Characterization of Deposited Platinum Contacts onto Discrete Graphene Flakes for Electrical Devices

Thesis by
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For years, electron beam induced deposition has been used to fabricate electrical contacts for micro and nanostructures. The role of the contact resistance is key to achieve high performance and efficiency in electrical devices. The present thesis reports on the electrical, structural and chemical characterization of electron beam deposited platinum electrodes that are exposed to different steps of thermal annealing and how they are used in four-probe devices of ultrathin graphite (uG) flakes (<100nm thickness). The device integration of liquid phase exfoliated uG is demonstrated, and its performance compared to devices made with analogous mechanically exfoliated uG. For both devices, similar contact resistances of $\sim 2\, \text{k}\Omega$ were obtained.

The electrical measurements confirm a 99.5% reduction in contact resistance after vacuum thermal annealing at 300 °C. Parallel to this, Raman characterization confirms the formation of a nanocrystalline carbon structure over the electrode. While this could suggest an enhancement of the electrical transport in the device, an additional thermal annealing step in air at 300 °C, promoted the oxidation and removal of the carbon shell and confirmed that the contact resistance remained the same. Overall this shows that the carbon shell along the electrode has no significant role in the contact resistance.

Finally, the challenges based on topographical analysis of the deposited electrodes are discussed. Reduction of the electrode’s height down to one-third of the initial value,
increased surface roughness, formation of voids along the electrodes and the onset of platinum nanoparticles near the area of deposition, represent a challenge for future work.
I want to thank my thesis advisor, Prof. Pedro Costa, for his continuous support during the complete duration of this research project. He welcomed me to do research and has continuously supported my learning and development. I especially thank him for his inspiring commitment and dedication.

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To my friends in KAUST and outside, I dedicate my gratitude for their friendship and encouragement. I would like to mention all of them here but that would certainly require more than this page.

I dedicate the effort behind this work to my beloved Blanca, for her encouragement, patience, and love.

My total gratitude goes to my family; I would not be here if it were not because of their efforts, lessons, and continuous support.

Finally thanks to God for allowing us to complete our dreams.

J.A.H.L.
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Gas injection system: GIS
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Laser beam lithography: LBL
Liquid metal ion source: LMIS
Liquid phase exfoliation: LPE
Mechanical exfoliation: ME
Metal ion free: MIF
Rapid thermal processing: RTP
Scanning electron microscopy: SEM
Transfer length method: TLM
Ultrathin graphite: uG
LIST OF SYMBOLS

Aluminum: Al
Carbon: C
Chromium: Cr
Cobalt: Co
Copper: Cu
Degree Celsius: °C
Gallium: Ga
Gold: Au
Iron: Fe
Nickel: Ni
Nitrogen gas: N₂
Ohm: Ω
Palladium: Pd
Platinum: Pt
Silicon: Si
Silicon carbide: SiC
Silicon dioxide: SiO₂
Silver: Ag
Titanium: Ti
Watt: W
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Chapter 1: Introduction

1.1 Graphene

Carbon, the sixth element of the periodic table, occurring naturally in different forms of allotropes, plays a major role in many aspects ranging from the environment and life to jewelry and industry [1]. In lately years, carbon materials especially at the nanoscale, have increased the attention of the scientific community because of their multiple interesting properties [2].

Graphene is one of the simplest forms of carbon and the thinnest possible; it is a single atom thick sheet of hexagonally arranged carbon atoms by sp² covalent bonding (Fig. 1.1) and is the unit building block of graphite [3].

![Graphene bond diagram showing carbon atoms with sp² bonding and dangling bonds.](image)

1.1.1 Historical Background and Context

The most recognized process to produce graphene from graphite is the mechanical exfoliation using Scotch™ tape; this method is famous because it was employed in the first
official isolation of single layer graphene [4][5]. This first milestone was achieved in 2004 by Novoselov, Geim, et al. [6]; the method consists in cleaving and peeling off graphene layers from a graphite stack using a piece of adhesive tape, repeating the step as many times as necessary to find from few layers to single layer graphene, and finally transferring the graphene layers by pressing the adhesive tape against a substrate.

Few years after the achievement, this new area of research was awarded the Nobel Prize in physics of 2010 [7], meanwhile, the mentioned scientific paper [6] has reached already more than twenty thousand citations [8][9]. It is important to say, that the knowledge of the existence of graphene and significant work around it was performed many years before [10] but without having the right recognition. This might happened because at that time it was a widely accepted fact that a single graphene layer (and any other free-standing atomic layer) would not be thermodynamically stable, and therefore impossible to isolate [6][11].

1.1.2 Properties

Graphene has been highlighted in many areas due to its different outstanding properties, as described in words of A. Geim:

“Graphene is a wonder material with many superlatives to its name. It is the thinnest known material in the universe and the strongest ever measured. Its charge carriers exhibit giant intrinsic mobility, have zero effective mass, and can travel for micrometers without scattering at room temperature. Graphene can sustain current densities six orders of magnitude higher than that of copper, shows record thermal conductivity and stiffness, is impermeable to gases, and reconciles such conflicting qualities as brittleness and ductility.” Andre Geim [12]
Thus, applications in several fields have been proposed and studied, ranging from electronics and flexible circuits to biomedical applications like DNA sequencing [13].

1.2 Graphene Dispersions: Towards Solution Processes

After demonstrating applications of graphene in the laboratory, the interest on production of graphene has been increased; the classical method of mechanical exfoliation with adhesive tape provides the highest quality of product but not the quantity desired, therefore other methods have been explored in order to produce graphene effectively and at the lowest possible cost. Chemical vapor deposition (CVD) on metallic substrates and epitaxial growth methods using SiC provide high-quality graphene, but their drawback is the limited scale and high cost. On other hand, solution processes as direct liquid phase exfoliation (LPE) of graphite have been demonstrated for large-scale production at a lower price [14].

Despite the fact that CVD and epitaxial growth provide a higher quality graphene, LPE has gained significant importance mainly in the development of printed electrical devices. LPE offers a meaningful economic advantage for several applications including thin film transistors [15], energy devices [16], optoelectronic and photonic devices [17]. According to G. Fiori et al. [18] LPE could be considered the preferred technique for nanoelectronic applications, only if the graphene flake size and thickness produced by this method is controlled successfully by sorting processes [19] that can guarantee the product.

With sights into that future, the present work relies on LPE method.

1.3 Graphene Devices

One of the most promising applications of graphene and related materials is in the field of electronic devices [20]; the outstanding electrical properties of graphene [6] and its relevant
small thickness make it a very good candidate for future technology where smaller, faster, and more efficient devices are aimed for.

Graphene has been tested already in several types of devices that currently are dominated by silicon technology, ranging from sensors, photonic devices, to field effect transistors [21]–[24]. Just as for the current silicon-based technology the role of the electrical contacts is very important; these contacts will be the interface between the subject material (carbon in this case) and the outer world, and so they have to show certain properties that metal contacts generally do. In order to achieve devices with sufficient electrical performance, typically it is expected at least a good ohmic contact and a low contact resistance [18], [25].

1.4 Metal Contacts and Platinum

The use of certain metals as electrical contacts for semiconductors is determined by the purpose of the device under consideration; the selection is influenced by electrical conductivity, chemical inertness, thermal conductivity, and even resistance to corrosion [26]; sometimes when the contacts are going to be exposed to mechanical forces, the property of wear resistance is also important [26].

According to N. Weiss et al. [23], gold (Au) is the natural choice as contact metal due to its high conductivity, low chemical reactivity, and other noble properties. Despite this fact, it is found in literature that several metals are being applied to graphene devices [27]–[34]; besides Au, also titanium (Ti), palladium (Pd), platinum (Pt), silver (Ag), nickel (Ni), chromium (Cr), copper (Cu), iron (Fe), cobalt (Co), and aluminum (Al) are all being used, certainly because they are available in the current technologies. These metals represent a variety of selection that opens up opportunities for different applications; however, it is not always possible to have access to all of those metals, and many research projects are
sometimes narrowed by what it is available under particular technology. As an example, Pt is commonly available in dual-beam scanning electron microscopy (SEM) systems, but Ni is less common; fortunately, when using these systems, Pt deposition is preferred over Au deposition when applied to device fabrication [35].

Platinum is the element number 78 on the periodic table, it is very low reactive, and has a bulk electrical resistivity ($\rho$) of $1.06 \times 10^{-7} \ \Omega \text{m}$ [36]. It is well known that Pt does not form carbides (unless exposed to extreme conditions) [37], and hence it becomes very relevant for its use in graphene devices.

1.5 Contact Resistance

As mentioned, one of the most crucial topics in the fabrication of graphene electrical devices is the interface between the graphene and the metal contact; the metal-semiconductor junction as it is known has to be ohmic and with the lowest possible resistance. The contact resistance in graphene devices has been one of the major limiting factors [32]–[34], understanding and controlling this parameter is crucial for the further development of high-performance devices.

