INTRODUCTION

Most part of the materials used in engineering are combinations of two or more components which exhibit the features of each constituent while also providing special characteristics not achieved by a single material alone. These materials, resulting of the combination of various components, are referred as composites.

During the last decades, composite materials have been subjected to permanent interest for their properties. Their can offer many advantages like weight reduction, high strength and high resistance.

In all the composites two constituents are distinguished:

- **Matrix:** Component presented continuously acting as a binder that usually is the major one. In general, the objective of a composite is to improve some of the properties of this constituent incorporating one or more components. Matrix holds the reinforcement in orderly patterns and helps to transfer load among the reinforcement. Likewise the reinforcement is protected against degradation by the matrix. Matrix phase can be metallic, ceramic or polymeric.
- **Reinforcement:** It is the structural constituent, which determines the internal structure of the composite. The role of the reinforcement is to improve matrix properties and consequently achieve the requirements of a particular application. Reinforcements can be presented in different forms as particulates, fibres or sheets.

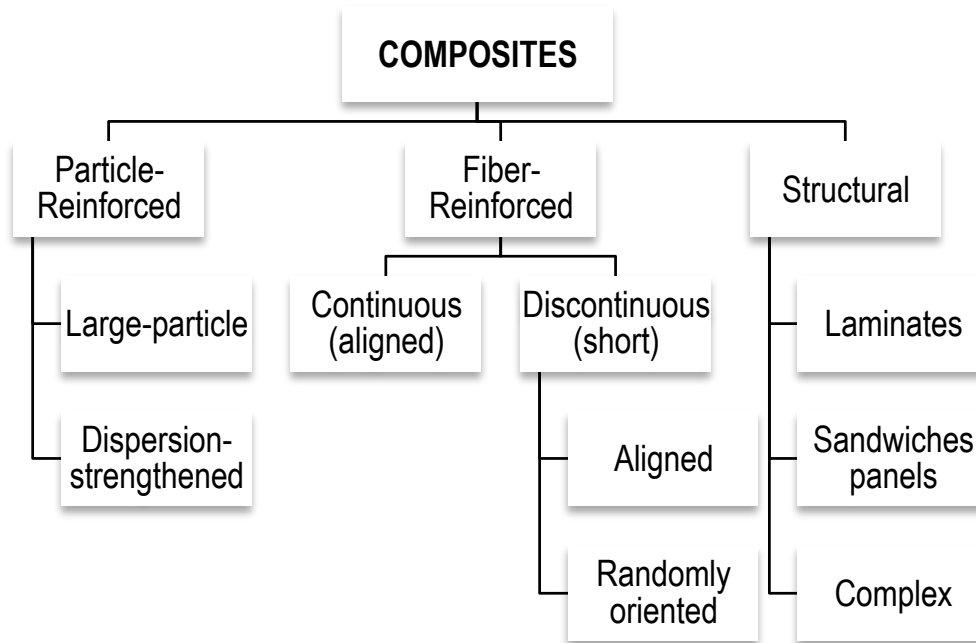


Figure 1. Classification of composites by geometry and type or reinforcement [1]

1.1. CARBON FIBRE REINFORCED POLYMERS

Carbon Fibre Reinforced Polymer (CFRP) is an extremely strong and light polymer, which contains carbon fibres as reinforcement. They are intensively used in many applications due to their good strength to weight ratio as aerospace applications, automobile applications, communication antenna and electronic circuit bands.

Thanks to their specific stiffness and strength, good chemical resistance and low density in comparison to metallic materials, CFRPs have been well developed and used as the structural material especially in aviation industry. Weight is a central issue in this industry but it is not the only one, strength and reliability must have also given due attention. That is why aircrafts manufactures are switching to advanced composite materials and it can be observed by considering the used of these materials throughout history. In 1970 when the first commercial Airbus A300 was made only three to four percent of its weight was manufactured with composites. Nowadays with the A380, composites represent a quarter of its weight and for the A350 this percentage has increased up to 50%. Along the same lines, Boing 787 Dreamliner used for its primary structure 50% of CFRPs, carbon sandwich and GFRP composites. [2-6]

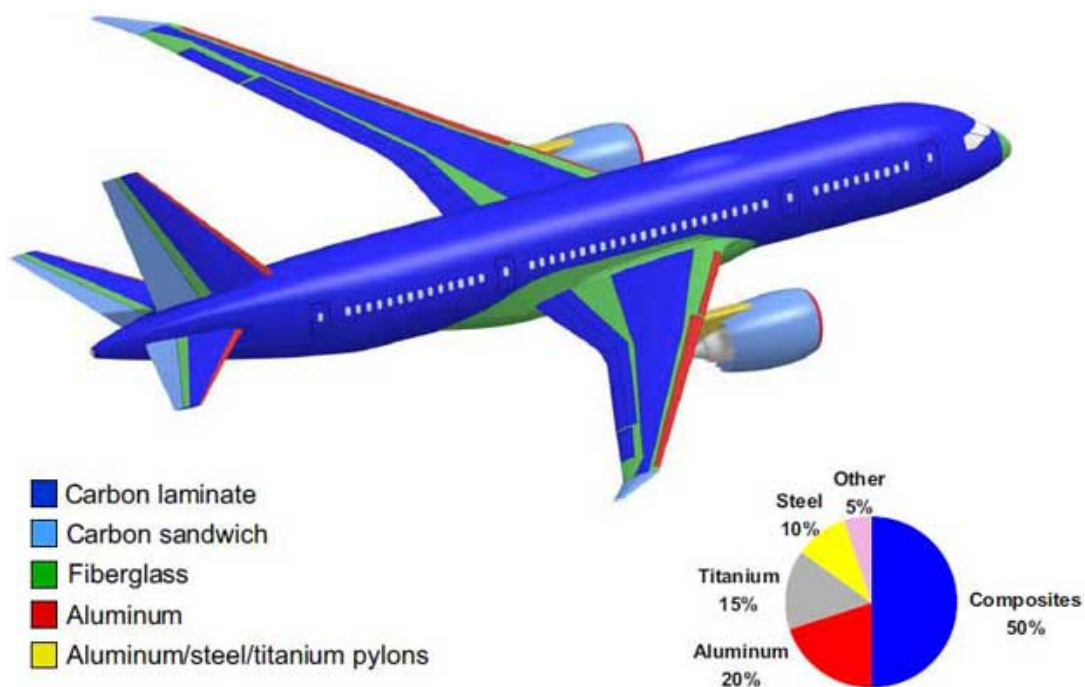


Figure 2. Materials used in Boeing 787 Dreamliner body [3]

Despite many wonderful properties of CFRPs, the lack of electrical conductivity in these materials has limited its use for certain applications. While metallic structures such as traditional aluminium airframes, are highly conductive, CFRP have a much lower electrical conductivity. Although carbon fibres are good conductors, the polymer matrix is an excellent dielectric and therefore reduces the overall conductivity of the composite.

1.1.1.EPOXY RESINS

Epoxy resin is a thermosetting polymer used in a wide range of applications. Thermosetting polymers harden when are heated and change into an infusible, insoluble polymer network by curing. When the curing starts, appear covalent bonds between adjacent molecular chains. These bonds difficult vibrational and rotational movement of the chains at elevated temperatures and only heating to an excessive temperature it is possible to break these connections and as a consequence the degradation of the polymer.

Due to this crosslinking, thermosetting polymers are generally harder, stronger and better suited to high-temperature applications up to the decomposition temperature since they keep their shape. However, thermosetting polymers are more brittle than thermoplastics.

1.1.2. CARBON FIBRE

Carbon fibre is a long, thin strand of material about 0.005-0.0010 mm in diameter and composed mostly of carbon atoms. Carbon can be presented in different allotropic forms but the most use for reinforce fibres is as graphite since the orientation of basal plane, where the covalent bond is stronger, provides high properties like high strength.

Carbon fibres are classified by the tensile modulus of the fibre; “low modulus” has tensile modulus below 240 GPa and “ultrahigh modulus” has tensile modulus of 500 – 1000 GPa. As a comparison, steel has a tensile modulus of about 200 GPa, ten times weaker than ultrahigh modulus carbon fibre. Moreover, carbon fibres have high fatigue properties compared to metallic structures and are lighter.

Carbon fibres need a superficial treatment to increase the bonding with epoxies and other materials used in composites. Generally, the fibres are slightly oxidized immersing it in gases such air, carbon dioxide or ozone; or in various liquids such as sodium hypochlorite or nitric acid. The addition of oxygen atoms to the surface provides better chemical bonding properties and also etches and roughens the surface for better mechanical bonding properties.

2. OBJECTIVES

The main objective of this work consists on studying the background and the state-of-art of improving electrical and thermal conductivity on CFRPs. This knowledge will be applied to provide to CFRP samples, with epoxy base, these improvements.

The measurements of the conductivity will be performed by the four probes method on the surface of the samples. We will study the influence of the thickness of the film with thermal and electrical conductivity.

3. BACKGROUND AND STATE-OF-ART

Carbon Fiber reinforced polymers are apparently an ideal material for aerospace and aircraft industry due to their properties such as high stiffness, great thermal and dimensional stability, super corrosion resistance and low weight. The density of CFRP is around 1.5 g/cm^3 , half that of aluminium ($2,70 \text{ g/cm}^3$) and six times lower than copper ($8,96 \text{ g/cm}^3$). As a result, CFRP offers extensive weight savings compared to metal materials.

However, the electrical conductivity is insufficient for certain applications like lightning strike protection. The low electrical conductivity due to the resin matrix makes CFRP unsuitable for direct use as waveguide elements. Methods for improving surface electrical conductivity in CFRP follow different approaches and they can be classified in two different types:

- Joining methods
- Coating methods

3.1. JOINING METHODS

Joining consist on attach two different materials achieving a durable union. Several techniques exist for joining hybrid materials as metal with CFRPs [7,8]. It is possible to classify these techniques in two groups as shown in Figure 3.

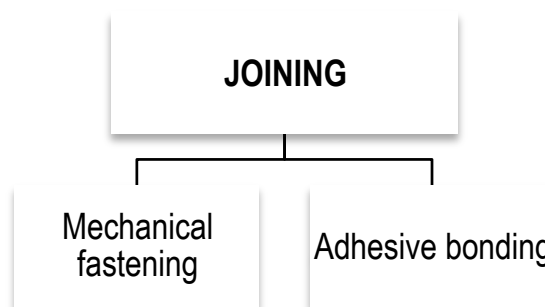


Figure 3. Techniques for joining metal and CFRPs

These techniques can be utilized individually or combined to ensure a successful and durable joint. Usually the composites used in aircraft are joined by combination of mechanical fastening and adhesives, whereas those used in automobile are often joined with adhesives. The most appropriate method will depend on application and service requirements.

3.1.1.MECHANICAL FASTENING

Mechanical fastening is currently the main method for joining hybrid materials in aircrafts and space applications due to the simplicity of the method and the easily adaptation for automatic process.

Mechanical fastening incorporates the use of additional clamping components without fusing the joint surface. Screws and rivets are the clamps most used for joint formation and special mechanical operations are required by this technique, such as drilling holes or making screw threads. These holes are areas of high stress concentrations and determine load capability of the whole structure.

One of the disadvantages of using mechanical fastening is the increasing component weight due to load management. The composite and metal thicknesses must be increased to accommodate the stress concentrations around the holes and fasteners points loads, thereby increasing the weight. Another disadvantage is corrosion and rust related problems.

3.1.2.ADHESIVE BONDING

Adhesive bonding is a solid state joining technique that relies on the formation of intermolecular forces between the workpieces and the adhesive itself for joint formation. The advantage of using adhesive bonding compared to mechanical fastening is that the entire bonded contact surface participates in load management; there are no holes that create stress concentrations. Adhesive bonding provides more efficient load management, so the thickness and weight of both materials can be reduced. In addition, the adhesive creates an interlayer that isolates one surface from another, which prevents from galvanic corrosion. On the other hand, adhesive bond joints are more disposed to environmental degradation from factors such as moisture, humidity and temperature.

However, the most limiting factor to use adhesive bonding is the difficulty of predicting the long-term durability of this kind of joint. Bonded joints often fail instantaneously instead of progressive when applied in engineering structures. [9]

Surface treatments are used to improve bond strength and joint durability in adhesive bonding. Typical surface treatments techniques include solvent cleaning, alteration of surface chemistry and abrasion.

3.2. COATINGS METHODS

Coatings consist on deposition a thin film onto a material usually referred as a substrate. Functional coatings are used to modify physical and chemical properties and morphology of a surface such as adhesion, wettability or corrosion resistance. Coatings add new properties to a material such as a magnetic response or electrical conductivity.

The advantage of coating technology lays in the fact that it marries two dissimilar materials, in this case CFRP+metal, to improve the performance of the tandem substrate/coating. Generally, mechanical strength and fracture toughness are provided by the substrate whereas the coating provides protection against environmental degradation.

Surface treatments are used to improve the adhesion between substrate and the coating. It is important to activate the surface because it will affect the properties, structure, adhesion and surface texture of the thin film deposited. Substrate surface morphology and composition can be modified by diffusion, plasma treatment, self-assembly, chemical etching and reactive heat treatment.

Frequently, coating process follows these steps:

1. Surface treatment
2. Synthesis or creation of the deposition species
3. Transport from source to substrate
4. Deposition onto the substrate and subsequent film growth.

Exist many techniques for coating and several classifications for the mechanisms used in the process (Figure 4). In this paper we will summarize the most commonly used techniques.

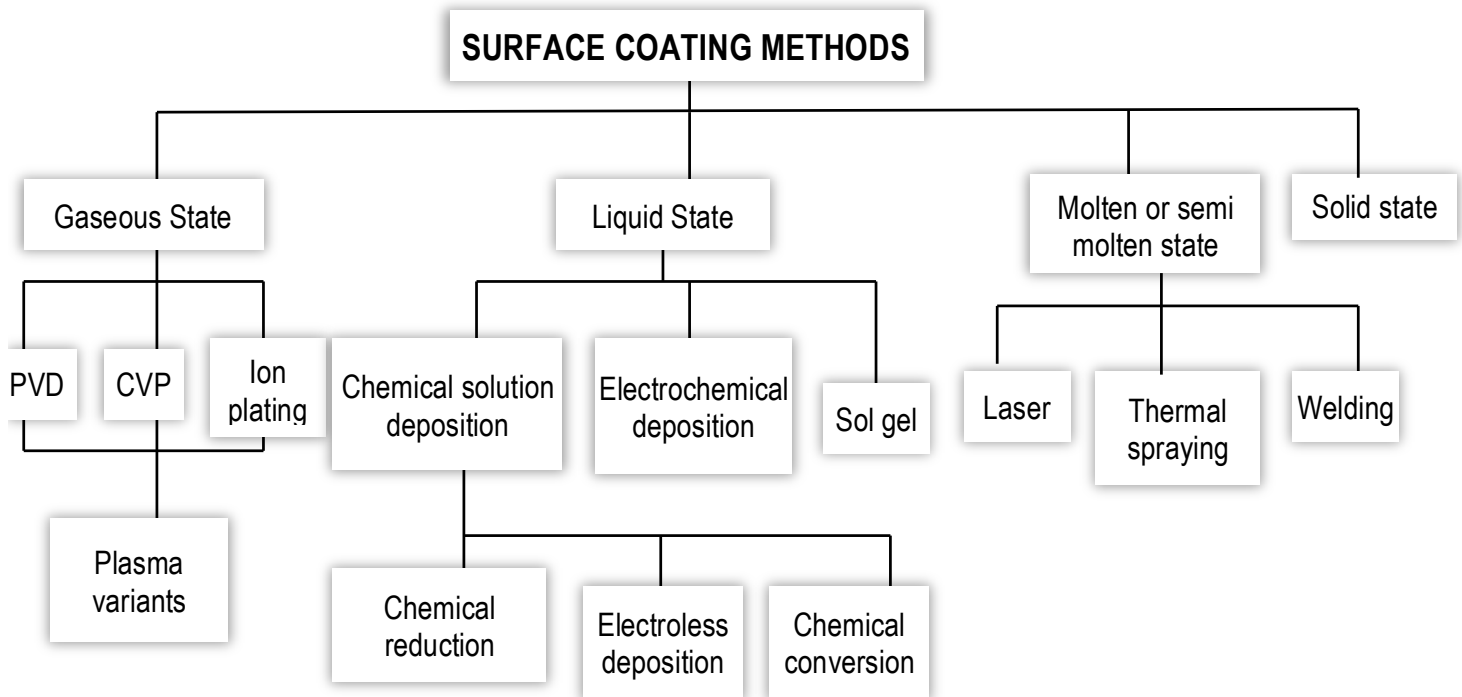


Figure 4. Classification of surface coating methods [10]

3.2.1. GASEOUS STATE PROCESSES

Gaseous state processes cover surface engineering techniques in which the coating or surface treatment material passes through a gaseous or vapour phase prior to depositing on to the surface.