The contact resistance can be measured by three main different types of methods [38] that can be named two-probe, transfer length, and four-probe method. Naturally, two-probe method is the simplest one needing only two contacts. In order to give a total resistance from which contact resistance can be estimated this method employs a series of measurements of the device voltage drop at different current values, however, it is limited by further required calculations including the knowledge of the material resistivity. Also it is limited by a low effectivity for structures of small contact area and small contact resistance.
The transfer length method (TLM) is widely used; it is based in a series of planar pair contacts situated at different distances between them. The resistance of progressing pairs is measured and plotted as a function of the distance between pairs; then this function is used to determine a transfer length parameter from which the contact resistance can be estimated. Lastly, the four-probe method also known as four-terminal Kelvin test is based on the use of two outer electrodes as a current source while the other two inner electrodes measure the potential drop between them. This method is useful due to its sensitivity, the capability of obtaining the actual resistance values almost directly and its relevance to semiconductor industry.

1.5.1 Two and Four-Probe Electrical Measurements

Due to its practical implementation, the four-terminal resistance measurement has been extensively used and studied [39], [40]; even variations of the method [41], [42] have been released with the intention of account for as many variables as possible and provide a better tool for the correct determination of the resistance. In the case of the present work, a four-probe approach has been chosen to evaluate the device and the contact resistance.

In two terminal configuration each electrode serves as both current and voltage probe, therefore, the device resistance \( R_T \) is calculated by a simple Ohm’s law, \( V = IR_T \), where \( V \) is the voltage drop across the device and \( I \) the current. Here the obtained resistance is a sum of the probe resistances \( R_P \), the contact resistances \( R_C \), and the subject material resistance \( R_G \), in this case, graphene:

\[
R_{2\text{-probe}} = R_T = 2R_P + 2R_C + R_G
\]

As it can be seen, at this point it is impossible to extract the contact resistance. The solution for this issue is the use of additional two probes to form an entire set of four; here the
current path is identical as before, but the voltage measurement will be through the additional probes. These additional probes will carry as well $R_p$ and $R_C$, but the current passing through them is so small due to the high impedance of the voltmeter (in the range of TΩ) that the voltage drop in the probes is negligible [41], and so the measurement gives the graphene value directly. Thus:

$$R_{4\text{-probe}} = R_G$$

Assuming highly conductive electrodes (metals) [29]:

$$R_{2\text{-probe}} = 2R_C + R_G$$

Hence:

$$\frac{R_{2\text{-probe}} - R_{4\text{-probe}}}{2} = R_C$$

Using the previous descriptions and in the case of having electrodes with a high resistance being used as probes, the voltage drop across them will be included in the four-probe measurement and therefore:

$$R_{4\text{-probe}} = R_G + 2R_P$$

Recalling:

$$R_{2\text{-probe}} = 2R_P + 2R_C + R_G$$

The same equation is obtained:

$$\frac{R_{2\text{-probe}} - R_{4\text{-probe}}}{2} = R_C$$

Moreover, the usage of this approach to calculate the contact resistance in graphene devices is reported as well in recent literature [29], [43].
1.5.2 Improving Contact Resistance: Post-Fabrication Treatments

The presence of a high contact resistance is mainly attributed in literature to surface contamination, improper metal/semiconductor contact and improper metal uniformity [18], [27], [28]. Regardless of the specific reason, there is a common post-fabrication treatment that have been demonstrated to reduce the contact resistance [27], [43]–[50], this one is thermal annealing.

Thermal annealing is a simple heat treatment that can be performed either in vacuum or specific gas atmosphere, where a sample is exposed to different ranges of temperature depending on the requirement. As per energy consumption, low temperatures (below 500 °C) are commonly used and preferred, however if there is a need to go to higher temperatures the benefit per cost is usually justified. Thermal annealing is carried out using ordinary furnaces or vacuum ovens that are available practically in each laboratory; therefore the implementation does not require very sophisticated equipment. Additionally, thermal annealing can easily be implemented due to the actual technology available in the semiconductor manufacturing industry, where already more powerful equipment like rapid thermal processing (RTP) is available [51].

1.6 Precedent

Previous to this work, a report in carbon nanotubes (CNT) devices described results [44], [52] that serve as the basis for the present investigation in graphene devices. The conclusions supported the use of dual-beam SEM systems as device fabrication tool. Deposition of Pt electrodes and the effect of vacuum thermal annealing were studied using electron beam induced deposition (EBID) and ion beam induced deposition (IBID), demonstrating the better performance by EBID electrodes. The results are based on device’s better electrical
transport and lower contact resistance, as well as a detailed chemical and structural characterization by Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), and electron energy loss spectroscopy (EELS). Electron beam lithography (EBL) electrodes were also implemented but it was found to be less efficient and with a lower device yield than EBID or IBID.

According to [44], it was found that after vacuum thermal annealing, the EBID Pt electrodes change their structure from a disordered Pt-C mixture to a structure made of a Pt core and a C shell. This transformation was observed to be accompanied by a decrease in the contact resistance, suggesting in this way the participation of C in the improvement of transport properties of the electrodes and devices.

1.7 Scope and Motivation

The present work is intended to develop the understanding of electrical contacts on graphene devices. Liquid phase exfoliated graphene flakes are going to be used for the device fabrication, and Pt electrical contacts will be deposited by EBID. Since isolating single graphene from LPE is still a challenge, ultrathin graphite [53] will also be acceptable for device fabrication. Because of the nature of EBID fabrication, the deposition should not be affected by the use of graphene nor ultrathin graphite.

Evaluation of the device will be performed through electrical characterization via determination of contact resistance using the four-probe technique; the measurements will be taken during different steps of vacuum and air thermal annealing. Chemical and structural characterization will be accompanying the results.

This work is motivated by the following reasons: Firstly, there is a need of reduction of contact resistance in graphene/carbon nanostructure devices. Secondly, there exists a lack of
information of the actual structural changes that may be responsible for reducing the contact resistance. Thirdly, there is an interest in the use of dual-beam SEM as a practical mask-less tool for device fabrication. Finally, this work provides useful information in the feasibility of using liquid phase exfoliated graphene for future devices.
2.1 Device Fabrication

The starting point for the elaboration of this thesis project is the fabrication of a device substrate where graphene can be integrated. The description of steps and considerations faced during the development of the device is presented as follows.

2.1.1 Design

The design of the substrate was based on a previous research [52] performed as part of the Laboratory for Carbon Nanostructures in KAUST. The main idea is the use of numbered electrical pads arranged in a matrix of nine by nine; this arrangement facilitates the use of carbon nanostructures suspended in solution because there are 64 potential areas to find these nanostructures, and therefore potential devices. The fact that the pads are numbered facilitates the localization by a combination of row and column. Additionally to the pads, the use of alignment marks was also continued, even if these marks were only to facilitate the operation of EBL technique, it was desired to have them in the case they were required.

In regards to the present work, circular pads with a diameter of 50 µm were used. These circular pads are arranged in a matrix of nine rows and nine columns with a distance between pads of 20 µm (Fig. 2.1 a); rows and columns are numbered from “1” to “9” and from “A” to “I” respectively to identify the sample location. A plus sign mark of 3 µm is situated in between each row and column to serve as an alignment mark. Apart from these, four lines of 50 µm width go along each cardinal point; east and west lines go up to 4 mm, while north and south lines go up to 2.36 mm. After north and south lines, it was added a hollow square
of 1.5 mm outer side and 1 mm inner side. A 100 µm plus sign was included in the center of the empty squares to help in alignment and location.

Concentric circles to the central matrix were added without interfering with the pads and numbering (Fig. 2.1 a); the most inner one with an internal radius of 331.3 µm and an external radius of 341 µm, was replicated 15 times with a consecutive scale factor of +1.1. The initial intention of the circles was to increase the wettability of the area of interest, but it was found to be also very useful to locate the central area when observing under the microscope.

Afterwards the device was framed in 1 cm² hollow square of 100 µm border width, and the lab signature was added near the center. Lastly, the device unit was replicated 52 times to fit into a four inches Si/SiO₂ wafer. The single device can be appreciated in Fig. 2.1 b.

The design was made using KLayout™ editor software, which is a free open-source resource available in “http://www.klayout.de”.

Fig. 2.1. Digital visualization of the device substrate design: a) Center of the device unit: matrix of pads of 50 µm diameter showing the numbering, the alignment marks, and the concentric rings. b) Device unit.
2.1.2 Photolithography: Laser Beam

The term photolithography refers to one process of microfabrication where light is used as a tool for exposure and transfer of a design or pattern onto a substrate. The transfer is made through a photoresist, which is chemically and physically changed after light exposure. Further metal layer deposition completes the fabrication of the design [54]. In this work, laser beam lithography (LBL) was used and was effectively implemented. A description of the working principle and the experimental conditions is described as follows.

2.1.2.1 Working Principle

The process of photolithography used in micro-fabrication starts by cleaning the wafer that will serve as a substrate, then a photoresist is spin-coated on top of the wafer and baked using a hot plate during few seconds (Fig. 2.2 a and b).

Using software from Heidelberg™ Instruments, the design described in previous pages is transferred to the laser beam writer Heidelberg™ µPG101™. The wafer covered with the photoresist is taken inside the laser writer and then it is exposed to the laser. The photoresist is being changed chemically where the light falls upon, and then this same area can be removed with a step called development (Fig. 2.2 c and d).

Fig. 2.2. Photolithography patterning process: a) Spin-coating of photoresist over the SiO₂/Si wafer. b) Baking the wafer and photoresist on a hot plate. c) Exposure of the photoresist/wafer to the laser beam to create the pattern. d) Immersing the wafer into the developer in order to remove the exposed photoresist.
The laser beam writer is composed of the power unit and the lithography unit [55], the first one is in charge of supplying the voltage required for operation, and the second one is in charge of the generation and handling of the laser beam and the substrate. Additional computer unit and air supply unit are also part of the system, but they are generic, and hence not to be described here.

The elements of the lithography unit [55] (Fig. 2.3) are the optics, the electronics, the write head, the write lens, and the stage. The optics are integrated by the diode laser, an acousto-optic modulator (AOM), mirrors and optical lenses. Additional camera and illumination optics for alignment purposes are found. Besides, the electronics module contains a mainboard processor that communicates with the computer to receive the pattern design; after processing the information, it manipulates the optics, the write head, and the stage. Everything in the moving system is being enhanced with a dry air supply that acts as a vibration dampener for each moving part, especially the stage and the write head. Additionally this pneumatic system enables a vacuum system to hold the substrate to the stage.

![Fig. 2.3. Schematic of laser beam writer working principle. Based on [52], [55], [56]](image-url)
After the exposure and the development of the design, the wafer is taken into the metal deposition system, where the patterned photoresist is covered with a metal layer. This metal is exclusively attached to the wafer where the photoresist was exposed to the laser. In order to complete the lithographic process, the remaining metal and photoresist are removed. There are few techniques to deposit the metal layer, but metal sputtering deposition was chosen due to its simple operation. Metal sputtering method is a type of physical vapor deposition that is characterized by the ejection of particles from a target surface; the ejection is caused by momentum transfer from incident energetic particles (of atomic size), and then the deposition of the ejected particles into a substrate takes place. In this case the target is a solid metal, which is vaporized (not by heat) and deposited on the patterned wafer [57].

As mentioned, the last step of the photolithography is the removal of the remaining photoresist by a method called lift-off; this is done basically by exposing the wafer to acetone and ultrasonication inside the water bath. Finally, the resulting microfabricated pattern is made of the deposited metal.

A most common schematic of this complete microfabrication process is illustrated in figure 2.4.

![Fig. 2.4. Common photolithography steps for microfabrication.](image)

### 2.1.2.2 Experimental Conditions

Operating clean room class-100 at KAUST Core Laboratories, the design previously proposed was fabricated under the following conditions:
Using a commercial 4” wafer of p-doped Si with SiO$_2$ thermal layer of 300 nm (Fig. 2.5).

- The wafer was cleaned inside a Petri dish with acetone during 3 minutes in bath sonication, then transferred to another dish containing isopropyl alcohol (IPA) and cleaned in the same way; finally, rinsed with deionized water and dried with N$_2$ flow (Fig. 2.6).

- The wafer was left into a vacuum oven at ~100 °C during 30 minutes in order to remove the moisture that might be already adsorbed on the surface.

- The wafer was covered with photoresist AZ5214 (Fig. 2.8 a) using spin-coating technique and the conditions described in Table 2.1, and Fig. 2.7.

Fig. 2.5. 4” Si wafer with 300 nm SiO$_2$.

Fig. 2.6. Cleaning process before microfabrication. a) Acetone cleaning. b) Isopropanol cleaning. c) Water rinsing and nitrogen drying. d) Moisture removal.
Table 2.1. Parameters for the spin-coating of AZ5214 photoresist.

<table>
<thead>
<tr>
<th>Step</th>
<th>Speed (rpm)</th>
<th>Ramp (rpm/sec)</th>
<th>Time (sec)</th>
</tr>
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<tr>
<td>1</td>
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<td>3</td>
</tr>
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<td>1500</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>6000</td>
<td>3000</td>
<td>30</td>
</tr>
</tbody>
</table>

Fig 2.7. Relation of spin-coating speed to photoresist thickness for AZ5214 [58].

- After spin-coating, the wafer was exposed to baking on the hot plate at 110 °C for 120 sec.
- The wafer was exposed using the laser beam writer μPG101™ Heidelberg™ (Fig. 2.8 b), with 10 mW at 85% of intensity. The diode laser is 405nm wavelength (violet). This step usually takes around 3.5 hours.

Fig. 2.8. a) Wafer covered already with AZ5214 photoresist. b) Laser beam writer.
- The exposed wafer was developed in AZ726 for ~30 sec, then rinsed with deionized water and dried with N\textsubscript{2} flow. AZ726 is a metal-ion-free (MIF) developer based on tetramethyl-ammonium hydroxide. Visual inspection using optical microscope was used at this point to verify the transfer of the pattern.

- Afterwards, the design was fabricated using metal sputtering deposition (Fig. 2.9 a, and Fig. 2.10 a) employing the AJA International Inc. ATC 2000 sputtering system (Fig. 2.9 b). The metals used were a Ti bottom buffer layer of 3 nm (~19 sec. of exposure) and a Pt top layer of 85 nm (~170 sec. of exposure).

Fig. 2.9. a) Pattern transferred showing metal layer covering the wafer. b) Metal sputtering system ATC 2000.

- The fabrication process was completed with the lift-off step by using water bath sonication of the wafer inside acetone for ~7 min (Fig. 2.10 b and c).

- Afterwards the wafer was diced according to the design units (Fig. 2.10 d) in order to proceed with the device fabrication.
2.1.3 Dispersion and Deposition of Graphite Flakes

The dispersion of graphene/graphite flakes was performed using ethanol as media. First, 1 mg of “graphene powder” (obtained from LPE [59]) was dissolved in 5 ml of ethanol obtaining a dispersion of concentration 0.2 mg/ml (Fig. 2.11 a).

Further dilutions were made from the initial dispersion, taking 1 ml from it (0.2 mg/ml) and adding 4 ml of pure ethanol for a final concentration of 0.04 mg/ml. In similar way a dispersion of concentration 0.02 mg/ml was prepared.

These dilutions were exposed to ultra-sonication in water bath for at least 30 min. (Fig. 2.11 b). In the author's experience, it is believed that longer times provide always better dispersion.

Fig. 2.11. Graphene dispersion: a) Before sonication. b) After sonication.
2.1.3.1 Drop-Casting and Spin-Coating

Once dispersions were prepared, the deposition of graphene took place. Preliminary attempts using simple drop-casting resulted not very effective; this was because graphene flakes have enough time to form clusters before the ethanol is evaporated. Because of this difficulty, spin-coating technique was adopted. This double-approach technique was effective to distribute the flakes uniformly, and helped as well with the removal of heavy undesired particles from the device substrate. The effectiveness of the deposition did not vary significantly between dispersions of different concentration; the only effect observed is the different abundance of the flakes proportional to the concentration. Nonetheless, it was observed that using less than 0.2 mg/ml provides cleaner substrates, which translates into cleaner pads and certainly better electrical measurements.

The deposition was performed pouring up to four drops of dispersion onto the substrate while doing the spin-coating with a top spin-speed of 3000 rpm for 10 seconds (Fig. 2.12). These conditions were enough to dry the ethanol drops.

Fig. 2.12. Graphene deposition by drop-casting and spin-coating.
2.1.4 Mechanical Exfoliation of Graphite

In order to compare the devices from LPE graphite with the more classical mechanical exfoliated (ME) graphite, the latest was implemented in this thesis project. Commercial Scotch™ tape and highly oriented pyrolytic graphite (HOPG) stacks were used (Fig. 2.13 b). First, the HOPG was placed on a piece of tape, this tape was bent to cover both sides of the HOPG flake and it was pressed with the fingers, then the tape was unfold obtaining thin graphite stacks. The HOPG flake was put aside, and the tape was then folded again, pressed and unfolded; this was repeated until thinner and transparent flakes of graphene/graphite were found by optical inspection (Fig. 2.13 a). At this point the tape was pressed against the substrate expecting to find flakes between the pads of the design; this has to be confirmed by visual inspection. The final step was the removal of glue residues out of the substrate; this was done by exposing the device substrate into acetone at 50° C. The effectiveness of this removal was not complete due to lack of total removal, but it was enough for the purpose of this work. However, if further cleaning is needed, exposing the substrate to 300° C vacuum or air annealing was found to be effective.

Fig. 2.13. Mechanical exfoliation of graphite: a) Exfoliated graphene/graphite as seen in optical microscope when still in the adhesive tape. b) HOPG stack.
2.1.5 Integration of Graphite into Devices

The integration of graphene/graphite flakes into devices involves the creation of a connection between the flakes and the outer world, which generally means metallic contacts. For the devices presented in this thesis, direct fabrication method using EBID was used to fabricate the electrodes between the flakes and the pads in the device substrate. This EBID technique, which is implemented using the dual-beam SEM, was chosen because it has been demonstrated to be useful for carbon materials [44][60], [61], and it is preferred over IBID [44], [62].