3.2.1.1. PHYSICAL VAPOR DEPOSITION (PVD)

PVD processes is a general term used to describe any method that use a vaporized form of the solid or liquid material to deposition as a thin solid film onto the surface of the substrate. PVD involves physical ejection of material as atoms or molecules, transported in the form of a vapor through a vacuum or low-pressure gaseous environment, and a condensation and nucleation of these atoms onto the surface of the substrate. With these processes it is possible to accomplish films with a thickness range of a few angstroms to a thousands of angstroms.

PVD processes can be categorized as [12]:

- Thermal vaporization
- Sputter deposition
- Arc vapor deposition

There are a lot of techniques from this processes and exists hybrids processes that combine the best attributes of each PVD and CVD process to achieve the requests.

Every PVD process follows three basic steps:

1. Creation of vapor-phase species by evaporation, sputtering or chemical vapor and gases
2. Transport vapor-phase species from the source to the surface of the substrate.
3. Nucleation. Film growth on the substrate.

Thermal vaporization

Thermal vaporization is a PVD process in which material reaches the substrate without collision with gas molecules in the space between the source and the substrate. The source material is evaporated in a vacuum allowing the vapor molecules to travel directly to the substrate, where they condense back to a solid state. The base pressure system maintained determines the quality of its vacuum. These levels are generally described as rough, low, medium, high, or ultra high (Table 2). In general, thermal evaporation is used to deposit metals and some compounds with low fusion temperature, e.g., Au, Al, Ti, Cr, and SiO.

Table 1. Vacuum quality pressure ranges [13]

Vacuum type	Pressure Range (Torr)⁽¹⁾
Low	760 – 0
Medium	0 – 10 ⁻³
High	10 ⁻³ – 10 ⁻⁸
Ultra High	10 ⁻⁸ – 10 ⁻¹²
Extreme High	< 10 ⁻¹²
Outer Space	≈ 10 ⁻¹⁶

(1) Torr = 101325/760 Pa

Many different vacuum system configurations exist however the main process footsteps can be summarized in four points:

1. Place a suitable material (the source) inside the vacuum chamber with a heater.

2. Seal and evacuate the chamber
3. Heat the source. When the temperature reaches the evaporation temperature, atoms or molecules start to leave the surface of the source and travel into the substrate. The equilibrium vapor pressure is an important property of the material because the vaporization rate from a hot surface into a vacuum depends on the temperature and the equilibrium vapor pressure of the material at that temperature.
4. Since the surface of the substrate is at much lower temperature, the molecules of the source will transfer their energy lowering their temperature and condense onto the surface. The deposition thickness will depend on the evaporation rate, the geometry of the source and the substrate and the time of evaporation.

Thermal vaporization has the advantage that is low cost, energy efficient and it is possible to deposit high purity films. On the other hand, line-of-sight and limited-area sources results in poor surface coverage on complex surface and in poor film-thickness uniformity over large areas without proper fixturing and movement.

Sputter Deposition

Sputter deposition is the deposition of vaporized particles from a nonthermal vaporization process where surface atoms are physically ejected due to a bombardment of energetic particles. Physical sputtering is driven by momentum exchange between the ions and atoms in the target material, due to collisions. The energetic atoms in the gas plasma collide with the target material and knock off source atoms, which then travel to the substrate and condense into a thin film. [16,20]

There are several sputtering systems although the basic model is the DC diode sputtering system.

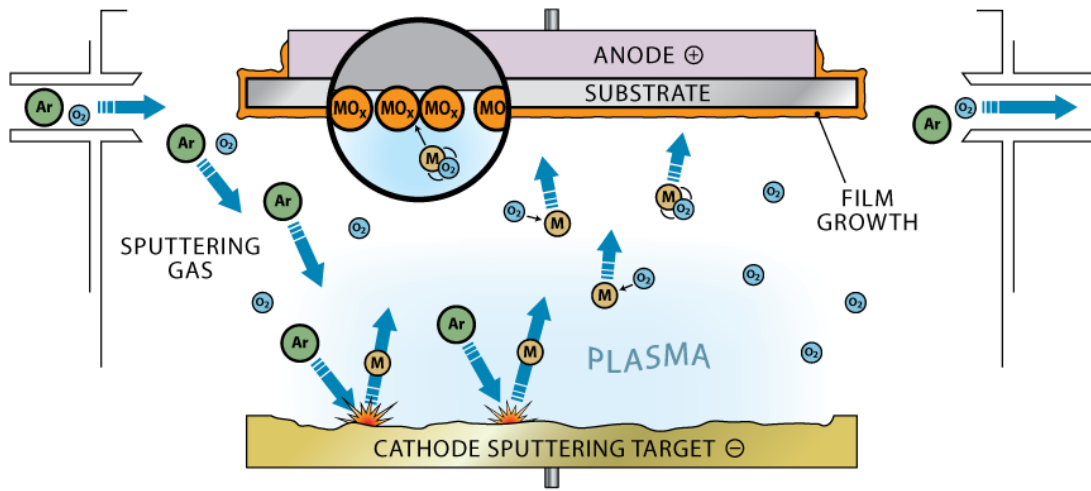


Figure 5. DC diode sputtering system [14]

DC diode sputtering system is composed of a pair of planar electrodes, cathode and an anode, where a high negative direct current voltage is applied. The top plasma-facing surface of the cathode is covered with a target material and the substrate is placed on the anode. When the current voltage is applied the glow discharge is initiated. The Argon ions in the glow discharge are accelerated at the cathode fall and sputter the target, resulting in the deposition of a thin film.

The advantage of using DC diode sputtering is the possibility of coating large areas uniformly, the possibility to coat a wide range of substrates and the DC diode plasma, which fills the entire deposition chamber, can be used to plasma clean the surface as part of the in situ cleaning. However, it should take into account the damage that ion bombardment causes to the substrate and the difficulty to produce high performance thick coating due to the high internal residual stress levels that this method causes.

Arc vapor deposition

Arc vapor deposition uses the vaporization from an electrode under arcing conditions as a source of vaporized material. Arcing conditions consist of a high-current low-voltage electrical current passing through a gas or a vapor of the electrode material.

In arc vaporization the atoms that are vaporized pass through a high-density electron cloud and a high percentage are ionized. Ion bombardment at the cathode and electron bombardment

at the anode heat the electrodes and most of the ejected material is thermally evaporated and some is ejected as molten droplets or solid particles from the cathode.

The usual configuration is the cathodic arc where the vaporization is from an arc that is moving over a solid cathodic surface. The cathode can be molten or solid with a water-cooled solid cathode. One of the problems with cathodic arc deposition techniques is the formation of molten micro-sized globules, called “macros” of the ejected material from the solid surface. These macros deposit on the film material and create bumps, which, when dislodged, create pinholes. Cathodic arc deposition has problems with the stabilization and the movement of the arc on the solid surface too. The arc movement may be random or “steered” using a magnetic field. There are a number of different steered arc source designs using magnetic fields to steer the arc. Steered arc sources generally produce fewer macros than random arc sources.

Another configuration is the anodic arc configuration, where the electrons melt and vaporize the anodic electrode. The electrons can arise from a heated thermoelectron emitting surface, a hot or cold hollow cathode, or an arc cathode. By bending the electron beam in a magnetic field the vaporized material may be kept from impinging on the electron source. [12,18]

The advantages of using arc vapor deposition are the activation that arc plasma produces to a reactive species making them more chemically reactive, and the formation of “film-ions” that allow them to be accelerated to high energies. However the formation of “macros” in cathodic arc deposition can be a determining factor in some materials and applications, also, in anodic arc deposition exist a high radiant heat loads in the system.

3.2.1.2. CHEMICAL VAPOR DEPOSITION (CVD)

In CVD the source atoms are removed by chemical means and low vacuum are typically used. In this technique, volatile reactants are flowed past the substrate by a carrier gas (e.g. H_2) in viscous regime vacuums. If the thermodynamics are favourable for diffusion and reaction at the substrate, a solid film is formed.

CVD films are grown under conditions that are closer to equilibrium than physical vapor deposition. A reaction that produces a solid phase must be thermodynamically favourable for the film grown. There are six reactions used in this technique: Pyrolysis, Reduction, Oxidation, Compound formation, Hydrolysis, Metalorganic, Disproportionation, Reversible transfer.

The strength of CVD lies in its ability to produce well adherent, uniform and dense surface layers. The grain orientation and size, coating composition and its properties can be varied by the selection of appropriate process parameters. Although, most metals are not compatible with CVD due to their resistivity, but many processes exists for semiconductors and insulators and the resulting coatings can be adhere over very complex substrate geometries.

Exist many different techniques for CVD but every technique follows these six steps:

- 1) Transport of the reactants to the boundary layer
- 2) Diffusion of the reactants through the layer
- 3) Absorption/diffusion on the surface of the substrate and chemical reaction
- 4) Nucleation of the film on the substrate
- 5) Desorption of by-products
- 6) Transportation of by-products to the outside

Table 2. Classification CVD techniques [11]

Activation Type	Equipment	Designation
Thermic	Resistance heating, induction, radiation	CVD or LPCVD
Plasma	Electric shock DC or AC	PACVD
Photons	Laser, Hg lamp	LCVD

LPCVD: Low pressure CVD
PACVD: Plasma assisted CVD
LCVD: Laser assisted CVD

3.2.1.3. ION PLATING

Ion plating is a coating process that uses concurrent or periodic bombardment of the substrate, and deposits film by atomic-sized energetic particles. The source of material to be deposited in ion plating can be from vaporization, evaporation, sputtering, arc erosion, laser ablation or other vapour sources. The energetic particles used for bombardment are usually ions of an inert or reactive gas; however, using an arc erosion source, ions of the film material can be used to bombard the growing film.

Ion plating is also called ion-assisted deposition (IAD), ion vapor deposition (IVD), beam-assisted deposition (IBAD) and ionized physical vapor deposition (IPVD). These definitions does not specify the source of the bombarding particles, neither the environment in which deposition take place; therefore the term “ion plating” is often accompanied by modifying terms as “sputter ion plating” or “vacuum ion platting” to indicate a particular conditions of the technique. [15,17]

Bombarding species are generally ions accelerated from plasma in the deposition chamber (plasma-based ion plating) or ions from an ion source (vacuum-based ion plating).

In plasma-based ion plating a negatively biased substrate is in contact with plasma and bombarding positive ions are accelerated from the plasma and arrive at the surface with spectrum energies. The substrate can be positioned in the plasma-generation region or in a remote location outside the active plasma-generation and usually performs as the cathode electrode.

In vacuum-based ion platting the ions for bombardment are formed in a separated ion gun and the film material is deposited in a vacuum. The source of vaporization and the source of energetic ions for bombardment may be separated. This process is also called IBAD.

Some of the advantages of using ion plating are the ability to obtain good adhesion in many otherwise difficult systems and that film properties are less dependent on the angle of incidence of the flux of depositing material than with sputter deposition or vacuum evaporation due to gas scattering, and sputtering effects. On the other hand it is difficult to obtain uniform ion bombardment over the substrate surface leading to film property variations over the surface and a high residual compressive growth stresses can be built into the film.

3.2.2. LIQUID STATE

Solution state processes cover surface engineering techniques in which the coating or surface treatment material passes through an aqueous phase prior on to depositing on to the surface.

The man benefit of these methods is that they have no upper limit on thickness, unlike the vapour deposition methods.

3.2.2.1. CHEMICAL SOLUTION DEPOSITION

Chemical solution deposition is a coating process which particles (atoms or molecules) from a solution settle onto a surface, resulting in the growth of a new phase.

Exist different techniques and types of reactions for this process:

- Homogeneous chemical reactions
- Electroless or autocatalytic deposition (reactions takes place on catalytic surface not in the solution)
- Conversion coating, where a reagent in solution reacts with the substrate to form a compound

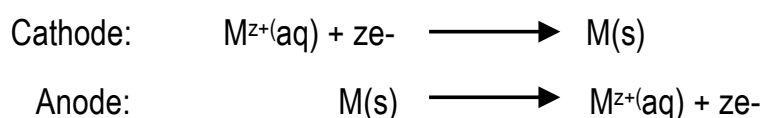
The most common technique is electroless nickel plating, usually used to protect components from corrosion. This process is an autocatalytic chemical reduction; this means that instead of using an outside source of electricity (like electroplating) uses a chemical bath to deposit the film onto the surface.

The main advantage of this type of process is that it does not use electrical power and it can be used to coat a non-conductive material. However the porous nature of electroless plating leads to inferior material structure compared to electrolytic processes.

3.2.2.2. ELECTROCHEMICAL DEPOSITION

Electrochemical deposition, also known as electroplating or electrodeposition, uses an outside electrical source to solidify ions of a solution by redox reactions. Most often, metallic cations are reduced at a cathode, while oxidation at an anode of the same metal replaces the reduced ions.

The process is carried out in an electrolytic cell, an apparatus consisting of positive and negative electrodes held apart and dipped into a solution containing positively and negatively charged ions (Figure 7).



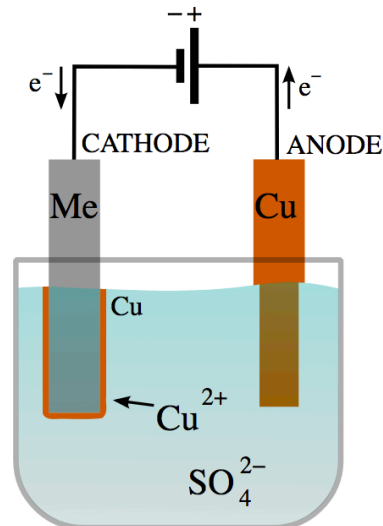


Figure 7. Scheme of electrolytic cell [21]

Michael Faraday, with electrolysis's laws in 1883, form the basis of this technology:

- 1) The amount of substance liberated at an electrode is directly proportional to the quantity of electricity passed: $M \propto Q$, where M is the quantity of substance liberated and Q is the quantity of electricity. This can be expressed as:

$$M = Z \cdot Q = Z \cdot I \cdot t$$

Where I is the current in Amperes, t is the time in seconds and Z is a proportionally constant called electrochemical equivalent of the substance (function of the valence and atomic weight of the substance).