2.1.5.1 Dual-Beam SEM

Dual beam systems incorporate both electron and ion beam sources, conferring them great versatility in applications, from single beam to paired tasks. Electron beam is used for imaging and deposition, while ion beam is used for deposition, milling, and imaging; both beams are used without the need of photoresists or masks, making them advantageous over other techniques of patterning. Probably the main application of this dual-beam system is in the field of structural analysis [63], nevertheless the fabrication capabilities are endless and practical. These mask-less fabrication capabilities are of a high importance for this work because they allow to deposit electrical contacts in order to perform transport measurements in micro and nanostructures [60]–[62], [64].

The following text is a brief description of the working principle of both, electron and ion beam sources, as well as the deposition mechanism.
A) Electron Beam Column

The electron beam column (Fig. 2.14) is generally composed of the electron gun, a pair of electromagnetic condenser lenses, an electromagnetic objective lens, deflectors, apertures, and the system for electron detection. The source of electrons from the gun is generally a sharp tungsten tip for field-effect emission, but it can also be a filament for thermionic emission. The electron gun can provide potentials ranging from 1 to 30 keV; the current of the beam is controlled by the resolution spot size, therefore providing currents of 1 to 100 pA for spot size of 1 to 10 nm; and currents of 1 to 10 nA for spot size of 0.1 to 100 µm.

During imaging the electron beam falls on the sample, and in this way starts generating the signal electrons from both the surface and up to 1 µm in depth, on the form of secondary and backscattered electrons respectively. In front of the final lens, there is a scan generator system that is responsible for deflecting the beam in a raster-scan motion across the sample; it operates in synchronization with the detection and computerized systems in charge of displaying the SEM image [65].

![Fig. 2.14. Schematic of the electron beam column. Based on [65] [66.](image)]
B) Ion Beam Column

The common ion beam column is composed of the ion gun, electrostatic condenser lens, electrostatic objective lens, apertures, deflectors, stigmation poles, and the ion/electron detection system. The ion beam column basically resembles the electron beam column, but instead of an electron source, it possesses a liquid metal ion source (LMIS) which generally is a Gallium ion (Ga⁺) [67], [63]. Instead of the sharp tungsten tip, the ion source has a sharp tungsten needle where the liquid gallium ions are extracted. Gallium is ideal to this mechanism mainly due to their low melting point of 30° C, low vapor pressure, and low volatility [67]–[69].

The ion beam is generated by the use of a high electric field, typically produced with an extraction voltage of 7 kV. The subsequent ion emission achieves potentials between 5 and 50 keV and beam currents between 1 pA and 10 nA. After extraction the ions are refined, condensed, and corrected with the optical system, to lastly, land on the sample substrate where the sputtering of sample atoms (milling), or the deposition of atoms to form structures (ion beam deposition) take place. The additional emission of some secondary electrons facilitates the imaging of the sample [68], [69].

When the electron and the ion beam column are integrated into the same system, they are known as dual-beam SEM. Regularly in these systems the electron beam is in a vertical position while the ion beam is set at 52° from the horizontal [52], [63].

C) Deposition Mechanism

As mentioned, the importance of dual-beam systems in this work is due to the capability of deposit metal as electrical contacts for micro and nanostructures. While both electron and
ion beam can be used for this purpose, only EBID was implemented based on previous results [44], [52].

EBID is a direct fabrication method considered bottom-up type, which is based on the dissociation of an organometallic gas precursor; this gas is supplied by the gas injection system (GIS) into the sample vacuum chamber. While the precursor molecules are being adsorbed on the surface of the sample due to the constant gas flow, the electron beam is dissociating (Fig. 2.15) them into the deposited metal and into some volatile organic products containing carbon [70]. In order to achieve the deposition, the accelerating voltage and current should be sufficient to break the bonds from the organometallic compound.

![Figure 2.15](image.jpg)

Fig. 2.15. Electron beam induced deposition schematic, including the precursor used in this work. Based on [71]

### 2.1.5.2 Experimental Conditions

Once graphene/graphite flakes were transferred to the device substrate, and after localizing them inside the pad matrix, the substrate was taken into the dual-beam SEM chamber of the FEI™ Helios NanoLab™ 650 system. Initial focus and stigmatism corrections were done
with the GIS needle inserted; the acceleration voltage and current were 5 kV and 1.4 nA respectively. The Pt precursor, methyl-cyclopentadienyl (trimethyl) platinum, (CH$_3$)$_3$(CH$_3$C$_5$Pt) or MePtC$_5$Me$_3$, was heated up to approximately 40 °C as required for deposition.

Once centered on the desired flake, a set of four electrodes were drawn using the software user interface; electrodes were set to be 200 nm width while the length was always dependent on the position and size of the flake. Electrode’s height was set to be 1 µm, however only ~80 nm were obtained. It is known from user’s experience that while using standard parameters of the Helios system, only a fraction of the deposition height is obtained. This effect might be due to incorrect calibration that it is out of the scope of this work.

According to the four-point resistance measurement theory, the electrodes on top of the graphene flake were designed to be equidistant between them and varying accordingly to the flake size. A schematic and one example of the device fabrication can be seen in figure 2.16 and figure 2.17.

![Fig. 2.16. EBID schematic for the integration of graphene flakes into the device.](image-url)
2.2 Post Fabrication Treatments: Thermal Annealing

An important step of this research relies in the thermal annealing as post-fabrication treatment. This method involves the use of heat as the tool to improve the structure and properties of the relevant material.

2.2.1 Experimental Conditions

The fabricated devices (Fig. 2.18 b) were exposed to thermal annealing at 100, 200, and 300 °C [44] under vacuum of 10 mbar during approximately 1 hour. The devices were kept under
vacuum until they were cooled down to room temperature. These treatments were carried out using both Büchi™ Glass Oven B-585 and Büchi™ Vacuum Pump V-700 (Fig. 2.18 a). After characterization of annealed devices, they were thermally annealed again at 300 °C in air conditions [35] (~20% O₂) for 15 minutes using a pre-heated Nabertherm™ Muffle LT 24/12/P-330 (Fig. 2.18 c). Then devices were allowed to cool down to room temperature.

**Fig. 2.18.** Thermal annealing setup: a) Oven and vacuum pump. b) Devices to be annealed. c) Muffle.

### 2.3 Characterization

Aiming to understand the structure and behavior of the deposited electrodes and the complete device, a series of characterization techniques were completed as follows.

#### 2.3.1 Electrical Characterization of Devices

**2.3.1.1 Equipment and Interface**

In order to characterize electrically the fabricated devices and electrodes, two main equipment were used: probe station Janis™ ST-500 (Fig. 2.19 a), and source meter Keithley™ 2602B (Fig. 2.19 d).
The probe station is equipped with four direct-current (DC) arms, each with a fine tungsten probe tip (Fig. 2.19 b). The arms are controlled by a delicate mechanical system to provide a high precision tip movement and landing, which is something significant for this work since the pads for landing the probes were fabricated of 50 µm diameter only.

The source meter provides the capability of doing several electrical testing, including the current versus voltage (I-V) curves that were of high importance for this work. These curves were measured using the built-in software interface (Fig. 2.19 c), which facilitated the data acquisition.

![Fig. 2.19. Electrical characterization setup: a) Probe station. b) Probe tip. c) Software interface for I-V curves. d) Source meter.](image)

### 2.3.1.2 Experimental Conditions

The I-V curves were constructed in two and four-probe modes, using two probes as high and low terminals and two probes as high-sense and low-sense terminals. The measurements were performed by supplying various ranges of input current, from -25 nA to 25 nA, -1 µA
to 1 µA, -10 µA to 10 µA, and -100 µA to 100 µA. All of these ranges were divided in 200 points, each with a pulse width of 990 µs, and a time per point of 200 ms. The source meter was set to limit the supply to 1 V to avoid device damaging.

2.3.2 Raman Spectroscopy

2.3.2.1 Working Principle

The vibrational and rotational frequencies that characterize different molecules can be studied by Raman spectroscopy. The Raman effect is named in honor to C.V. Raman who discovered this phenomenon in 1928 along with K.S. Krishnan [72].

In regards to carbon materials, Raman technique has become a very relevant tool for characterization. It has been found to be fast, non-destructive, of high resolution and capable of providing a very high amount of structural and electronic information, in such a way that it is possible to distinguish different kinds of carbon materials [73].

In Raman spectroscopy, a sample is illuminated by a monochromatic light source (laser light) of known frequency ($v_0$), then the sample scatters this light and this interaction is collected, dispersed and analyzed by a highly sensitive spectrometer; the spectrometer shows not only the original frequency $v_0$ (elastic scattering known as Rayleigh scattering) but also pairs of new frequencies ($v_0 \pm v_R$) called Stokes and anti-Stokes (Fig. 2.20), where $v_R$ represents the characteristic frequency shift. These new frequencies are known as Raman scattering (inelastic scattering), composing the Raman spectra [74], [75].

The Raman spectrum is comprised of Raman lines or peaks that correspond to the intensity of the Raman scattering frequencies. These peaks are affected mainly by the molecular and the crystal lattice vibrations; therefore, it is useful to determine chemical composition, type of bonds, phase, and crystal structure [74], [75].
Fig. 2.20. Elastic Rayleigh scattering, and inelastic Raman scattering illustrating Stokes and anti-Stokes. Based on [76]

2.3.2.2 Experimental Conditions

Raman analysis was performed using Witec™ Alpha 300 RA Raman spectroscopy system (Fig. 2.21), equipped with a solid-state green laser (532 nm wavelength) at 0.1 mW of intensity. Single point spectra were obtained from the ultrathin graphite flakes before device fabrication and after the various annealing steps. Raman mapping was completed as well, before and after the different annealing steps. The conditions for mapping scan were set to be 150 points per line, on 150 lines, an average mapping size of 20 µm x 20 µm, 0.005 ms of integration time, and 100x amplification lens. Using the operating software, further data analysis was completed in order to elaborate the device mapping at the characteristic bands of carbon [73]: G band (~1582 cm\(^{-1}\)) corresponding to the bond stretching in all sp\(^2\) carbon atom pairs, also called graphitic band; D band (~1355 cm\(^{-1}\)) corresponding to a measure of disorder in graphite; and 2D band (~2710 cm\(^{-1}\)) corresponding to a D band overtone.
(although not related to disorder) and the second most prominent peak found in graphite after G band; 2D band is used as signature of the number of graphene layers [73], [77].

2.3.3 Atomic Force Microscope

2.3.3.1 Working Principle

The atomic force microscope (AFM) uses an atomic sharp tip to image a sample surface in a raster-scan way; it relies upon its high sensitivity to inter-atomic forces to collect surface information. The detection method uses the deflection of a laser that has been previously focused and aligned on the back of a cantilever that holds the sharp tip, therefore, as soon as the tip is moved up or down by the inter-atomic forces the laser bends and this deflection is translated to changes in the surface height. In order to be accurate, the force between the tip and the substrate is maintained constant with the help of a piezoelectric system, thus obtaining a topography mapping of the sample [78], [79]. Since AFM relies on the measurement of micro forces between the tip and the sample, it can be used in both contact and non-contact mode.
2.3.3.2 Experimental Conditions

An AFM Park-Systems™ XE-100 Series (Fig. 2.22) was used to measure mainly the height of the deposited materials that were used to fabricate the devices. Non-contact mode was used with Park Systems NCHR tips.

![AFM Image](image)

Fig. 2.22. AFM: a) User interface showing 1) Cantilever and laser on top; 2) Device substrate. b) AFM showing 3) AFM head where cantilever is attached; 4) Piezoelectric base.

2.3.4 Scanning Electron Microscope

2.3.4.1 Working Principle

The working principle has been described in section 2.1.5.1, part A, *Electron beam column*.

2.3.4.2 Experimental Conditions

A SEM system, FEI™ Nova Nano 650 (Fig. 2.23 a), was used to capture SEM images of the flakes (Fig. 2.23 b) and devices before and after thermal annealing. The operating conditions were 4 kV and 24 pA, or 7kV and 24 pA, at 5 mm working distance. Additional SEM images
were captured using FEI™ Helios NanoLab™ 650 system with 5 kV and 1.4 nA at 4 mm working distance.

Fig. 2.23. SEM: a) Nova Nano 650 SEM. b) Ultrathin graphite flake SEM image.

2.3.5 Energy Dispersive X-ray Spectroscopy

2.3.5.1 Working Principle

Energy dispersive X-ray spectroscopy (EDXS) is commonly used for elemental identification of unknown and known samples based on the characteristic X-ray emission of each element. The X-rays from the sample are generated because of a series of events: First, an electron beam falls over the sample providing electrons with enough potential to excite ground-state atoms. As soon as excited electrons move up from the inner shell of the atom, outer electrons fill the hole created and X-ray photons are emitted [80]. Due to its nature, EDXS is mainly carried inside electron microscopes, where a silicon detector inside the SEM chamber collects the generated X-rays; further analysis of the signal is done, and the processing reveals the EDXS spectra formed by intensity versus X-ray energy.
2.3.5.2 Experimental Conditions

Point EDXS analysis and EDXS elemental mapping were carried out using FEI™ Nova Nano SEM with EDAX™ detector (Fig. 2.24). The analyses were carried out at 7 kV or 5 kV, with 3, 3.5, or 5 spot size in high vacuum. The parameters were varied depending on the sample. Dead time and amplification time were set to achieve counts of ~1000 counts per second (cps) in the best cases, but for lower currents even ~200 cps were used.

Fig. 2.24. EDAX detector attached to the SEM chamber.
Chapter 3: Results and Discussion

In order to evaluate single-electrode resistance, individual electrodes connecting a pair of pads were fabricated in various width sizes: 0.01 µm, 0.05 µm, 0.1 µm, 0.2 µm, 1 µm, and 1.5 µm. The fabrication condition for all of the electrodes was EBID at 5 kV and 1.4 nA while the length of the electrodes was 20 µm, and the as-deposited thickness 70 nm average.

Electrical resistance was calculated from measured Ohmic I-V curves; those were made from -25 nA to 25 nA before annealing, and from -1 µA to 1 µA, and -10 µA to 10 µA after thermal annealing (300 °C during 1 hour, 10 mbar).

The measured values (Fig. 3.1) confirm the common inverse relation between the resistance of the electrode and the cross-sectional area \( R = \frac{\rho l}{A} \) [81], this gives priority to thicker electrodes when the best conduction is desired; however, in order to keep miniaturization, it was decided to implement 0.2 µm electrode width for the devices in this work.

Several devices were fabricated using ultrathin graphite exfoliated from expandable graphite [59] and were characterized by electrical resistance in 2 and 4-probe configuration along different annealing steps.
In a first batch, devices were exposed to thermal annealing at 100 °C, and it was observed only a small relative improvement on the resistance of the device (Table 3.1). Additionally and contrary to what is desired the contact resistance was increased (Fig. 3.2 a), although in a very small relative proportion.

<table>
<thead>
<tr>
<th>Device</th>
<th>2-Probe</th>
<th>4-Probe</th>
<th>Contact resistance</th>
<th>2-Probe</th>
<th>4-Probe</th>
<th>Contact resistance</th>
</tr>
</thead>
<tbody>
<tr>
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<td>11.67</td>
<td>10.77</td>
<td>0.45</td>
<td>11.52</td>
<td>10.49</td>
<td>0.52</td>
</tr>
<tr>
<td>Average (Std. Dev)</td>
<td>11.55 (±1.0)</td>
<td>10.60 (±1.1)</td>
<td>0.48 (±0.06)</td>
<td>11.23 (±0.96)</td>
<td>10.07 (±1.09)</td>
<td>0.58 (±0.07)</td>
</tr>
</tbody>
</table>

Table 3.1. Electrical resistance of devices before and after thermal annealing at 100 °C. Value in parenthesis represents the standard deviation.

In a previous report [82] using the same precursor and type of deposition (EBID), the application of heat up to 150 °C did not positively affect or purify the platinum structures, in this case, the electrodes. Particularly in this work, the effect of the annealing at 100 °C is not significant when comparing these resistance values (in MΩ range), to those reported [44], [52], [62] (in kΩ range) in similar structures fabricated by IBID without any post treatment. Hence, a higher annealing temperature is justified.

The same devices were then exposed to 200 and 300 °C thermal annealing in vacuum, and afterwards, their electrical resistance was measured using ranges of -10 μA to 10 μA, and -100 μA to 100 μA. A different set of new devices was exposed to the same conditions of heat treatment and characterization. The results (Table 3.2 and Fig. 3.2 b) show that at these conditions, a significant reduction in electrical resistance is obtained. Now the actual values go from MΩ range to few kΩs.
Table 3.2. Electrical resistance of devices before and after thermal annealing at 200 and 300 °C.