- 2) If the same quantity of electricity is passed through different electrolytes, then the mass of substance liberated deposited in the electrodes are proportional to their respective equivalent weight or chemical equivalent

The advantages of electrochemical deposition process are that have high deposition rates, the thickness can be controlled adjusting the electrochemical parameters and it is possible to achieve a uniform thick film. However the difficulty of plating non-conductive films and the higher voltages for some substance, increasing the costs, makes it not suitable for some process. [22-24,26,28,31]

3.2.2.3. SOL-GEL PROCESSING

The sol-gel process is the creation of an oxide network by progressive condensation reactions of molecular precursors in a liquid medium. There are two ways to prepare sol-gel coatings: [32]

- Inorganic method: evolution of networks through the formation of a colloidal suspension and gelation of the sol to form a network continuous liquid phase
- Organic method: use a solution of monomeric metal in alcohol or other low-molecular weight organic solvent

Usually sol-gel coating processes consist in 4 steps:

- 1) Dispersion of the colloidal particles in a liquid to form a sol
- 2) Deposition of the sol to coat the substrate by spraying, dipping or spinning
- 3) Polymerization of the particles in the sol through the removal of the stabilizing components and the production of a gel in a state of continuous network
- 4) Formation of the film by the pyrolysis of the remaining organic or inorganic component

Sol-gel chemistry tends to be particularly sensitive a parameters such as pH, type of solvent, temperature and agitation.

This technique is widely use as a protection from corrosion or as a decorative coating and electro-optic components, and can be applied to glass, metal and other types of substrates.

Some of the advantages of this method are that can produce thick coatings to provide corrosion protection and can produce high purity products. Despite all the advantages, this technique never arrives at its full industrial potential due to some limitations such as the difficulty of the control of porosity and the maximum coating thickness (0,5 μm).

3.2.3. MOLTEN AND SEMI-MOLTEN STATE PROCESS

Molten and semi-molten state process cover surface engineering techniques in which the coating material is heated rapidly (melted) and projected at high velocity onto a surface.

This category includes laser surface treatments, as a pre-treatment of the surface, thermal spraying and welding.

3.2.3.1. LASER SURFACE TREATMENT

Laser surface treatment is used as a pre-treatment of the surface to increase adhesion between the surface and the coating material or as an alternative technique to the conventional coating methods. [33,36]

The principle of laser surface treatment is the modification of a surface as a result of interaction between a beam of light, with high power density, and the surface within a special atmosphere (vacuum, protective or processing gases).

The methods of laser surface treatment of materials have been classified in to two different types:

- Thermal process: with no change of surface composition (no material addition), like laser cutting, welding, tempering, annealing, melting and transformation hardening
- Thermo-chemical process: with change in composition of surface (material addition) like laser cladding.

Laser surface encompass several applications that are mainly related to enhancing one of the surface dependent properties like friction, fatigue and resistance to wear, hardness or corrosion

Some of the advantages of this technique are the production of a dense surface layer with no porosity, a higher bonding between the surface and the layer than coating techniques such as spraying or electrodeposition. Despite this, this technique is not widely employed because of the small areas that can be processed in a single pass.

3.2.3.2. THERMAL SPRAYING

Thermal spraying includes a group of coating processes in which metallic and non-metallic materials are spray deposited as fine particles in a molten or semi-molten condition or even in fully solid state to form a coating.

In the process, a heat source, which can be a combustion flame, an electric arc, or an ionized gas, is used to melt the feedstock material (powder, wire, stick, suspension/solution) and accelerate the particles toward the solid surface of the substrate, which is the material or component to be coated. [32]



Figure 7. Thermal spray process [44]

Coating materials in thermal spraying include pure metals, metal alloys, oxide ceramics, plastics, composites, and blended materials. Materials suitable for thermal spraying include practically all materials, except compounds that decompose irreversibly during melting and the ones that do not have a stable melt state and vaporize excessively in the spray process.

Exist different thermal spraying techniques classified as the feed stock material, the thermal energy source and the kinetic energy produced. The main techniques are [44]:

- Flame spraying
 - Typical coatings: Iron based alloys, molybdenum, nickel based alloys, copper and copper alloys, aluminium, zinc and Al/Zn alloys
 - Benefits: Can coat large structures and have a high production spray rate.
- Electric arc spraying
 - Typical coatings: Iron based alloys, nickel based alloys, copper and copper alloys, aluminium, zinc and Al/Zn alloys
 - Benefits: No combustible gas supply is required and have an excellent coating bond strength and density
- High velocity flame spraying:
 - Typical coatings: Nickel and cobalt based alloys, stellite, triballoy, Inconel, iron bases alloys.
 - Benefits: Excellent tenacity bonded coatings, low oxide metallic coatings and very high coating thicknesses are achievable.

- Cold spraying:
 - Typical coatings: Ductile materials (Zn, Al, Ni, Tr, Cu, Ag), Ductless metals alloys (NiCr, CuAl) and high end materials (Nobium, Tantalum)
 - Benefits: Do not use combustible gases or flame, high thermal and electrical conductivity coatings are achievable and have high rates and efficiencies.

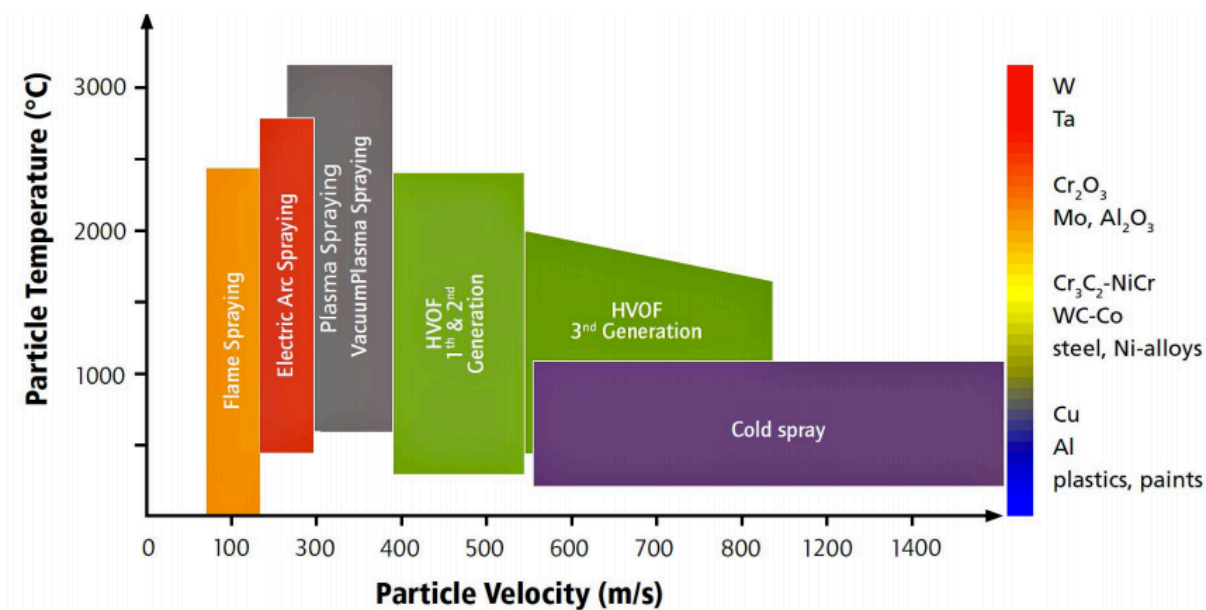


Figure 8. Thermal spray process positioning [44]

The resulting coating properties are always a combination of the thermal spray process conditions and the composition and properties of the feedstock material. Since thermal spraying is in most cases a deposition technique that does not increase much the temperature of the substrate during processing, it allows the use of many different substrate materials other than metals and alloys, even polymers and their composites.

3.2.3.3. WELDING

Welding is also considered a joining method. Various welding techniques can be used to deposit thick films onto a substrate. More conventional techniques like metal arc welding, gas tungsten arc welding, gas metal arc welding and submerged arc welding have been used for

metals and ceramic composites. New emerging techniques such as ultrasonic welding, laser welding, friction spot welding and friction stir welding have demonstrated good adhesion with polymers.

Welding can only be employed with thermoplastic polymers. Thermosets polymers, like epoxy, degrade in the process, meanwhile thermoplastics can be melted and soften by heat. For that reason, in this work only a brief mention it is done for this process. For more information is possible to consult [7-8].

3.2.4. SOLID STATE PROCESS

Diffusion is another coating process used especially for corrosion protection with metals. This process is done on metal components under elevated temperature. Detailed information can be found in [45].

4. ELECTRICAL AND THERMAL CONDUCTIVITY

The main objective of this work is to improve the electrical and thermal surface conductivity of CFRPs, therefore, it is important to understand how this properties work and what can make them diverge.

4.1. ELECTRICAL CONDUCTIVITY

The electrical conductivity, σ [$\Omega^{-1}\text{m}^{-1}$], of a material is defined as the amount of electric charge transferred per unit time across unit area under the action of a unit potential gradient:

$$J = \sigma \cdot E \quad (1)$$

Where J is the current density (current per unit area) and E is the potential gradient. This is another way of expressing Ohm's law, which is more commonly stated as: $V = I \cdot R$, where V is the electrical potential [V], I [A] is the current, and R [Ω] is the resistance of a material.

For an isotropic material:

$$\sigma = 1/\rho \quad (2)$$

Where ρ is the resistivity of the material [$\Omega \cdot \text{m}$], an intrinsic property that quantifies how strongly the material opposes the flow of electric current.

For a sample of length l , and cross section area A , the resistance, R , is calculated by:

$$R = \rho \frac{l}{A} \quad (3)$$

Charge carriers can be electrons, in metals, semiconductors and insulators, ions, in ceramics, and holes in semiconductors. The mobility of this charge carriers, μ , which is defined as their drift velocity per unit field, depends on a variety of factors including: Atomic bonding, lattice imperfections, microstructure and temperature.

4.1.1. THE NEARLY FREE ELECTRON MODEL

In 1900 Paul Drude presented a model of electrical conductivity assuming that electrons move straight lines and undergo collisions of negligible duration. This model assumes that electrons do not collide with each other; instead, they collide with immobile array of positive ion cores. It also assumes that all valence electrons contribute to the conductivity.

Although this model works well for a number of metals, it cannot explain the conductivity of other materials. In order to overcome these limitations in 1927 Arnold Sommerfeld proposes the free electron model, a modification of the Drude model (also known as the Drude-Sommerfeld model).

In this model the valence electrons are treated as quantum mechanicals waves, but the periodic potential of the crystal is ignored. This model improves the classical Drude model but still fails to explain the existence of semiconductors and insulators.

In the free nearly electron model the concept of electronic band structure is introduced to explain why some materials are insulating and other semiconductors (Figure 9). The band structure describes the range energies that an electron may have (energy bands or allowed bands) and ranges of energy that it may not have (band gaps).

The nearly free electron model explains the electrical properties of a solid material as consequence of its electronic band structure, namely, the distribution of the outermost electronic bands and the way they are filled by the electrons. The band containing the electrons with the

highest energy is the valence electrons, called the valence band and the conduction band is the next energy band, which is often empty of electrons.

Only electrons with energies greater than the Fermi energy can be accelerated in the presence of an electric field. These are the electrons involved in the conduction process, which are called free electrons. In semiconductors and insulators is another charged electronic entity called holes. Holes have energies smaller than E_f (Fermi energy) and also participate in electronic conduction. Electrical conductivity is a direct function of the number of free and holes electrons. In addition, the distinction between conductors and non-conductors (insulators and semiconductors) lies in the number of free electrons and charge-carrying holes.

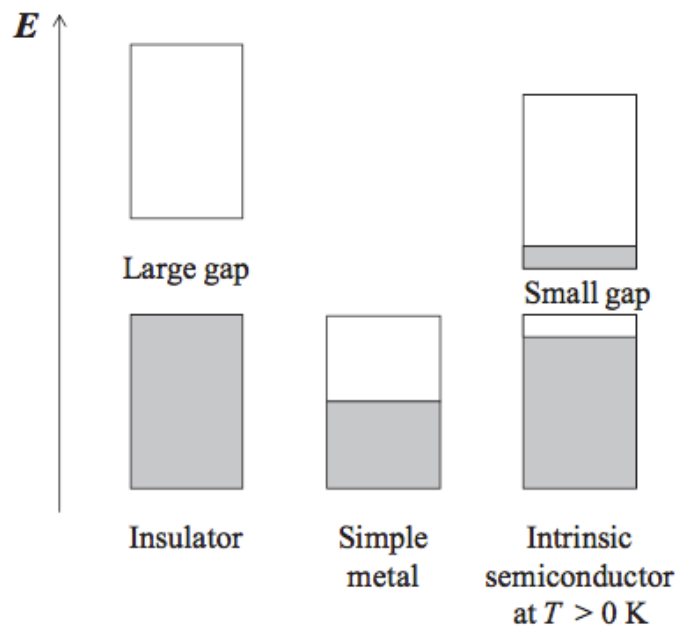


Figure 9. Flat Band Diagrams for different materials [1]

4.1.2.ELECTRICAL CONDUCTIVITY IN METALS

For an electron to become free, it must be excited or promoted to one of the empty energy states available above E_f . Metals have a band structure as shown in figure 9, they have empty energy states contiguous to the highest energy level, E_f , and overlapping bands. Thus, little energy is required to promote electrons at low energy levels, as shown in figure 10. Generally, the energy provided by an electric field is enough to excite a large number of conduction electrons to these conducting states.

Metal bond assumed that all valence electrons have freedom of movement and are evenly distributed throughout the ion network. Even though these electrons are not locally attached to any particular atom, they must, however, experience some excitation to become completely free conductors. Thus, even when only a fraction is excited, this gives rise to a relatively large number of free electrons and, consequently, to a high conductivity.

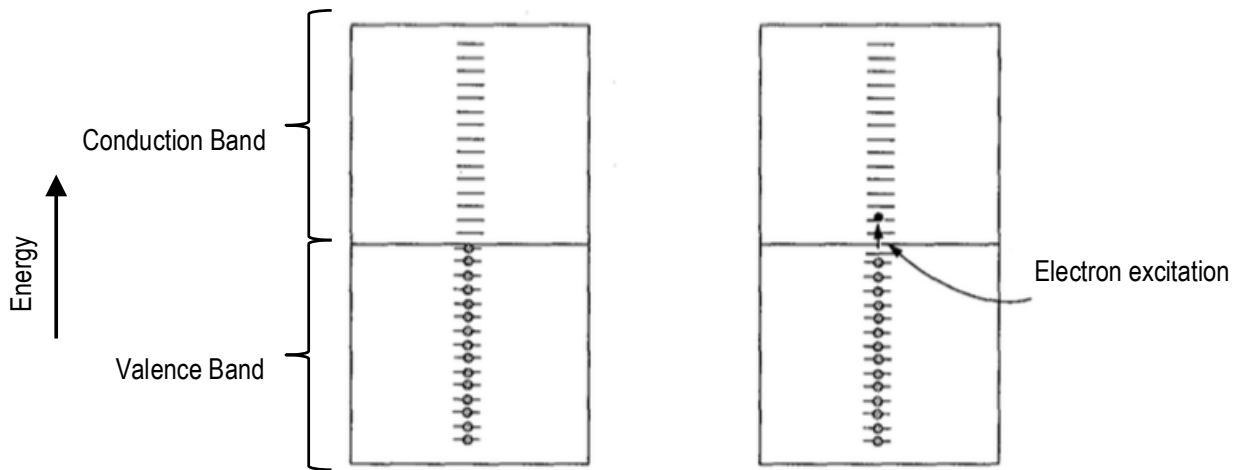


Figure 10. Electron Band of a metal before and after electron excitation [1]

4.1.2.1. FACTORS AFFECTING ELECTRICAL CONDUCTIVITY

Conductivity or resistivity of metals and alloys varies with defects, temperature, alloying and processing.