<table>
<thead>
<tr>
<th>Device</th>
<th>2-Probe</th>
<th>4-Probe</th>
<th>2-Probe</th>
<th>4-Probe</th>
<th>2-Probe</th>
<th>4-Probe</th>
</tr>
</thead>
<tbody>
<tr>
<td>GESP03_EF89</td>
<td>10277.04</td>
<td>9168.29</td>
<td>554.37</td>
<td>48.74</td>
<td>0.92</td>
<td>23.91</td>
</tr>
<tr>
<td>GESP04_HI78</td>
<td>12705.48</td>
<td>11858.97</td>
<td>423.25</td>
<td>7.07</td>
<td>0.05</td>
<td>3.51</td>
</tr>
<tr>
<td>GESP07_DE89</td>
<td>11668.27</td>
<td>10764.97</td>
<td>451.65</td>
<td>4.86</td>
<td>0.05</td>
<td>2.41</td>
</tr>
<tr>
<td>GESP11_CD12</td>
<td>11775.00</td>
<td>10840.30</td>
<td>454.85</td>
<td>11.95</td>
<td>0.19</td>
<td>5.88</td>
</tr>
<tr>
<td>GESP11_CD45</td>
<td>12547.16</td>
<td>11677.82</td>
<td>434.67</td>
<td>12.93</td>
<td>0.08</td>
<td>6.43</td>
</tr>
<tr>
<td>GESP11_DE67</td>
<td>10207.80</td>
<td>9304.21</td>
<td>451.78</td>
<td>6.71</td>
<td>0.14</td>
<td>3.29</td>
</tr>
<tr>
<td>GESP11_DE89</td>
<td>11453.04</td>
<td>10639.29</td>
<td>406.87</td>
<td>6.13</td>
<td>0.10</td>
<td>3.01</td>
</tr>
<tr>
<td>GESP08_AB89</td>
<td>11321.35</td>
<td>10286.26</td>
<td>517.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GESP08_EF23</td>
<td>10850.08</td>
<td>10007.61</td>
<td>421.23</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GESP09_CD12</td>
<td>8143.08</td>
<td>7361.44</td>
<td>390.82</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>11092.20</strong></td>
<td><strong>10190.90</strong></td>
<td><strong>450.70</strong></td>
<td><strong>14.05</strong></td>
<td><strong>0.22</strong></td>
<td><strong>6.92</strong></td>
</tr>
<tr>
<td><strong>(Std. Dev.)</strong></td>
<td><strong>(±1259.74)</strong></td>
<td><strong>(±1258.02)</strong></td>
<td><strong>(±47.56)</strong></td>
<td><strong>(±14.44)</strong></td>
<td><strong>(±0.29)</strong></td>
<td><strong>(±7.08)</strong></td>
</tr>
</tbody>
</table>

The decrease in electrical resistance after thermal annealing in EBID electrodes and structures of platinum and carbon, is attributed in literature to structural modifications [35], [44], [71], [82]–[87] highlighting the following points:
During deposition of platinum, a significant amount of amorphous carbon is being trapped becoming a dielectric matrix for the Pt particles and therefore for the electrical paths.

During annealing in vacuum at 300 °C, amorphous carbon is diffused outwards and Pt particles are partially sintered into a more crystalline rod, becoming a core-shell-like structure where the shell is made of carbon with a higher degree of order.

During annealing in air/oxygen at 300 °C, amorphous carbon is diffused outwards and being removed while leaving behind a highly purified Pt electrode (higher Pt concentration). However the removal of carbon creates voids along the electrode, and these are believed to affect the conductivity.

In both vacuum and air annealing, the height of the electrode is considerably reduced even down to one-third the original thickness because of the diffusion, loss of carbon, and the rearrangement of Pt particles.

Micrometer-scale carbon deposits from EBID, show conductive partially graphitized crystallites after annealing in a range from 300 to 350 °C (much lower annealing temperatures than for bulk carbon).[84], [85]

The presence of amorphous carbon inside the electrode and its further extraction/removal to purify the Pt electrode, plus the sintering of the Pt particles into a more solid structure during thermal annealing, can describe the difference in resistance values between fresh devices (MΩs) and those that have been annealed (kΩs). This behavior have been seen for the same electrodes in carbon nanotubes devices [44] where a detailed transmission electron microscopy analysis shows the particle dynamics. However, when describing the role of the carbon after annealing there is clearly two paths and non-consensus: one suggests that after annealing in vacuum, the formation of a shell-like structure of partially ordered carbon
optimizes the charge transport. In the other hand, it is believed that the annealing in air promotes the oxidation and removal of carbon, and therefore the increase of purity and conductivity of the Pt electrode. Consequently, a series of structural analysis was carried out in the present devices, focusing on the presence of carbon and its modifications through the different annealing steps.

In order to confirm the presence of deposited C and Pt, EDXS study was carried out on fresh devices, both by mapping and point analysis at 7kV. It was effectively found that besides Pt, C signature is present in the as-deposited electrodes (Fig 3.3 and 3.4, Table 3.3).

![Fig. 3.3. Left: EDXS elemental mapping of the as-deposited device showing Pt and C from the electrodes and flake, as well as Si and O from the substrate. Right: SEM image of the same device.](image1)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CK</td>
<td>11.91</td>
<td>23.99</td>
</tr>
<tr>
<td>OK</td>
<td>28.28</td>
<td>42.76</td>
</tr>
<tr>
<td>SiK</td>
<td>35.04</td>
<td>30.18</td>
</tr>
<tr>
<td>PtM</td>
<td>24.77</td>
<td>3.07</td>
</tr>
<tr>
<td><strong>Matrix Correction ZAF</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Left: Fig. 3.4. EDXS point spectra analysis of the as-deposited electrode. Right: Table 3.3. EDXS point composition analysis of the as-deposited single electrode.
Once the presence of C was confirmed, Raman spectroscopy mapping was used to analyze the devices in order to track the diffusion of C material along the deposited electrodes. Raman mapping was performed to fresh devices, and then after each 100, 200, and 300 °C vacuum thermal annealing steps. The characterization was performed using a green laser of wavelength 532 nm, at around 0.1 mW of power intensity.

The images above (Fig. 3.5) show the evolution of the characteristic carbon Raman signature along different annealing steps.
The characteristic peaks (or bands) of carbon in the Raman spectra are called D, G, and 2D; and are generally located at ~1355 cm\(^{-1}\), ~1582 cm\(^{-1}\), and ~2710 cm\(^{-1}\) respectively [88], [89]. D peak is related to the degree of disorder, becoming null in perfect graphite; however in the case of amorphous carbon D peak indicates ordering [88]. G peak is called graphitic peak and corresponds to the bond-stretching vibration of sp\(^2\) C atoms pairs; therefore is present in all sp\(^2\) sites (not only on C rings), and provides a measure of graphitization. 2D peak is considered an overtone of the D peak and it is always present on graphite; opposite to D peak, 2D peak does not require defects for its activation [77].

In the specific case of G peak, Fig. 3.5 shows an additional mapping of G at 1608 cm\(^{-1}\); this is because the transition of amorphous carbon towards any degree of graphitization is expected the show a peak at ~1620 cm\(^{-1}\), which for small graphitic grains merges with the regular G peak (1582 cm\(^{-1}\)) [88]. In order to assess correctly the C shell structure on the electrode, it is necessary to consider the formation of this wider G peak.

Another additional mapping is the so-called “G band combined”, which is an image overlap of the 1582 cm\(^{-1}\) and 1608 cm\(^{-1}\) G mappings. This combination was performed using the software provided by Witec™, and it is solely intended to illustrate better the G band of the complete device.

According to the information obtained from the D and G bands, it is possible to confirm the formation of a C structure covering the electrodes. It is also evident that the effect of vacuum thermal annealing at 100 °C is not significant, contrasting with a clear transition at 200 °C and slightly more after 300 °C.

After different annealing steps, electrode’s D and G bands follow the same trend observed on the electrical measurements; this is the reason why a previous report [44], [52] associates the C shell structure with the improvement of transport properties of the device. Despite
this fact, the role of C as a conductor is well known to depend on the degree of graphitization and can be confirmed only after validating the C structure of the present samples.

When looking at the electrodes, certainly the G band mapping confirms the presence of sp² bonds, however, the intensity of D band reveals only short graphitic structures and a significant degree of graphitic disorder. These observations suggest that carbon appears in the form of nanocrystalline graphite, which is a transition between the amorphous phase and fully graphitized C [88]. In order to confirm the previous statements, the Raman spectra of the electrodes (Fig. 3.7) were analyzed.

![Raman spectra of annealed electrode](image)

Left: Fig. 3.6. Raman spectra corresponding to the deposited electrode as indicated in the picture on the right. The shadowed areas indicate D band and G band.

Right: Fig 3.7. Raman mapping at G band: blue square indicating the area where the above spectra were taken.

As seen in the Fig. 3.6, the first thing that raises attention is the presence of a G peak in as-deposited electrodes, which suggests that C is already partially nanocrystalline even before thermal annealing; this is likely due to the electron beam irradiation [90] during the process of fabrication. Nevertheless, the intensity of carbon peaks on the electrode, increases with
the increment of annealing temperature, confirming the outward diffusion of C and the formation of the shell structure.

One important way of assessing the degree of graphitization is by measuring the intensity ratio between D and G peaks. According to Ferrari and Robertson [88] when amorphous carbon evolves to fully nanocrystalline graphite, the I(D)/I(G) ratio goes up to a value of 2. According to the present spectra the ratios for as deposited electrode and its further annealing steps are 0.56, 0.6, 0.61, and 0.73 respectively; therefore, it is clear that the graphitization of the shell structure is very low, although increasing.

As a side note, low values of I(D)/I(G) ratio can also be expected when I(G) is very high compared to I(D), as shown in graphite. This fact can be illustrated taking the Raman spectrum of the ultrathin graphite flake and compare it to the electrode Raman spectrum as shown in the following figure.