Crystalline defects act as scattering centres for conduction electrons in metals, increasing the number of defects also increases resistivity, decreasing conductivity. It has been experimentally found that the resistivity of a metal is the sum of the contributions of the thermal vibrations, the impurities and the degree of plastic deformation, namely, the dispersion mechanisms act independently of each other. This rule is known as Matthiessen rule and can be expressed as:

$$\rho_{TOTAL} = \rho_{thermal} + \rho_{defect} + \rho_{impurity} \quad (4)$$

Temperature Effect

For pure metals, resistivity depends linearly on temperature:

$$\rho_t = \rho_0 + aT \quad (5)$$

Where ρ_0 and a are constants for each metal.

The dependence of this thermal component of resistivity with temperature is because when temperature increases, increases the thermal vibrations and other irregularities of the network (for example vacancies), which act as scattering centres of the electrons.

Impurities effect

The resistivity component due to impurities is related to the concentration of its impurities, C_i , expressed as atomic fraction (%atoms/100):

$$\rho_i = AC_i(1 - C_i) \quad (6)$$

Where A is a constant independent of the composition and is a function of both the impurity and the solvent.

Effect of atomic level defects

Imperfections in crystal structures scatter electrons reducing the mobility and therefore, the conductivity of the metal. The resistivity component due to defects is expressed as:

$$\rho_d = BC_i(1 - C_i) \quad (7)$$

Where B is the defect resistivity coefficient and C_i is the concentration of defects in atomic fraction (%defects/100)

Effect of atomic level defects

Strengthening mechanism and metal processing techniques affect electrical properties of a metal in different ways (figure 11):

Considering the following ratio:

$$S = \frac{\rho}{\rho_0} \times 100 \quad (8)$$

Where ρ_0 is the resistivity of pure metal without defects and ρ is the resistivity of the metal being considered, S will change depending on the increase in the number of dislocations that causes electron scattering.

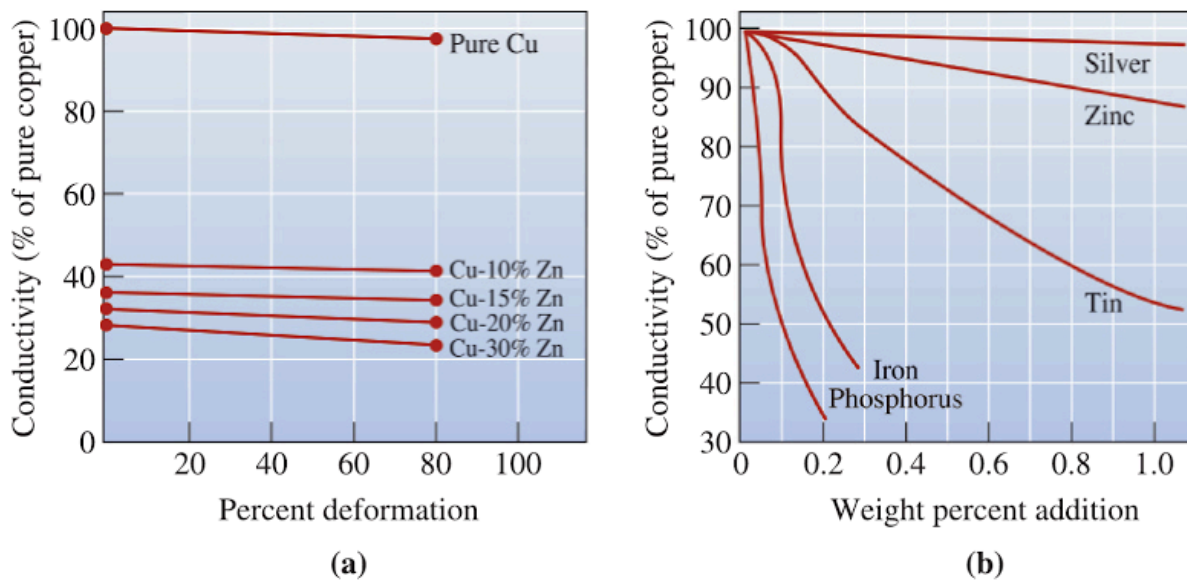


Figure 11. a) The effect of strengthening and cold work on the electrical conductivity of copper and b) the effect of the addition of selected elements on the electrical conductivity of copper [40]

4.1.3. ELECTRICAL CONDUCTIVITY IN INSULATORS AND SEMICONDUCTORS

Insulators and semiconductors don't have empty states contiguous to the maximum of the valence band. To become free, the electrons must overcome a forbidden range of energy to access the first energy states of the conduction band (figure 12). This is possible only if the energy equivalent to the difference between these two states, which is approximately equal to the energy of the gap, is supplied to the electron.

The number of electrons excited thermally (by heat energy) to the conduction band depends on the gap range of energy, as well as the temperature. At a given temperature, the greater is E_g (gap energy) the lower is the probability that a valence electron will pass into an energetic state within the conduction band, resulting in a smaller number of conduction electrons. In other words, the longer the gap energy interval, the lower the electrical conductivity for a given temperature.

Therefore, the distinction between semiconductors and insulators lies in the value of the gap range; In the case of semiconductors is small, whereas in insulating materials is relatively large.

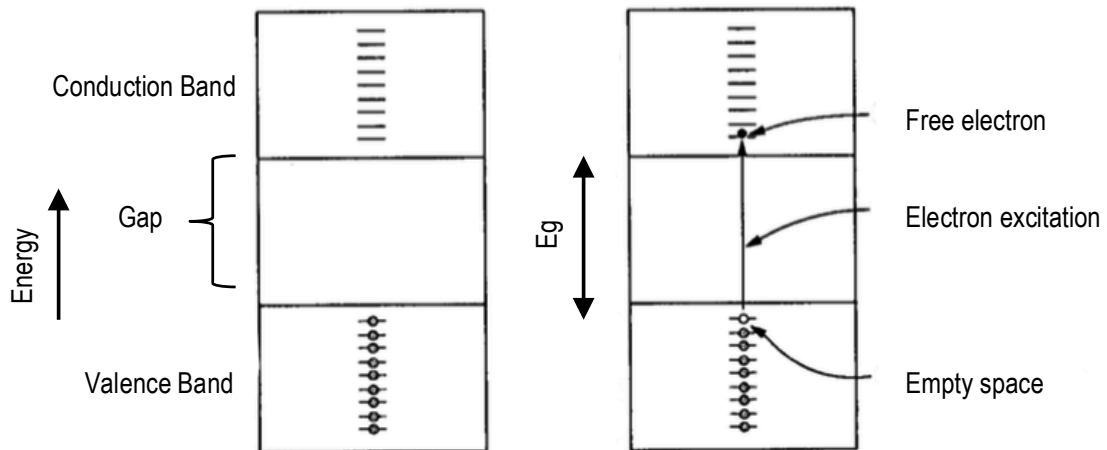


Figure 12. Electron Band of a semiconductor before and after electron excitation [1]

Conductivity of insulators and semiconductors can also be seen from the perspective of chemical bonding models. In insulating materials, the interatomic bond is ionic or strongly covalent. Thus, the valence electrons are strongly attached to or shared by individual atoms. These electrons are very localized and are not at all free to move within the crystal. The bond in the semiconductors is covalent (or predominantly covalent) and is relatively weak; this means that valence electrons are not tightly bound to atoms. As consequents, in semiconductors, these electrons are more easily switched off by thermal excitation than in insulators.

4.2. THERMAL CONDUCTIVITY

Thermal conductivity, K [$\text{Wm}^{-1}\text{K}^{-1}$], is the property of the materials that indicates the ability to conduct heat. It is evaluated in terms of Fourier's first law of heat conduction, which gives the heat flux proportional to the temperature difference, surface area, and length of the sample:

$$H = \frac{\Delta Q}{\Delta t} = KA \frac{\Delta T}{l} \quad (9)$$

Where Q/t is the rate of heat transfer, A is the surface area and l is the length.

Heat transfer, the movement of thermal energy from a hotter to a colder body, occurs only through three modes:

- Conduction: involves the transfer of thermal energy by combination of diffusion of electrons and phonon vibrations (applicable in solids)
- Convection: involves the transfer of thermal energy in moving medium. The hot gas/liquid moves through the cooler medium (normally due to density difference)
- Radiation: involves the transfer of thermal energy by electromagnetic radiation.

Factors to influence thermal conductivity:

- Chemical composition
- Atomic structure
- Phase changes
- Grain size
- Temperature and pressure

4.2.1.THERMAL CONDUCTIVITY IN METALS

Metals have a relatively high concentration of free conduction electrons, and these can transfer heat as they move through the lattice. Therefore, the method of conduction in metals is the same for thermal and electrical conduction, by the movement of valence electrons.

Wiedemann-Franz law relates thermal and electrical conductivity to temperature. This law states that the ratio of the electronic contribution of the thermal conductivity (K) to the electrical conductivity (σ) of a metal is proportional to the temperature (T)

$$LT = \frac{K}{\sigma} \quad (10)$$

Where L is a proportional constant, also known as the Lorenz number:

$$L = 2,45 \times 10^{-8} W \Omega K^{-2}$$

For metals, thermal conductivity decreases when temperature increases since it is mainly a function of the motion of free electrons. As the temperature increases, the molecular vibrations increase, reducing the mean free path. So, they obstruct the flow of free electrons, thus reducing the conductivity.

4.2.2.THERMAL CONDUCTIVITY IN NON-METALS

Non-metals have a relatively few free electrons, so thermal conductivity occurs by a different mechanism; the energy transfer involves lattice vibrations or phonons.

A phonon is a quantum mechanical description of an elementary vibrational motion, in which a lattice of atoms or molecules uniformly oscillates at a single frequency. Atoms in solids are coupled to each other by bonds so, atomic vibrations are also coupled. This atomic vibrations lead to waves, known in classical mechanics as a normal mode.

Two different types of phonons exist, optical and acoustic. The frequency of acoustic phonons is around that of sound, and for optical phonons, close to that of infrared light.

When a non-metal is heated, the heat absorbed in the hot region of the material generates phonons, which travels toward the cold region transferring energy. Phonons can collide with other phonons, crystal defects and impurities, which difficult their propagation along the direction of the heat flow. Therefore, thermal conductivity is proportional to the mean free path that a phonon travels before losing its momentum.

Materials with strong covalent bonds, like diamond, have higher thermal conductivity, due to the strongly coupled atoms, than weak bonds between chains like polymers.

In case of non-metals, thermal conductivity increases with temperature since the method of conduction is molecular vibrations.

5. EXPERIMENTAL PROCEDURE

At the beginning of this work, the background and the state-of-art of different existing techniques to improve surface electrical and thermal conductivity has been studied. As it was mentioned above, there are two different approaches to the problem: joining two different materials or coating a thin film onto a material. In this work we will compare the two different approaches using three different techniques:

- Joining: Adhesive bonding
- Coating:
 - Gaseous State: Sputtering
 - Solution State: Electrochemical deposition

Experiments were performed on CFRP with epoxy resin as matrix. It is reasonable to say that each sample has the same chemical and mechanical properties.

5.1. ADHESIVE BONDING

Adhesive bonding is a process well known for automobile and aircraft industry to improve superficial properties. The choice of adhesive joints as assembly method allows better stress distribution as well as durable, lightweight bonding. Exist a wide range of adhesives for joining CFRP's with metals and a lot of studies for superficial treatments to improve bond strength and joint durability [7-9]. Many researchers have studied the modification of composite surfaces by means of solvent cleaning, abrasion, pee-ply, tear-ply, acid chemical etching or plasma treatments.

A simulation of an adhesive bonding of CFRP with a metal has been prepared using an adhesive tape of copper and another of aluminium.

Two samples of CFRP with copper adhesive tape 12 mm wide and two samples of aluminium adhesive tape 15 mm wide will be tested with the four probe method to compare their electrical conductivity.

Every sample has been cleaned with ethanol and DI water and subsequently dried to have a clean surface where to join the adhesive tape.

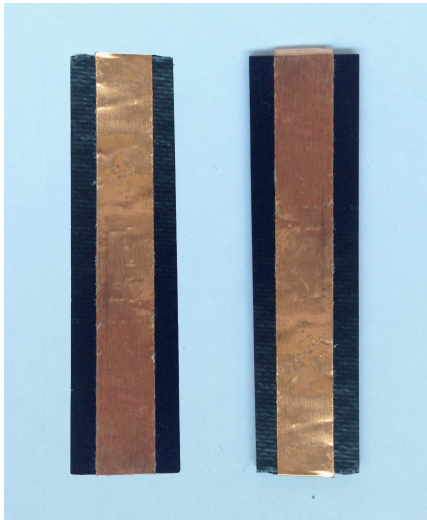


Figure 13. CFRP with copper adhesive tape



Figure 14. CFRP with aluminium adhesive tape

5.2. SPUTTERING

Sputtering is a PVD technique with a wide range of applications in the semiconductor, optical and industrial coating. Many sputtering systems exist to accomplish a uniform film. In this project we used Pulsed Direct Current Magnetron Sputtering (PDCMS) granted by the department of Applied Physics and Optics (FAO) of the Universitat de Barcelona.

PDMCS is particularly effective for the sputtering of metals and dielectric coatings. The main advantage of this method is that it reduces or eliminates the formation of arcs, which can cause damage on the deposited film as well as on the DC power system. PDMCS is recently been employed in many different applications because of its high plasma density at the substrate, the wide range of process parameters alternation, and also for its stable and high deposition rate of insulators and semiconductors compared to other methods.