![Raman spectra of annealed electrode and ultrathin graphite flake](image)

Fig. 3.8. Raman spectra illustrating the comparison in I(D)/I(G) ratio intensities from the ultrathin graphite flake and the electrode.
An additional thermal annealing was carried out in order to provide a definite statement about the structure of the carbon shell over the electrode. The process took place after the vacuum annealing; now it was performed in air atmosphere (~21% O₂) during 15 minutes at 300 °C. Raman spectrum and mapping were collected afterwards.

Fig. 3.9. Raman mapping of LPE ultrathin graphite device. Columns: D, G, and 2D bands; rows: 300 °C vacuum annealing and 300 °C air annealing. The column in the middle: G band combined, is obtained by overlapping adjacent images.

Fig. 3.10. Raman spectra corresponding to the deposited electrode. Including air thermal annealing at 300 °C.
As it can be seen in the Raman data (Fig. 3.9 and Fig. 3.10), both amorphous and partially nanocrystalline phase were removed almost in total; the spectra and mapping reveal an almost negligible G peak. In other words, the presence of carbon peaks coming from the electrode are almost null; this fact is due to the rapid oxidation and further removal of carbon during the short heat treatment. The presence of Pt is also relevant for this process since it is known for its properties as a catalyst of C oxidation, even for graphite oxidation [91]. The removal of carbon from the electrode paved the way for a second round of electrical measurements where the role of C as conductor could be electrically assessed. The electrical measurements were performed in the same way as the previous readings.

<table>
<thead>
<tr>
<th>Device</th>
<th>Resistance after 300 °C thermal annealing (kΩ)</th>
<th>Resistance after air 300 °C thermal annealing (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2–Probe</td>
<td>4–Probe</td>
</tr>
<tr>
<td>GESP04_HI78</td>
<td>4.20</td>
<td>0.03</td>
</tr>
<tr>
<td>GESP07_DE89</td>
<td>3.28</td>
<td>0.03</td>
</tr>
<tr>
<td>GESP11_CD45</td>
<td>7.97</td>
<td>0.20</td>
</tr>
<tr>
<td>GESP11_DE67</td>
<td>3.86</td>
<td>0.04</td>
</tr>
<tr>
<td>GESP11_DE89</td>
<td>3.52</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>4.55</strong></td>
<td><strong>0.07</strong></td>
</tr>
<tr>
<td><em>(Std. Dev.)</em></td>
<td><em>(±1.73)</em></td>
<td><em>(±0.06)</em></td>
</tr>
</tbody>
</table>

Table 3.4. Electrical resistance of devices before and after thermal annealing in air at 300 °C.

As it can be seen from the table 3.4, there were not significant changes before and after thermal annealing in air (Fig. 3.11). Hence, the carbon structure that was over the electrode does not play a role in the electrical resistance of the device. If any observation can be made is that the resistance values after annealing in air are slightly lower and in a very low proportion; average contact resistance is decreased only by 30 Ω (error = ± 5 Ω).
As per the previous results, it can be confirmed that the degree of graphitization of the C shell structure is very low; the Raman analysis confirms that it has only a partial nanocrystalline character, and the heat oxidation confirms majority composition of amorphous carbon. The presence of the C shell along the electrode more likely does not enhance electrical conductivity; this was confirmed since it has not been found a difference between devices annealed at 300 °C in vacuum and devices annealed at 300 °C in air. Thus, the reduction in the contact resistance relies only on the removal of dissolved carbon from the electrode and the sintering of Pt particles into a solid rod.

Another variable that was important for the present work is the use of LPE ultrathin graphite flakes. In order to evaluate the suitability of these flakes and their effect on the structural changes of the electrodes, it was necessary to fabricate blank devices. These blank devices were fabricated using mechanically exfoliated (ME) ultrathin graphite as a standard material and were subjected to the same conditions, measurements, and post-fabrication treatments. The only difference was that 100 °C thermal annealing was skipped since this temperature was shown to be worthless concerning resistance reduction.
The following tables (Table 3.5 and 3.6) show the values obtained in devices fabricated with ME ultrathin graphite. The data presented (Fig. 3.12 a and b) obeys the same trend observed in PLE ultrathin graphite devices, obtaining lower electrical resistance after higher thermal annealing. The reduction of resistance of both PLE and ME devices is in the range of 99.5% after 300 °C thermal annealing.

<table>
<thead>
<tr>
<th>Device</th>
<th>Resistance before annealing (kΩ)</th>
<th>Resistance after 200 °C annealing (kΩ)</th>
<th>Resistance after 300 °C thermal annealing (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-Probe</td>
<td>4-Probe</td>
<td>Contact resistance</td>
</tr>
<tr>
<td>GM05_AB78</td>
<td>11760.09</td>
<td>10821.71</td>
<td>469.19</td>
</tr>
<tr>
<td>GM05_EF12</td>
<td>12319.97</td>
<td>11032.59</td>
<td>643.69</td>
</tr>
<tr>
<td>GM05_EF34</td>
<td>11631.06</td>
<td>10672.56</td>
<td>479.26</td>
</tr>
<tr>
<td>GM05_FG89</td>
<td>11208.65</td>
<td>9866.61</td>
<td>671.02</td>
</tr>
<tr>
<td>GM05_GH78</td>
<td>12094.20</td>
<td>11058.21</td>
<td>518.00</td>
</tr>
<tr>
<td>GM05_HI23</td>
<td>11747.62</td>
<td>10905.30</td>
<td>421.16</td>
</tr>
<tr>
<td>GM05_HI67</td>
<td>12777.28</td>
<td>11759.98</td>
<td>508.65</td>
</tr>
<tr>
<td>GM05_HI89</td>
<td>11132.85</td>
<td>10207.97</td>
<td>462.44</td>
</tr>
<tr>
<td>GM05_CD89</td>
<td>11759.32</td>
<td>10412.20</td>
<td>673.56</td>
</tr>
<tr>
<td>GM05_AB12</td>
<td>11309.46</td>
<td>10682.74</td>
<td>313.36</td>
</tr>
</tbody>
</table>

Average (Std. Dev.)

Table 3.5. Electrical resistance of devices before and after thermal annealing at 200 and 300 °C.

Fig. 3.12. Variation of the contact resistance in devices: (a) after 200 and 300 °C vacuum thermal annealing. (b) Before and after thermal annealing in air at 300 °C. Values inside a rectangle denote average values.
Resistance after 300 °C annealing (kΩ) | Resistance after air 300 °C thermal annealing (kΩ)
--- | ---
**Device** | **2-Probe** | **4-Probe** | **Contact resistance** | **2-Probe** | **4-Probe** | **Contact resistance**
GM05_AB78 | 4.49 | 0.08 | 2.21 | 4.46 | 0.08 | 2.19
GM05_EF12 | 3.75 | 0.08 | 1.84 | 3.72 | 0.08 | 1.82
GM05_EF34 | 3.90 | 0.05 | 1.93 | 3.84 | 0.05 | 1.89
GM05_FG89 | 4.47 | 0.19 | 2.14 | 4.37 | 0.15 | 2.11
GM05_GH78 | 5.85 | 0.08 | 2.89 | 5.84 | 0.08 | 2.88
GM05_HI23 | 3.18 | 0.09 | 1.54 | 3.16 | 0.09 | 1.53
GM05_HI67 | 5.27 | 0.24 | 2.51 | 6.16 | 0.27 | 2.95
GM05_HI89 | 2.47 | 0.24 | 1.12 | 2.44 | 0.24 | 1.10
**Average**<br>(Std. Dev.) | 4.17 | 0.13 | 2.02 | 4.25 | 0.13 | 2.06
(|±0.07|) | (±0.52) | (±1.18) | (±0.08) | (±0.59)

Table 3.6. Electrical resistance of devices before and after thermal annealing in air at 300 °C.

Looking at table 3.6, the only observation is that the average contact resistance has increased; this is due to the device GM05_HI67, which shows an abnormal increase in both 2 and 4-probe resistance after air annealing. Considering the trend in 13 previous devices, it is certain to say that this mismatch might be due to a false reading, improper probe contact, or handling artifact. If one allows dismissing this device from the table, the average contact resistance for vacuum annealing is then 1.95 kΩ and for air annealing 1.93 kΩ, matching with the expected value. This observation is illustrated in Fig. 3.12 b.

After the electrical characterization, Raman mapping and spectroscopy were performed. The results (Fig. 3.13, 3.14, 3.15) show the same behavior observed before on LPE ultrathin graphite devices; C is transformed towards a nanocrystalline phase but in a very low proportion; then it is almost entirely removed by thermal oxidation.
Fig. 3.13. Raman mapping of ME ultrathin graphite device. Columns: D, G, and 2D bands; rows: different thermal annealing steps including 300 °C air annealing. The column in the middle: G band combined, is obtained by overlapping adjacent images.

Left: Fig. 3.14. Raman spectra corresponding to the deposited electrode including air thermal annealing at 300 °C.