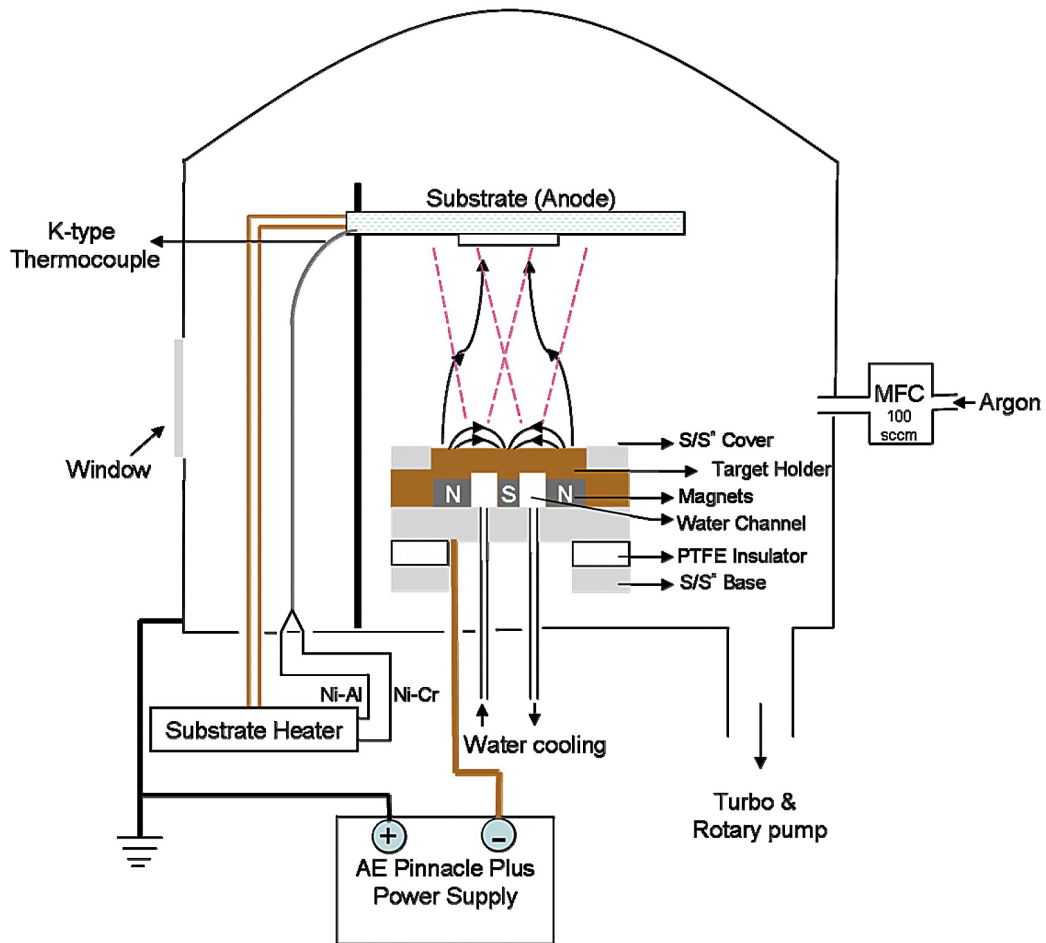


Figure 15. Schematic representation of Pulsed DC Magnetron Sputtering [20]

The system consists of a cylindrical stainless steel vacuum chamber with a pump to create the vacuum (Figure 15). A magnetron with an aluminium target serves as the sputter source.

The main process of this method can be summarize in three points:

1. Surface treatment: Oxygen plasma. This treatment breaks the molecular bonds on the surface of the substrate and creates reactive free radicals, which react with the oxygen forming chemical functional groups. Therefore, oxygen plasma increases surface energy and thus promotes adhesion by providing specific interactions across the adhesive-adherent interface. The ionized gas generated by plasma allows several effects, which are mainly cleaning, activation, and oxidation of polymeric surfaces without affecting bulk properties.
2. Cleaning the chamber: Prior to the sputtering the system is purged with argon gas to ensure a clean surface of the sample.

3. Sputtering: Deposit a film of aluminium onto the surface of the sample (described in **3.2.1.1. PVD**). The tests were performed at room temperature, 100 KHz, $0,51\pm0,01$ A and 228 ± 1 V (All the parameters of the test are summarized in Annex 1)

Three samples where sputtered with this method in three different sputtering times (1800s, 3600s, 4500s), to achieve different thickness coatings.

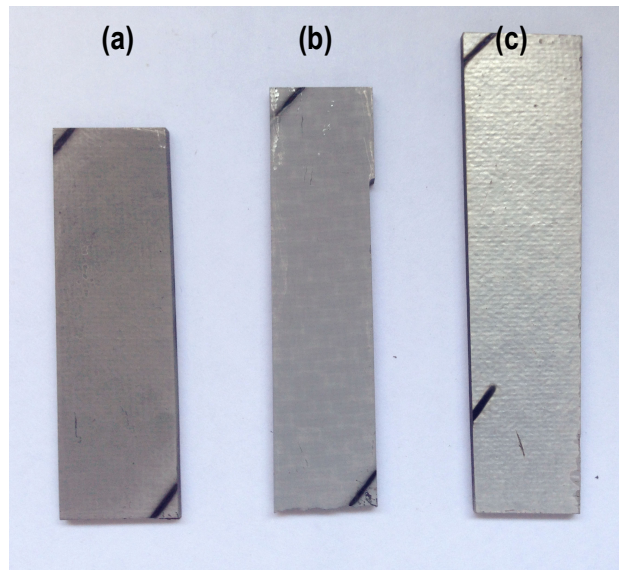


Figure 16. Aluminium sputtered samples. a) 1800s b) 3600s c) 4500s

5.3. ELECTROCHEMICAL DEPOSITION

Copper is an excellent choice for electrochemical deposition, since it has a very high plating efficiency, resulting in excellent coverage even on difficult-to-plate parts. It is highly conductive and also acts as thermal expansion barrier by absorbing the stress produced when different thermal expansion coefficients undergo temperature changes, and this is particular helpful with plastic substrates. The major advantage of electrochemical deposition of copper is the simplicity of the process; it can take place at room temperature, the voltage required for the deposition is lower in acid solutions and the thin film properties can be controlled.

For copper deposition, CFRP ($4,4\pm0,2 \times 1,4\pm0,1$ cm) and pure copper (10x4 cm) were used as the cathode and anode respectively. The samples of CFRP were grinded mechanically (grid 320P) to generate an activation of the surface, improving the adherence. Then they were cleaned with ethanol and rinsed with deionized water.

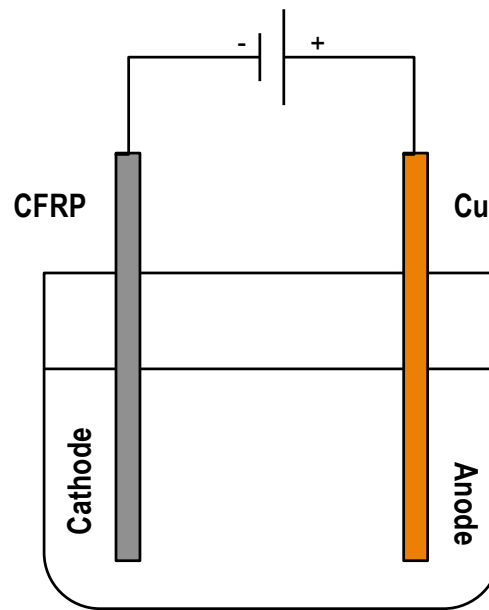


Figure 17. Scheme of the electrolytic cell

The distance between copper anode and the samples was 3cm, and the submerged area of the anode was three times that of the cathode. Two-electrode electrolytic cell was used with 225g/L of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and 70g/L of H_2SO_4 , operating at room temperature. Copper sulphate provides a source of copper ions and sulphuric acid makes the bath conductive and acts as a charger.

The voltage applied to the electrolytic cell was 2,5V. The samples were tested in three different times to achieve different film thicknesses (3, 5, and 7minutes).

These operating conditions are extracted from “Electrodeposition of Copper,” *Mod. Electroplat. Fifth Ed.* [26]

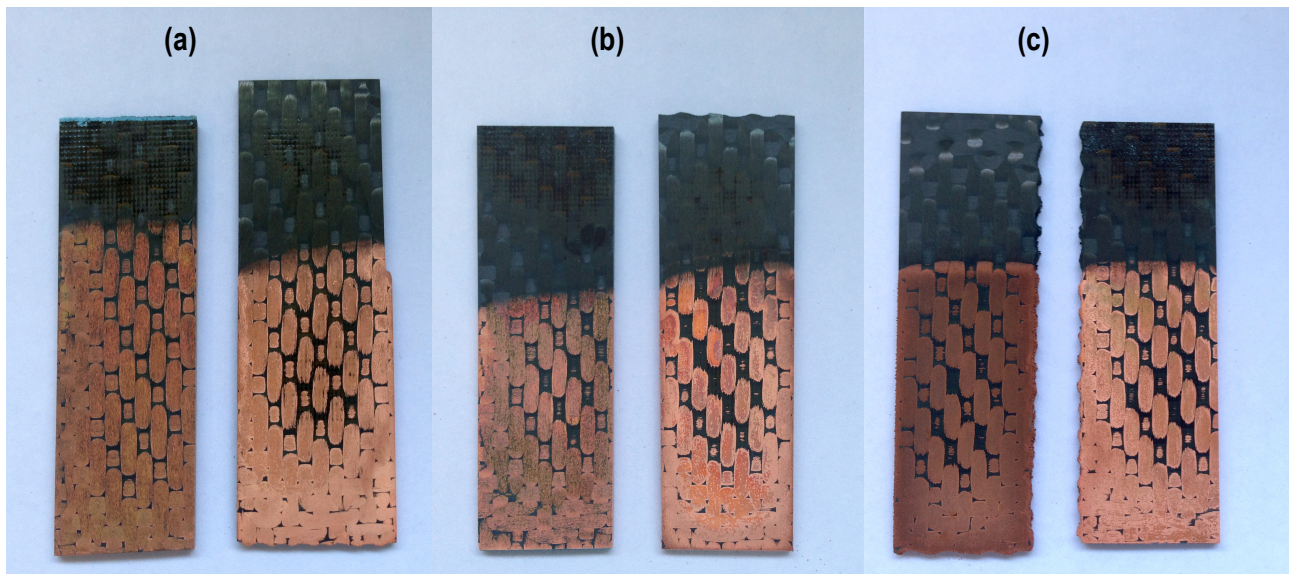


Figure 18. Samples of electrochemical deposition of Copper. a) 3 min, b) 5 min c) 7 min

5.4. FOUR-POINT PROBES METHOD

The four-point method was developed by Lord Kelvin and upgraded by Frank Wenner at the beginning of the 20th century to measure the resistivity of the planet Earth. In 1954, Leopoldo Valdes used this idea to measure the resistivity of semiconductors. This method has proven to be a convenient tool for the measurements of resistivity for semiconductors and for samples of all kinds of shapes. [41,43]

The advantage of four-points method is that it allows to eliminate the effect of the resistance of the cables and contact potentials, as well as to evaluate the magnitude of these potentials. This method makes use of two linked circuits as shown in figure 19. The four probes are placed on a flat surface of the material to be measured. Current is passed through the two outer electrodes and the floating potential is measured across the inner pair.

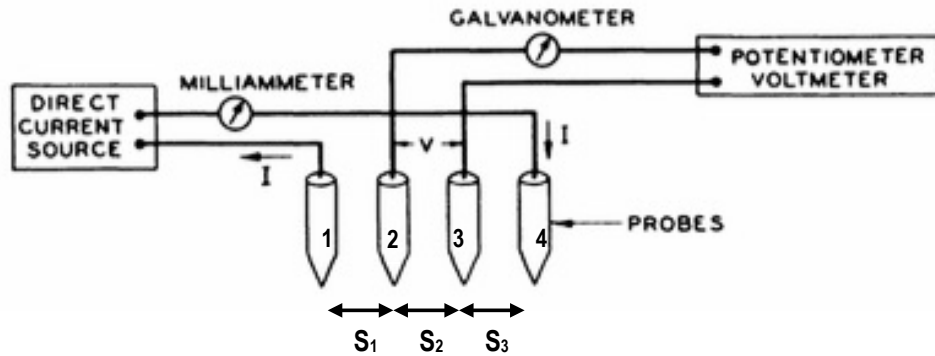


Figure 19. Circuit used for resistivity measurements [41]

In order to use the four-point probes method it is necessary to assume that:

- The resistivity of the material is uniform on the area of measurements.
- The surface on which the probes rest is flat with no surface leakage.
- The four probes used for resistivity measurements contact the surface at points that lie in a straight line
- The diameter of the contact between the metallic probes and the semiconductor should be small compared to the distance between probes
- A non-conducting boundary is produced when the surface of the coating is in contact with an insulator.

To measure the resistivity of our samples we will treat them as if they were a semi-infinite volume of material and then we will apply a correction factor. Figure 20 shows the geometry of this case. Four probes are spaced, s_1 , s_2 and s_3 , and current I is passed through the outer probes (1 and 4). The floating potential V is measured across the inner pair of probes 2 and 3.

The floating potential V_f at any point, is the difference between potential induced by each of the electrodes, since they carry currents of equal magnitude but in opposite directions:

$$V_f = \frac{\rho I}{2\pi} \left(\frac{1}{r_1} - \frac{1}{r_4} \right) \quad (11)$$

Where r_1 is the distance from probe number 1, and r_4 is the distance from probe number 4.

The potential difference V between probes is then the difference of the floating potentials at probe 2 (V_{f2}) and probe 3 (V_{f3}) substituting the proper distances:

$$V = V_{f2} - V_{f3} = \frac{\rho I}{2\pi} \left(\frac{1}{s_1} + \frac{1}{s_3} - \frac{1}{s_2+s_3} - \frac{1}{s_1+s_2} \right) \quad (12)$$

When the point spacing is equal ($s_1=s_2=s_3=s$) the equation above simplifies to:

$$\rho = \frac{V}{I} 2\pi s \quad (13)$$

If the resistivity is measured on a thin slice-non-conductive bottom surface as our case, we will have to apply a boundary condition to correct the deviations due to the new geometry of the samples.

Two boundary conditions must be met on this case; the top surface of the slice must be a conducting surface and the bottom of the surface must be a non-conducting surface. The method proposed by Valdes is by the method of images that requires for each current source an infinite series of images along a line normal to the planes passing through the current source.

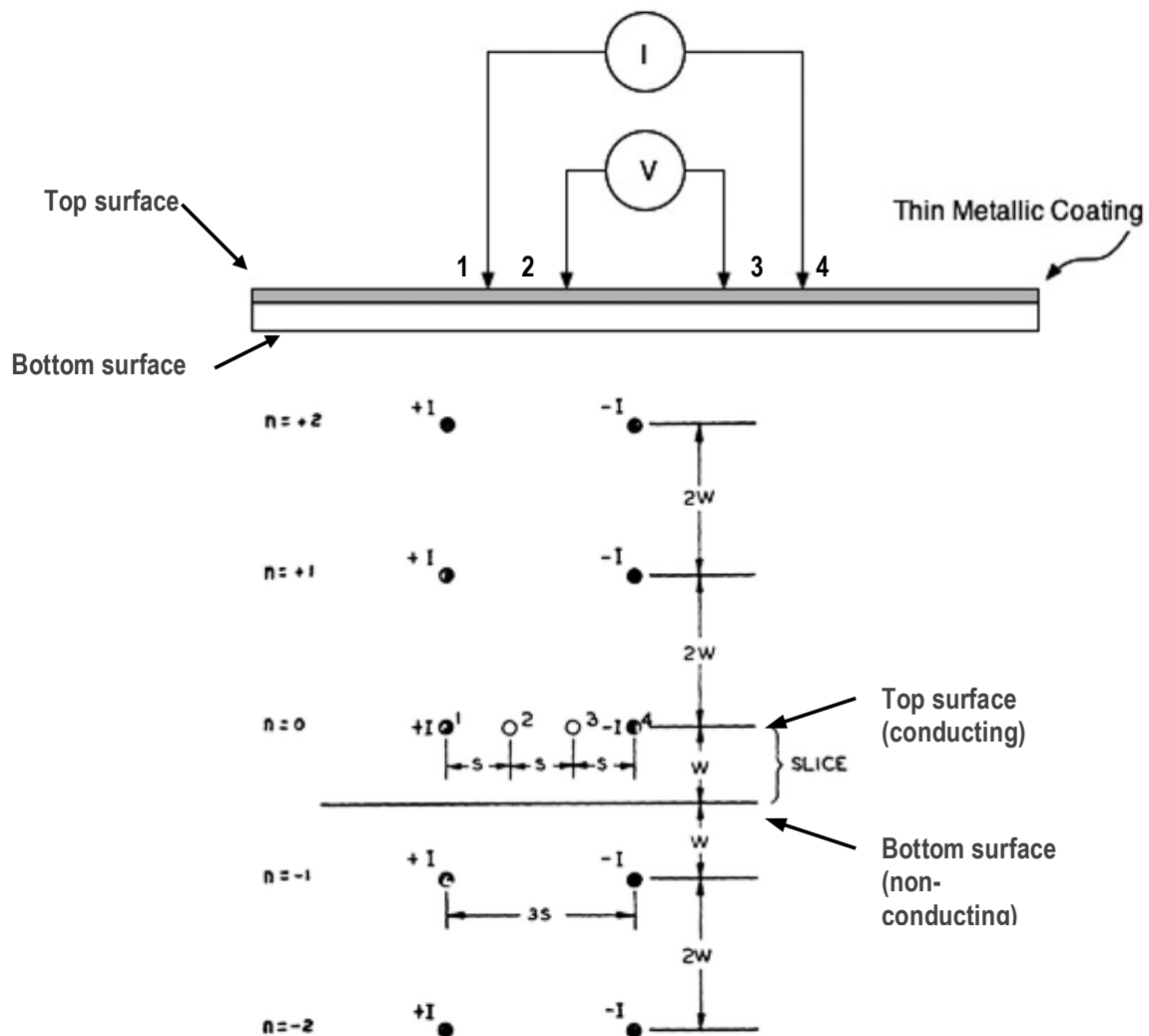


Figure 20. Image for the case of the resistivity probes on thin slice with a non-conducting bottom surface [41]

In this analysis, equal probe spacing s shall be assumed and the width of the slice is w . Figure 20 shows where the polarity and spacing of the first few images are.

With this model it is possible to calculate the resistivity as:

$$\rho \cong \frac{\rho_0}{G_7\left(\frac{w}{s}\right)} \quad (14)$$

Where ρ_0 is computable from (13) and G_7 :

$$G_7\left(\frac{w}{s}\right) = 1 + 4 \frac{s}{w} \sum_{n=1}^{n=\infty} \left(\frac{1}{\sqrt{\left(\frac{s}{w}\right)^2 + (2n)^2}} - \frac{1}{\sqrt{\left(2\frac{s}{w}\right)^2 + (2n)^2}} \right) \quad (15)$$

This function $G_7(w/s)$ is tabulated in table 3 and plotted in Figure 22. For smaller values of w/s the function can be approached to:

$$G_7\left(\frac{w}{s}\right) = \frac{2s}{w} \ln 2 \quad (16)$$

Table 3. Values for G_7 [41]

w/s	$G_7(w/s)$
0,100	13,863
0,141	9,0704
0,200	6,931
0,333	4,159
0,500	2,780
1,000	1,504
1,414	1,223
2,000	1,094
3,333	1,0228
5,000	1,00070
10,000	1,00045

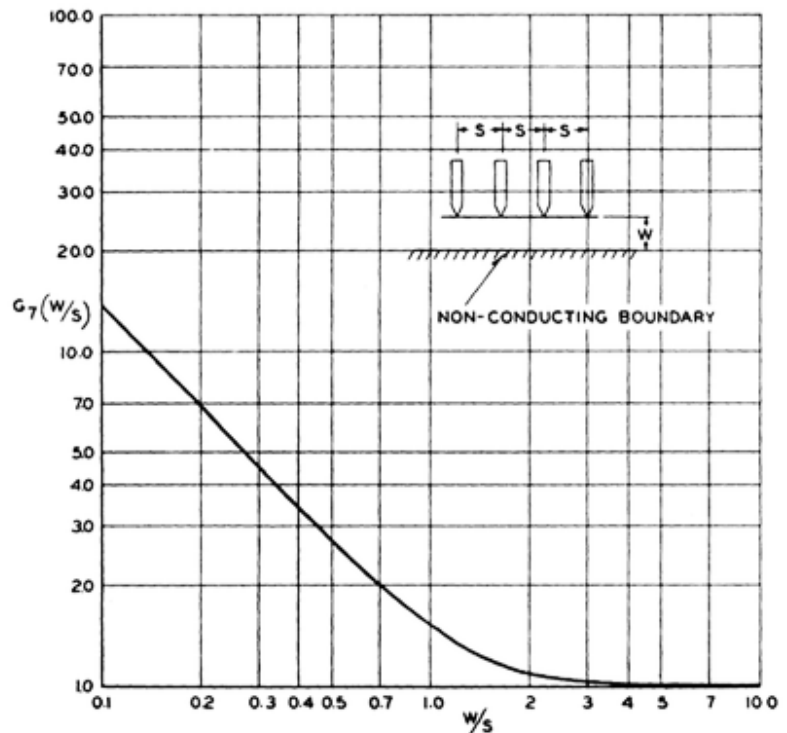


Figure 21. Correction divisor for a non-conducting boundary [41]

6. RESULTS AND DISCUSSION

6.1. COATING TECHNIQUES RESULTS

The two coating methods used in this work, sputtering and electrochemical deposition, were characterized with an optical microscopy to compare the difference between the surfaces.

The first difference we can observe with optical micrograph images is the thickness of the samples. Sputtered samples have a thickness between $2,99\text{ }\mu\text{m}$ – $4,40\text{ }\mu\text{m}$ in contrast with electrodeposition that have a thickness between $21,57\text{ }\mu\text{m}$ – $45,81\text{ }\mu\text{m}$. It is common to express coating thicknesses in angstroms for PVD's and it is due to their deposition rates. In many cases deposition rates are faster for electrochemical depositions ($0,4 - 180\text{ }\mu\text{m}/\text{min}$ for electrochemical deposition and $0,012 - 24\text{ }\mu\text{m}/\text{min}$ for sputtering), therefore, it can be quite difficult to deposit a coating of few hundreds of angstroms.

Another main difference between the two techniques it is the uniformity of the film. As we can see in Figure 22, electrochemical depositions only coat the surface where carbon fibres are exposed. To use this technique, the substrate has to be conductive to ensure the reduction of copper on the cathode. In contrast, with sputtering any substrate material can be coated.

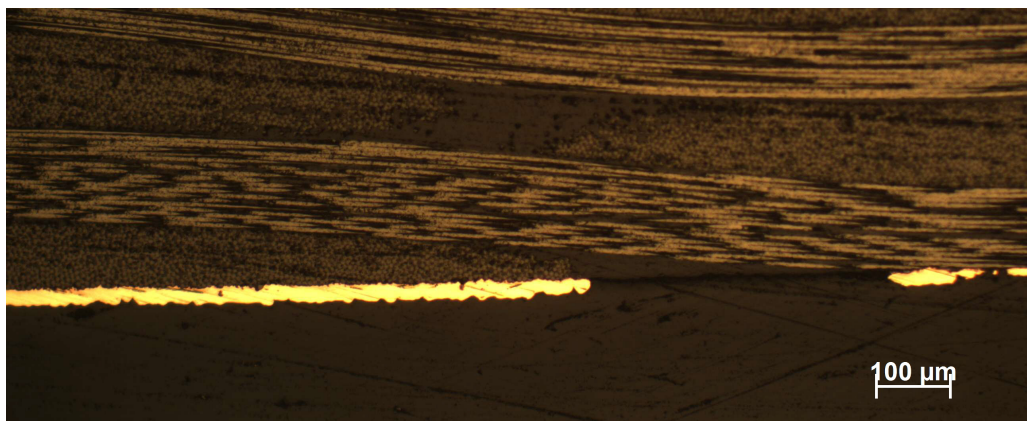


Figure 22. Optical micrograph image of electrochemical deposition surface with carbon fibre coated by copper and epoxy uncoated

It is possible to observe on the optical micrograph images, that more time sputtering or electrodepositing more thickness of the film. Although, for electrochemical deposition its fair to said that the optimal time would be around 5 – 7 minutes. At 3 minutes we can see a seed layer due to the nucleation of copper, but over time the film smothers and the layer is more uniform. At these thicknesses we couldn't observe any detachment of the coatings but it is a factor to take into account. If stress peaks are higher than the adhesion coating-substrate it will be detachment.

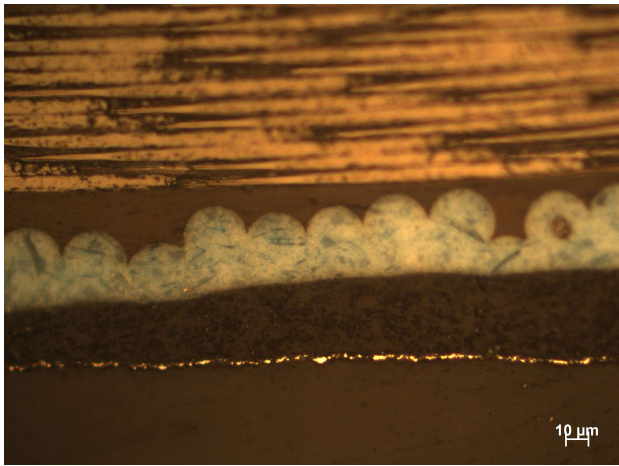


Figure 23. Optical micrograph image of sputtered surface 1800s

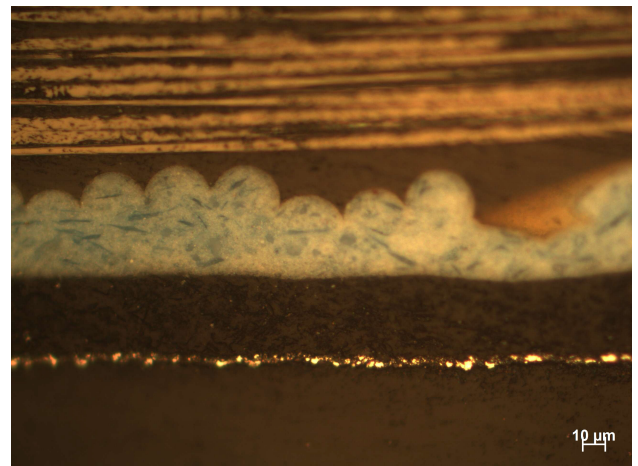


Figure 24. Optical micrograph image of sputtered surface 3600s

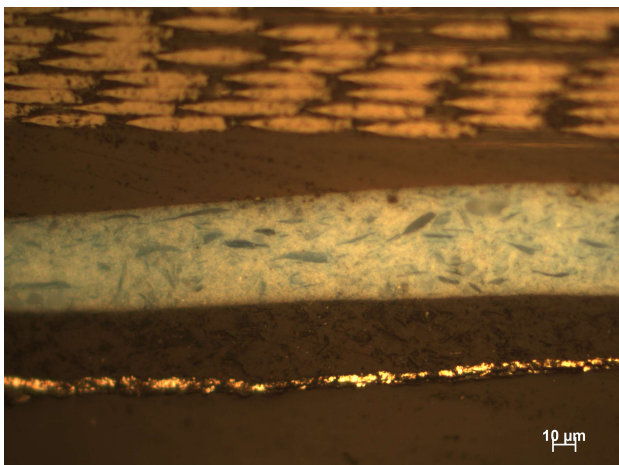


Figure 25. Optical micrograph image of sputtered surface 4500s

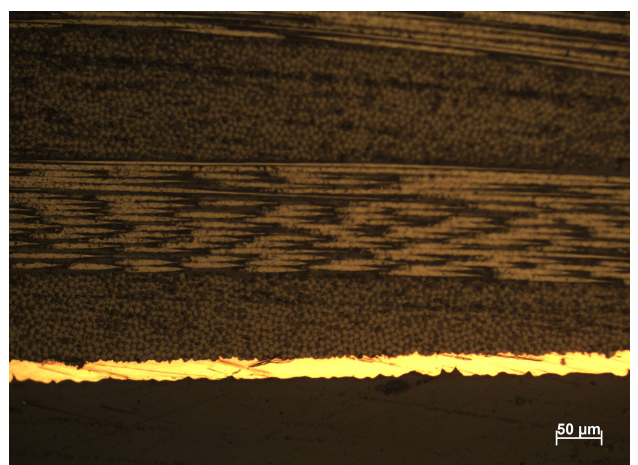


Figure 26. Optical micrograph image of electrochemical deposition surface 3 min

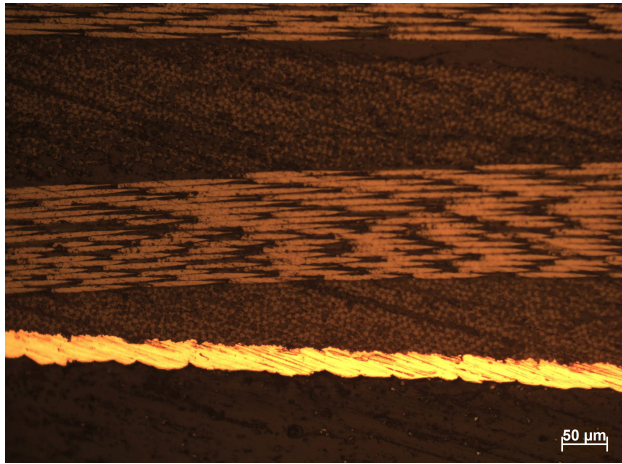


Figure 27. Optical micrograph image of electrochemical deposition surface 5 min

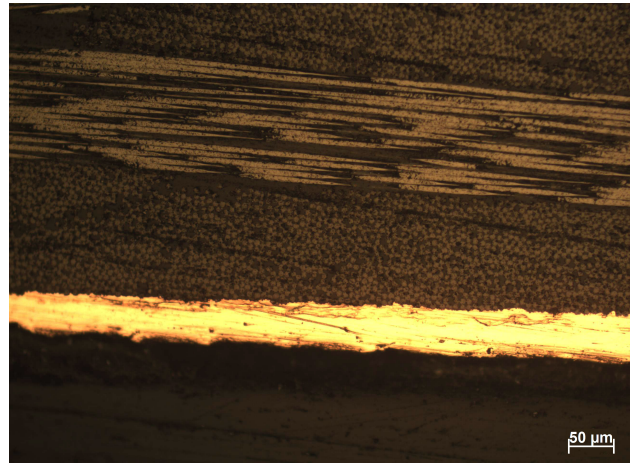


Figure 28. Optical micrograph image of electrochemical deposition surface 7 min

6.2. ELECTRICAL CONDUCTIVITIES RESULTS

We determined the resistivity, and therefore the electrical conductivity, by 4-points probe method of all the different techniques and compared with results before the treatments and with the tabulated values. Weight gain has also been determined since one of the reasons to switch to CFRP's is their good strength-weight ratio.