Right: Fig 3.15. Raman mapping at G band. Blue square indicating the area where the spectra were taken.
The comparison between LPE and ME devices was accompanied by the Raman spectra of the ultrathin graphite flakes. The following figure 3.16 a and b, shows the Raman spectra of the flakes before and after annealing where it can be seen that there is not affectation by the heat treatment. Additionally, it can be seen that by comparing both samples and annealing condition, there is not shift on the peak’s position.

Fig. 3.16. Raman spectra corresponding to the deposited ultrathin graphite flakes obtained by a) ME, and b) LPE. Spectra correspond to D, G, and 2D regime.
As a summary of the observations, EBID Pt electrodes react favorably to 300 °C thermal annealing in both PLE and ME ultrathin graphite devices. There is not substantial electrical difference for the annealed electrodes with the C shell structure and electrodes without it; nonetheless, both have in common the sintered Pt core. The C shell structure does not enhance electrical conduction on the electrode, and it is composed of a large proportion of amorphous C with distinguishable nanocrystalline graphite sites. LPE ultrathin graphite does not have an adverse impact on the electrical performance of the electrodes; the heat treatment has the same resistance reduction rate in LPE and ME ultrathin graphite devices. Lastly, devices fabricated with LPE ultrathin graphite perform in average as well as the devices fabricated with ME ultrathin graphite.

In order to complete the characterization of the devices, AFM and SEM analysis were performed. The goal was to study the structural changes of the electrode after annealing at 300 °C (Fig. 3.20), and in this way provide more information about the suitability of the fabrication method. AFM mapping (Fig 3.17 and 3.18) reveals changes in the morphology. The deposited electrodes suffer from roughness increase due to the partial sintering of Pt particles while also a significant height reduction was observed. The AFM reveals a decrement of around two thirds, from an average 71 nm to 21 nm final height. Additionally, the thickness of the flakes is reported (Table 3.7).

![AFM mapping](image)

**Fig. 3.17.** AFM mapping corresponding to the fresh deposited electrode. Approximate height is 88nm.
Fig. 3.18. AFM mapping corresponding to the annealed electrode. Approximate height is 29nm. The blue circle is highlighting the change on the scale; see also Fig. 3.17.

Right: Fig. 3.19. Electrode height reduction after thermal annealing at 300 °C.

Left: Table 3.7. Graphite flake thickness and type.

<table>
<thead>
<tr>
<th>Device</th>
<th>Flake thickness (nm) and type</th>
</tr>
</thead>
<tbody>
<tr>
<td>GESP04_HI78</td>
<td>22 – LPE</td>
</tr>
<tr>
<td>GESP07_DE89</td>
<td>110 – LPE</td>
</tr>
<tr>
<td>GESP08_AB89</td>
<td>25 – LPE</td>
</tr>
<tr>
<td>GESP08_EF23</td>
<td>30 – LPE</td>
</tr>
<tr>
<td>GESP09_CD12</td>
<td>10 – LPE</td>
</tr>
<tr>
<td>GESP11_BC67</td>
<td>32 – LPE</td>
</tr>
<tr>
<td>GESP11_CD12</td>
<td>15 – LPE</td>
</tr>
<tr>
<td>GESP11_CD45</td>
<td>20 – LPE</td>
</tr>
<tr>
<td>GESP11_DE89</td>
<td>19 – LPE</td>
</tr>
<tr>
<td>GESP11_EF78</td>
<td>90 – LPE</td>
</tr>
<tr>
<td>GM05_AB12</td>
<td>4 – ME</td>
</tr>
<tr>
<td>GM05_AB78</td>
<td>15 – ME</td>
</tr>
<tr>
<td>GM05_CD89</td>
<td>15 – ME</td>
</tr>
<tr>
<td>GM05_EF12</td>
<td>38 – ME</td>
</tr>
<tr>
<td>GM05_EF34</td>
<td>16 – ME</td>
</tr>
<tr>
<td>GM05_FG89</td>
<td>7 – ME</td>
</tr>
<tr>
<td>GM05_GH78</td>
<td>40 – ME</td>
</tr>
<tr>
<td>GM05_HI23</td>
<td>8 – ME</td>
</tr>
<tr>
<td>GM05_HI67</td>
<td>5 – ME</td>
</tr>
<tr>
<td>GM05_HI89</td>
<td>31 – ME</td>
</tr>
</tbody>
</table>

The reduction in electrode's height is attributed in literature to the loss of C from the electrode [35] showing a decrease of around two thirds the original value, however, it was observed the same rate of reduction in vacuum annealed devices during this work and in a previous report [44]. Because of these reasons, the reduction of the electrode’s height is attributed mainly to the sintering of Pt particles, accompanied by the outward diffusion of C. AFM also reveals the consolidation of the halo surrounding the electrode that can be seen mainly in the annealed electrode. Fig. 3.19 shows a nearly 5 nm height halo that extends
around 100 nm outside of the electrode. This halo is inherent to beam deposition methods [92] and can be reduced by the appropriate deposition parameters, however, it is detrimental for miniaturization.

SEM analysis reveals that the halo is not made by a film but by several Pt islets (Fig. 3.22). These islets are clearly delimited from the electrode and are found only after annealing. In association to this, it was unexpectedly found the formation of Pt nanoparticles (Fig. 3.21 and Fig. 3.22) outside of the halo; these nanoparticles extended along several nanometers. Another observation was the significant formation of voids (Fig. 3.22) along the electrode after the annealing. These voids are referred in literature [35] to be formed due to the loss of carbon after oxidation, therefore, it was expected that vacuum annealing would have restricted the formation of these; nonetheless, the voids were still found. These facts need to be studied further, but at this point and with the conditions used in this work, they are detrimental for high-quality device fabrication.

Fig. 3.20. SEM images of ultrathin graphite device before (a) and after (b) annealing.
Fig. 3.21. SEM images of ultrathin graphite device: (a) flake before fabrication. (b)(c)(d) Detail of device after annealing; diffusion of Pt nanoparticles over the flake and substrate can be appreciated.

Fig. 3.22. SEM images of ultrathin graphite device: (a) Detail of the voids and Pt islets. (b) Detail of the Pt nanoparticles on flake and substrate.
Chapter 4: Conclusion

The present research work reports the electrical, structural, and chemical characterization of EBID Pt electrodes, used in four-probe devices of ultrathin graphite, exposed to different steps of thermal annealing.

During Pt deposition, a significant amount of C is being trapped inside the electrode; the fact is confirmed by EDXS. After device fabrication, application of vacuum thermal annealing at 100, 200, and 300 °C, promotes the outward diffusion of C into a solid C shell structure covering the Pt electrodes. Raman analysis reveals the presence of C sp² sites, but based on an I(D)/I(G) ratio of ~0.73, the shell structure can only be considered partially nanocrystalline. The electrical measurements confirm the reduction in contact resistance after 200 and 300 °C vacuum thermal annealing, suggesting that the C shell might be enhancing the electrical transport of the device. Despite this fact, an additional thermal annealing at 300 °C in air, promotes the oxidation and removal of the C shell and allows to confirm that the contact resistance remains the same. Thus, the C shell along the electrode is not involved in the transport phenomena.

The same experimental conditions were applied to both LPE and ME uG devices in order to evaluate the performance of the first one and its contribution to the electrodes. Both types resulted in an average of ~2kΩ contact resistance after 300 °C thermal annealing. The reduction of resistance of both LPE and ME devices was in the range of 99.5% after the heat treatment, hence, it is clear that the LPE uG used in this work presents a comparable performance to the one obtained by ME.

Additional characterization by AFM and SEM confirms the reduction of the electrode's height into one-third of the original size. It is also observed the undesired formation of voids along the electrode and the appearance of Pt nanoparticles along the surrounding area
including the graphite flake. These facts symbolize a disadvantage for EBID deposition when high-performance devices are aimed, however, in the author's experience, this deposition technique offers different areas of optimization and improvement where further efforts can be made.

4.1 Future Work

The future direction of this work should be the optimization of deposition parameters that may help to mitigate the structural damage found along the electrodes. Firstly, it is suggested to increase the electrode's height. This might reduce the formation of voids due to the increased number of Pt particles available in a single rod; however, this might require longer deposition times, and therefore, a higher possibility of undesired deposition outside the area of the electrode.

The formation of the C shell along the electrode might be advantageous for some applications. Up to this point it was demonstrated that it does not enhance conductivity but also does not affect the same, therefore, it might be useful to protect the metal electrode from chemical reactions like oxidation, specially when applied to more reactive metals that are available for EBID; for instance tungsten.

Another topic that should be explored is the deposition of graphene flakes into the substrate. Up to now there was no way to control the location, the thickness, and the size of the LPE flakes. Developing a technique to attack these issues might accelerate the introduction of LPE technology into device fabrication.

The ultimate future work would be to be able to integrate CNTs and graphene into the same device, taking advantage of their properties, and the EBID deposition.
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[92] W. Disney, “Around here we don’t look backwards for very long. We keep moving forward, opening up new doors and doing new things, because we’re curious... and curiosity keeps leading us down new paths.”