Table 4. Tabulated values for cooper, aluminium and CFRP [46]

Technique	Resistivity (Ωm)	Electrical Conductivity (S/m)	Density (kg/m^3)	Thermal conductivity (W/Km)
Cooper	$1,71 \cdot 10^{-8}$	$5,85 \cdot 10^7$	8960	400
Aluminium	$2,82 \cdot 10^{-8}$	$3,55 \cdot 10^7$	2700	237
CFRP	$6,67 \cdot 10^{-4}$	$1,5 \cdot 10^3$	1800	24

Table 5. Conductivities results by 4-probe method

Technique	Resistivity (Ωm)	Electrical conductivity (S/m)	Film Thickness (μm)	Weight increase (g/m^2 film)	
CFRP	$5,80 \cdot 10^{-3}$	$1,72 \cdot 10^2$	--	--	
Adhesive cooper tape	$6,10 \cdot 10^{-8}$	$1,64 \cdot 10^7$	70	3,56	
Adhesive Aluminium tape	$9,39 \cdot 10^{-8}$	$1,07 \cdot 10^7$	70	1,87	
Electrochemical deposition (copper)	3 min	$1,94 \cdot 10^{-6}$	$5,17 \cdot 10^5$	21,57	1,88
	5 min	$3,96 \cdot 10^{-7}$	$2,53 \cdot 10^6$	28,23	1,97
	7 min	$2,37 \cdot 10^{-7}$	$4,22 \cdot 10^6$	45,81	2,64
Sputtering (Aluminium)	1800s	$3,76 \cdot 10^{-7}$	$2,66 \cdot 10^5$	2,99	0,18
	3600 s	$7,18 \cdot 10^{-7}$	$1,39 \cdot 10^6$	3,19	0,19
	4500 s	$6,86 \cdot 10^{-7}$	$1,46 \cdot 10^6$	4,38	0,29

It can be seen in table 5 and in figure 29 and 30, that higher conductivities are achieved by increasing the thickness of the film. This is because by increasing the thickness we get more uniformity in the film and it is easier for electron carriers of charge to move. The dependence of resistivity, and therefore conductivity, on the thickness is strongly influenced by the interaction of the conduction electrons with the surface; the conduction mechanism and the surface roughness play an important role.

The reasons for this change in electrical conductivities when the film is thicker is due to increase surface interactions as well as scattering effects. Free paths of conduction electrons are reduce due to increased scattering effects. Several research studies have developed models to characterize and explain the behaviour of the electrical resistivity of metallic thin films as a function of the thickness [42].

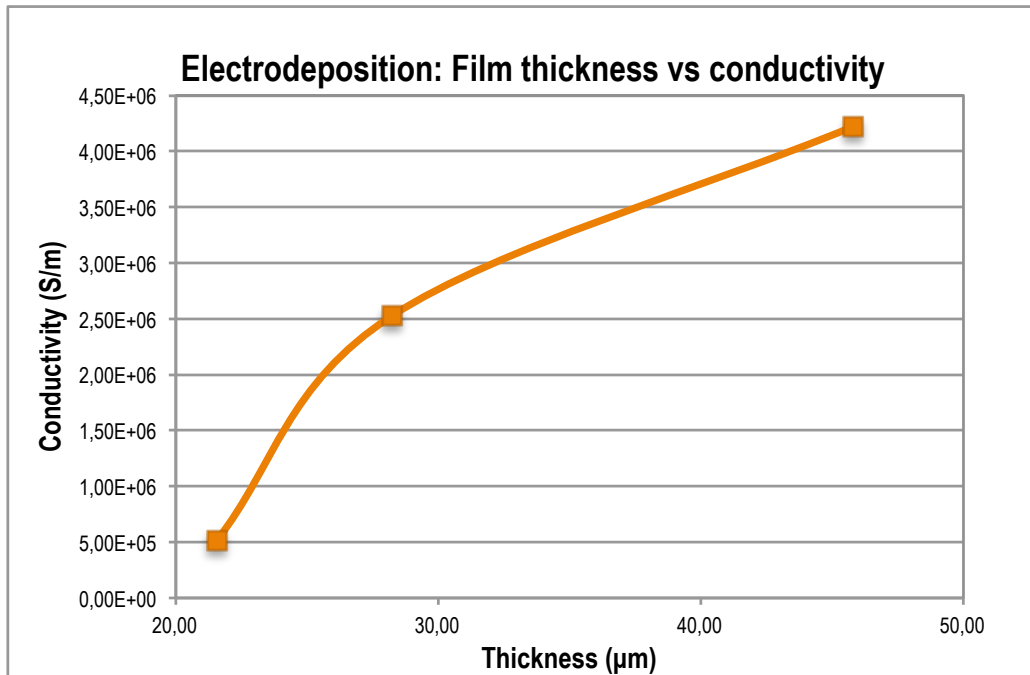


Figure 29. Film thickness vs. conductivity for electrochemical deposition of copper in CFRP

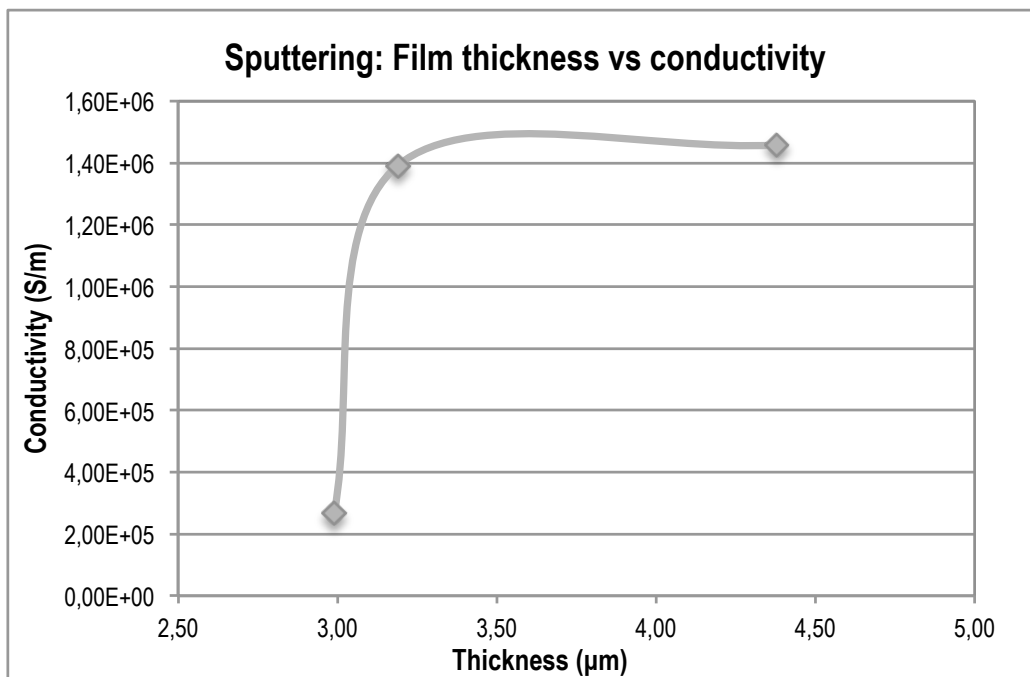


Figure 30. Film thickness vs. conductivity for sputtering of aluminium in CFRP

Comparing the conductivity of the different methods of aluminium and copper, it is easy to see that copper have better results but at the same time it is heavier than aluminium (Figure 31). Aluminium has a lower density than copper, and although it has a lower conductivity it's possible to achieve similar values for the same weight increasing the thickness of the film.

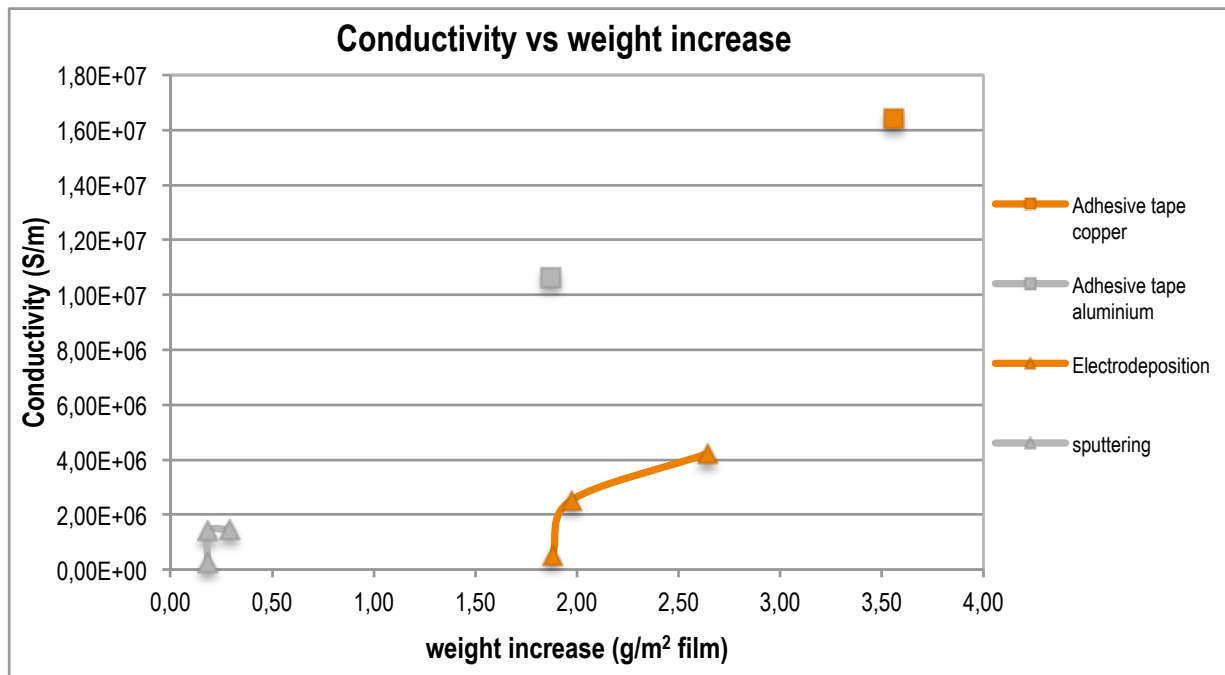


Figure 31. Conductivity vs. gain weight

Adhesive technique has reached better results than sputtering and electrochemical deposition. One of the main reasons its due to the film uniformity and thickness. As we see in the optical micrograph images, electrochemical deposition and especially sputtering do not have a smooth surface and still have some uncoated gaps.

6.3. THERMAL CONDUCTIVITIES RESULTS

To compare thermal conductivity, since we have metallic films onto the samples, we use Wiedemann-Franz law, which relates thermal and electrical conductivity to temperature.

$$LT = \frac{\kappa}{\sigma} \quad (10)$$

As with electrical conductivity, thermal conductivity in metals depends on the movement of free electrons. So the thermal conductivity is influenced by the thickness of the film; thinner films reduce free paths of conduction electrons decreasing thermal conductivity.

Table 5. Thermal conductivities using Wiedemann-Franz law

Technique	Electrical conductivity (S/m)	Thermal conductivity (W/Km)	Film Thickness (μm)
Adhesive cooper tape	$1,64 \cdot 10^7$	118,63	70
Adhesive Aluminium tape	$1,07 \cdot 10^7$	77,40	70
Electrochemical deposition (copper)	3 min $5,17 \cdot 10^5$	3,74	21,57
	5 min $2,53 \cdot 10^6$	18,30	28,23
	7 min $4,22 \cdot 10^6$	30,53	45,81
Sputtering (Aluminium)	1800s $2,66 \cdot 10^5$	1,92	2,99
	3600 s $1,39 \cdot 10^6$	10,05	3,19
	4500 s $1,46 \cdot 10^6$	10,56	4,38

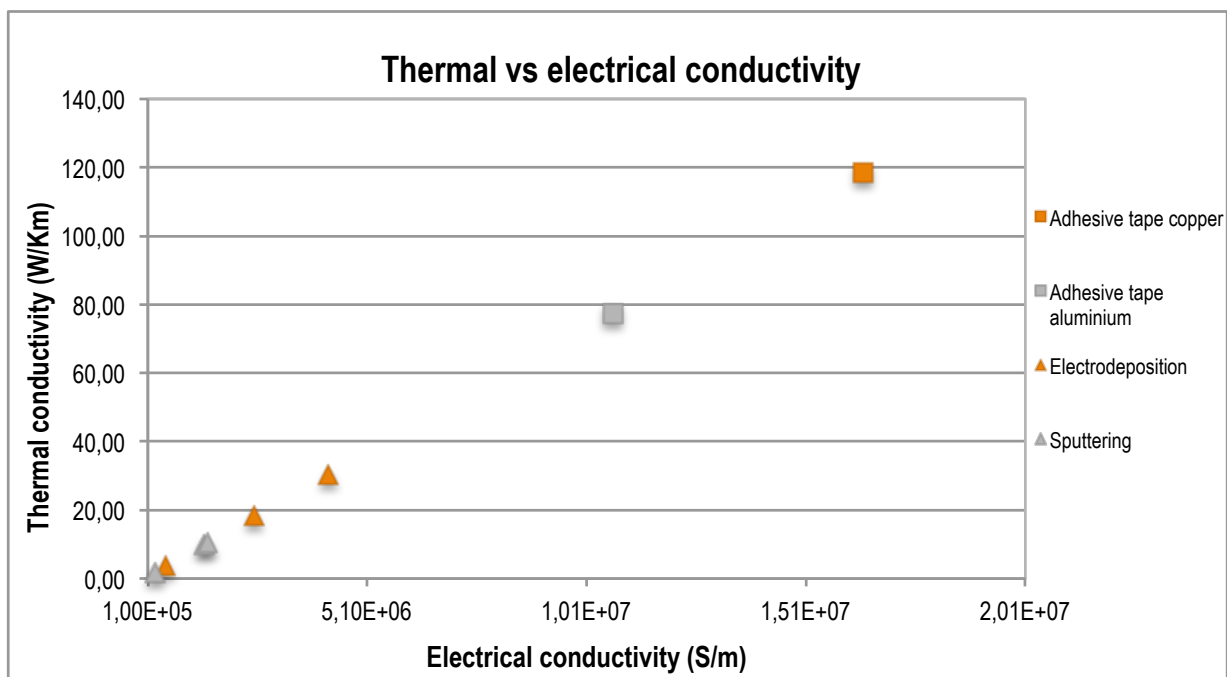


Figure 32. Thermal conductivity vs. electrical conductivity

The tests done in this project showed that copper is still a better choice to lightning strike efficient protection, but it should be found a good method to achieve uniform and thin films to reduce the increasing weight of copper coating. Aluminium can also be a good choice if weight reduction is the main point, but the risk of galvanic corrosion in contact with carbon fibre and the

strong reactivity of this metal is a concern. It would be possible to add an isolation layer of fibreglass but it would probably increase the weight.

The aircrafts industry has approach the issue using the most conductive materials in zones where lightning is most likely to attach, and lightweight materials with higher conductor resistance in zones that rarely see a direct strike (like fuselage). [3-5, 47-49]

7. CONCLUSIONS

- Electrochemical deposition achieves thicker films than sputtering due to their deposition rates.
- Electrochemical deposition can only coat conductive substrates. For non-conductive substrates, sputtering and adhesive joining reach more uniform metallic films.
- More time sputtering or electrochemical depositing, thicker films will be achieved. Moreover, it is possible that appear some detachment would appear.
- The optimal time for electrochemical deposition in our conditions will be between 5 – 7 minutes. At 7 minutes is possible to see a smooth an uniform film.
- Thermal conductivity in metals is related to electrical conductivity; both depends of the movement of free electron
- Electrical and thermal conductivity are highly dependent by the thickness of the film. Thinner metallic films have poor electrical and thermal conductivity because of the reduction of free paths of conduction electrons due to the increased scattering effects.
- It is possible to reach better result with copper than with aluminium with any method. However the weight of the material is highly increased.

REFERENCES AND NOTES

- [1] M. Cruells, N.Llorca, P. Molera, A. Roca and J. Viñals, "Ciència dels materials" Second edit., 2011.
- [2] B. Sandhya, A. Ramesh, B. D. Prasad, C. Mohannaidu, and A. Prof, "A review on Carbon Fibres," *Int. J. Adv. Eng. Glob. Technol.*, no. 4, pp. 476–484, 2015.
- [3] J. Hale, "Boeing 787," *Boeing.com/commercial/aeromagazn*
- [4] "Airbus" <http://www.airbus.com/innovation/proven-concepts/in-manufacturing/>
- [5] X.-S. Yi, *Development of multifunctional composites for aerospace application*. Elsevier Inc., 2015.
- [6] J. Pora, "Composite Materials in the Airbus A380," *Airbus, Large Aircr. Div.*, 2001.
- [7] J. Jahn, M. Weeber, J. Boehner, and R. Steinhilper, "Assessment Strategies for Composite-metal Joining Technologies – A Review," *Procedia CIRP*, vol. 50, pp. 689–694, 2016.
- [8] P. Kah, R. Suoranta, J. Martikainen, and C. Magnus, "Techniques for joining dissimilar materials: Metals and polymers," *Rev. Adv. Mater. Sci.*, vol. 36, no. 2, pp. 152–164, 2014.
- [9] R. Balkova, S. Holcnerova, and V. Cech, "Testing of adhesives for bonding of polymer composites," *Int. J. Adhes. Adhes.*, vol. 22, no. 4, pp. 291–295, 2002.
- [10] P. M. Martin, "Handbook of deposition technologies for films and coating," *Science applications and technology* third ed., 2010.
- [11] J.-T. Wang, *Chemical Vapor Deposition and Its Applications in Inorganic Synthesis*. Elsevier B.V., 2017.
- [12] D. M. Mattox, "Physical vapor deposition (PVD) processes," *Met. Finish.*, vol. 93, no. 1 SUPPL. 1, pp. 394–408, 1995.
- [13] Sandhya, B, Ramesh, A. Prasad, B Durga, Mohannaidu, C and Prof, Assoc , "International Journal of Advanced Engineering and Global technology", 2015
- [14] LNF Wiki, University of Michigan "http://lnf-wiki.eecs.umich.edu/wiki/Sputter_deposition"
- [15] D. M. Mattox, *Ion Plating and Ion Beam-Assisted Deposition*. 2010.
- [16] D. Depla, S. Mahieu, and J. E. Greene, *Sputter Deposition Processes*, Third Edit. Elsevier Ltd., 2010.
- [17] P. Martin, *Ion Plating*, Third Edit. Elsevier Ltd., 2010.
- [18] P. Martin, *Deposition Technologies: An Overview*, Third Edit. Elsevier Ltd., 2010.
- [19] S. C. Lofgran, "Thin film deposition and vacuum technology," p. 67, 2013.
- [20] K. and H. S. Wasa, "Sputtering Systems."
- [21] Wikipedia electroplating, <https://en.wikipedia.org/wiki/Electroplating>
- [22] D. Grujicic and B. Pesic, "Electrodeposition of copper: The nucleation mechanisms," *Electrochim.*

Acta, vol. 47, no. 18, pp. 2901–2912, 2002.

- [23] M. Volmer and A. Weber, "Nucleation and Growth of Metals," vol. 195, pp. 195–229.
- [24] B. Kalska-Szostko, "Electrochemical Methods in Nanomaterials Preparation," *Recent Trend Electrochem. Methods Nanomater. Prep.*, no. Dc, pp. 261–280, 2012.
- [25] Z. Guo, L. Sang, Z. Wang, Q. Chen, L. Yang, and Z. Liu, "Deposition of copper thin films by plasma enhanced pulsed chemical vapor deposition for metallization of carbon fiber reinforced plastics," *Surf. Coatings Technol.*, vol. 307, pp. 1059–1064, 2016.
- [26] J. W. Dini and D. D. Snyder, "Electrodeposition of Copper," *Mod. Electroplat. Fifth Ed.*, pp. 33–78, 2011.
- [27] A. Weber, "Surface coating methods," pp. 7–32.
- [23] L. . Samuels, "Electroplating," *Corrosion*, p. 12:3-12:50, 1994.
- [24] P.-H. Haumesser, "The Precipitation of Metals: Thin Film Electroplating and Nanoparticle Synthesis," *Nucleation Growth Met.*, pp. 59–70, 2016.
- [25] S. Karthikeyan, A. E. Hill, J. S. Cowpe, and R. D. Pilkington, "The influence of operating parameters on pulsed D.C. magnetron sputtering plasma," *Vacuum*, vol. 85, no. 5, pp. 634–638, 2010.
- [26] K. Osborne, "Electroplating," *VIII-Metals-G-Electroplating*, pp. 1–8, 2011.
- [27] L. L. Hench and J. K. West, "The sol-gel process," *Chem. Rev.*, vol. 90, no. 1, pp. 33–72, 1990.
- [28] J. D. E. Physique, I. V Colloque, M. Engineering, P. O. Box, and M. Science, "Coating by laser surface treatment (*)," vol. 3, 1993.
- [29] G. Archambault, B. Jodoin, S. Gaydos, and M. Yandouzi, "Metallization of carbon fiber reinforced polymer composite by cold spray and lay-up molding processes," *Surf. Coatings Technol.*, vol. 300, pp. 78–86, 2016.
- [30] S. Griehl, T. Müller, and R. Winkler, "Thick metallization-layers on polymers through vacuum-technology," *Surf. Coatings Technol.*, vol. 169–170, pp. 24–26, 2003.
- [31] M. A. Montealegre, G. Castro, P. Rey, J. L. Arias, P. Vázquez, and M. González, "Surface Treatments By Laser Technology," *Contemp. Mater.*, vol. 1, no. 1, pp. 19–30, 2010.
- [32] P. Vuoristo, *Thermal Spray Coating Processes*, vol. 4. Elsevier, 2014.
- [33] R. N. A and K. R. V, "Material science: electrochemistry," *Univ. Cambridge*, 2014.
- [34] M. Ciobanu, J. P. Wilburn, M. L. Krim, D. E. Cliffel, and C. I. N. Electrochemistry, "Chemistry Fundamentals," *Departmenr Chem. Vanderbilt Univ.*, 1893.
- [35] G. J. H, "Material Science: Electrical properties of materials," *Univ. Cambridge*, 2014.
- [36] L. B. Valdest, "Resistivity Measurements on Germanium for transistors," *Proc. I-R-E*, vol. 29, pp. 1429–1434, 1952.
- [37] D. Lakshminarayana and R. R. R. Desai, "Thickness dependence of electrical resistivity and activation energy in AgSbTe₂ thin films," *J. Mater. Sci. Mater. Electron.*, vol. 4, no. 2, pp. 183–186, 1993.
- [38] A. P. Schuetze, W. Lewis, C. Brown, and W. J. Geerts, "A laboratory on the four-point probe

- technique," *Am. J. Phys.*, vol. 72, no. 2, pp. 149–153, 2004.
- [44] "Flame spray technologies", <https://www.fst.nl/about/thermal-spray-proces-what-is-thermal-spray/>
- [45] M.S.J. Hashmi, "Comprehensive materials finishing," vol. 1, 2016
- [46] R. Ramsdale, "Engineer's handbook", <http://www.engineershandbook.com/aboutus.htm>
- [47] S. Black, "Lightning strike protection strategies for composite aircraft"
<http://www.compositesworld.com/articles/lightning-strike-protection-strategies-for-composite-aircraft>
- [48] J.A. Segui, "Boeing Simulates Thermal Expansion in composites with expanded metal foil for lightning protection of aircraft structures" https://www.comsol.com/story/download/191749/Boeing_CN2014.pdf
- [49] M. Gagné and D. Therriault, "Lightning strike protection composites," *Progress in Aerospace Science*, 2013

APPENDICES

APPENDIX 1: PARAMETERS OF SPUTTERING TESTS

Substrate	Carbon fiber	Researcher	Fernando Pantoja
Sample code	17D1901	Date	19/04/2017
		Hour	12:47

Objective Clean the target and deposit film

Clean with O2 plasma, Al films

Sample geometry	Width	11	mm
	Height	43	mm
	Thickness	2	mm
	Diameter		mm

Result



Thin film 1

Previous vacuum*	1.73*10^-3	Pa	Pulsed power	60	W
Previous flux	1	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	30	Pa	Pulsed current	0.14+0.01	A
Base-turbo pressure	10+1	Pa	Pulsed voltage	410+30	V
Sample-target		cm	Sample temperature	RT	°C
time	300	s			

Target 1	Carbon fiber (cleaning)	Gas 1	O2	Gas 2	
Deposit rate		nm/s	Flux (sccm)	10	Flux (sccm)

Thin film 2

Previous vacuum*	3*10^-4	Pa	Pulsed power	120	W
Previous flux	1	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	0.99	Pa	Pulsed current	0.52	A
Base-turbo pressure	1.17*10^-1	Pa	Pulsed voltage	228.8	V
Sample-target	8	cm	Sample temperature	RT	°C
time	600	s			

Target 2	Al(cleaning)	Gas 1	Ar	Gas 2	
Deposit rate		nm/s	Flux (sccm)	20	Flux (sccm)

Thin film 3

Previous vacuum*	6*10^-4	Pa	Pulsed power	120	W
Previous flux	2	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	11.2	Pa	Pulsed current	0.51	A
Base-turbo pressure	0.99	Pa	Pulsed voltage	228.7	V
Sample-target	8	cm	Sample temperature	RT	°C
time	1800	s			

Target 3	Al	Gas 1	Ar	Gas 2	
Deposit rate		nm/s	Flux (sccm)	20	Flux (sccm)

Thin film 4

Previous vacuum*		Pa	Pulsed power		W
Previous flux		min	Pulsed frequency		KHz
Substrate cleaning		min	Pulse width		ns
Reactor pressure		Pa	Pulsed current		A
Base-turbo pressure		Pa	Pulsed voltage		V
Sample-target		cm	Sample temperature		°C
time		s			

Target 4		Gas 1		Gas 2	
Deposit rate		nm/s	Flux (sccm)		Flux (sccm)

Comments

With O2 plasma: Butterfly valve 25%

* with gas and bypass lines open

Substrate	Carbon fiber	Researcher	Fernando Pantoja
Sample code	17D2001	Date	20/04/2017
		Hour	09:22

Objective Clean the target and deposit film

Clean with O2 plasma, Al films

Sample geometry	Width	11	mm
	Height	47	mm
	Thickness	2	mm
	Diameter		mm

Result



Thin film 1

Previous vacuum*	$1.01 \cdot 10^{-4}$	Pa	Pulsed power	60	W
Previous flux	2	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	30	Pa	Pulsed current	0.12	A
Base-turbo pressure	5.45	Pa	Pulsed voltage	374	V
Sample-target		cm	Sample temperature	RT	°C
time	60	s			

Target 1	Carbon fiber	Gas 1	O2	Gas 2	
Deposit rate		nm/s	Flux (sccm)	10	Flux (sccm)

Thin film 2

Previous vacuum*	$3 \cdot 10^{-4}$	Pa	Pulsed power	120	W
Previous flux	1	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	0.99	Pa	Pulsed current	0.52	A
Base-turbo pressure	$1.17 \cdot 10^{-1}$	Pa	Pulsed voltage	228.8	V
Sample-target	8	cm	Sample temperature	RT	°C
time	3600	s			

Target 2	Al/cleaning	Gas 1	Ar	Gas 2	
Deposit rate		nm/s	Flux (sccm)	20	Flux (sccm)

Thin film 3

Previous vacuum*	$2.56 \cdot 10^{-4}$	Pa	Pulsed power	120	W
Previous flux	2	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	11	Pa	Pulsed current	0.52	A
Base-turbo pressure	0.99	Pa	Pulsed voltage	228.9	V
Sample-target	8	cm	Sample temperature	RT	°C
time	3600	s			

Target 3	Al	Gas 1	Ar	Gas 2	
Deposit rate		nm/s	Flux (sccm)	20	Flux (sccm)

Thin film 4

Previous vacuum*		Pa	Pulsed power		W
Previous flux		min	Pulsed frequency		KHz
Substrate cleaning		min	Pulse width		ns
Reactor pressure		Pa	Pulsed current		A
Base-turbo pressure		Pa	Pulsed voltage		V
Sample-target		cm	Sample temperature		°C
time		s			

Target 4		Gas 1		Gas 2	
Deposit rate		nm/s	Flux (sccm)		Flux (sccm)

Comments

With O2 plasma: Butterfly valve 29%

* with gas and bypass lines open

Substrate	Carbon fiber	Researcher	Fernando Pantoja
Sample code	17D2002	Date	20/04/2017
		Hour	12:02

Objective Clean the target and deposit film

Clean with O2 plasma, Al films

Sample geometry	Width	11	mm
	Height	47/54	mm
	Thickness	2	mm
	Diameter		mm

Result



Thin film 1

Previous vacuum*	5.8*10^-4	Pa	Pulsed power	60	W
Previous flux	2	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	30	Pa	Pulsed current	0.13	A
Base-turbo pressure	7.15	Pa	Pulsed voltage	430	V
Sample-target		cm	Sample temperature	RT	°C
time	60	s			

Target 1	Carbon fiber (cleaning)	Gas 1	O2	Gas 2	
Deposit rate		nm/s	Flux (sccm)	10	Flux (sccm)

Thin film 2

Previous vacuum*	3*10^-4	Pa	Pulsed power	120	W
Previous flux	1	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	0.99	Pa	Pulsed current	0.52	A
Base-turbo pressure	1.17*10^-1	Pa	Pulsed voltage	228.8	V
Sample-target	8	cm	Sample temperature	RT	°C
time	3600	s			

Target 2	Al(cleaning)	Gas 1	Ar	Gas 2	
Deposit rate		nm/s	Flux (sccm)	20	Flux (sccm)

Thin film 3

Previous vacuum*	3.8*10^-4	Pa	Pulsed power	120	W
Previous flux	2	min	Pulsed frequency	100	KHz
Substrate cleaning		min	Pulse width	2016	ns
Reactor pressure	10.6	Pa	Pulsed current	0.52	A
Base-turbo pressure	0.99	Pa	Pulsed voltage	227.7	V
Sample-target	8	cm	Sample temperature	RT	°C
time	4500	s			

Target 3	Al	Gas 1	Ar	Gas 2	
Deposit rate		nm/s	Flux (sccm)	20	Flux (sccm)

Thin film 4

Previous vacuum*		Pa	Pulsed power		W
Previous flux		min	Pulsed frequency		KHz
Substrate cleaning		min	Pulse width		ns
Reactor pressure		Pa	Pulsed current		A
Base-turbo pressure		Pa	Pulsed voltage		V
Sample-target		cm	Sample temperature		°C
time		s			

Target 4		Gas 1		Gas 2	
Deposit rate		nm/s	Flux (sccm)		Flux (sccm)

Comments

With O2 plasma: Butterfly valve 29%

* with gas and bypass lines open