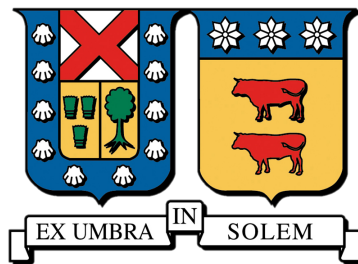


MASTERS THESIS

Graphene-coated Nanoprobes for Conductive Atomic Force Microscopy

Thesis submitted as required to obtain the degree of
MASTER OF SCIENCE IN PHYSICS.



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ABSTRACT

Atomic force microscopy (AFM) is a powerful technique that enables the study of surface topography at the nanoscale and, depending on the operating mode, the characterization of local electrical properties. However, electrical measurements require AFM probes with conductive coatings. These coatings present several limitations, including reduced conductivity stability, limited mechanical robustness, and relatively high fabrication costs. In this context, this research evaluates the feasibility of graphene (Gr) as an alternative coating material for AFM probes. Silicon nanoprobe tips coated with graphene are proposed as an additional option for conductive AFM probes, expanding the range of materials that can be used to provide electrical conductivity to AFM tips.

Graphene is first synthesized using chemical vapor deposition (CVD), producing a suspended two-dimensional graphene sheet at a water–air interface. The graphene film is then transferred from this interface onto the apex of an AFM probe using a hydraulic micromanipulator coupled to the AFM system through a polymer-free transfer approach.

In this work, mono-, bi-, and multilayer graphene were successfully synthesized and transferred onto eight AFM probes. Scanning electron microscopy (SEM) was employed to analyze the morphology of the probes and verify the presence of the graphene coating on the tip apex. The synthesized graphene was further characterized using Raman spectroscopy. The structural quality and number of graphene layers were evaluated through the intensity ratios I_D/I_G and I_{2D}/I_G respectively. Optical microscopy was additionally used to analyze the graphene coverage on the AFM chip, allowing the evaluation of its suitability for establishing electrical contacts required for conductive atomic force microscopy (C-AFM) measurements. Finally, the performance of the Gr-coated probes was evaluated through local topographic and conductivity measurements using C-AFM on a floppy disk test sample. This sample consists of Fe_2O_3 particles mixed with carbon black embedded in a polyurethane matrix, providing a surface with electrical heterogeneity ideal for conduction testing.

The results show that bilayer and multilayer graphene coatings fabricated through a single immersion of the AFM probe into the graphene film produce topographic images that remain comparable to those obtained with the reference conductive probe, despite a reduction in lateral resolution. The corresponding conductivity maps reveal a heterogeneous distribution of conductive regions, with measurable current signals in the nA and pA ranges for the bilayer and multilayer graphene coatings, respectively.

These findings indicate that a single-immersion transfer process is capable of producing electrically conductive Gr-coated probes suitable for C-AFM measurements. Overall, the coating process and its implementation in conductive AFM measurements proved to be successful.

DEDICATION AND ACKNOWLEDGMENTS

Dedication

To my parents, María Cristina and Eliceo, and to my brother Víctor, for their unconditional love, for always being my support system, and my number one fans. Everything I have achieved has been built upon the foundation of their love and values. I thank God for the blessing of their presence in my life.

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INTRODUCTION

In the field of atomic force microscopy (AFM), particularly in electrical modes such as conductive-AFM (C-AFM), commercial conductive probes present several limitations. These include progressive mechanical wear, the bimetallic effect associated with electrical measurements, and the degradation of metallic conductive coatings. These limitations are primarily driven by anodic oxidation [1] at the tip-sample junction due to ambient humidity, as well as electromigration induced by high current densities [2]. Such processes lead to the formation of insulating oxide layers or the physical delamination of the metallic coating, resulting in a loss of electrical sensitivity and directly impacting the stability, reproducibility, and operational lifetime of the probes. Consequently, the reliability of nanoscale electrical characterization is compromised. For this reason, we propose graphene as a new coating material for these AFM tips.

Graphene is a material that has attracted significant interest within the scientific community over the past decades due to its exceptional properties, including high electrical and thermal conductivity, good mechanical strength and optical transparency (Table 1.1). These characteristics make it a promising candidate for a wide range of applications, such as solar cells [3], nanoelectronics [1], sensing technologies [4], and as a potential coating material for AFM probes.

In this thesis, the fabrication and characterization of nanometric AFM tips coated with graphene are investigated, with the aim of analyzing their performance and evaluating their potential for electrical AFM modes. The main objective of this work is to

integrate graphene with silicon nanoprobe, which requires its synthesis, characterization, and subsequent transfer onto the AFM tips, in which a polymer-free transfer method is implemented. Following the transfer process, a series of morphological and structural characterization steps are carried out, with particular emphasis on structural analysis to assess the suitability of the system for C-AFM applications. This work seeks to investigate the feasibility of our transfer method and to analyze the probe quality for topographical imaging and electrical conductivity measurements.

1.1 Atomic Force Microscopy

Developed in the 1986 by Gerd Binnig, Calvin F. Quate and Christoph Gerber [5], atomic force microscopy (AFM) emerged as part of the scanning probe microscopy (SPM) family and that followed the scanning tunneling microscopy (STM). The AFM made it possible to visualize the topography of both conducting and insulating surfaces, often achieving atomic-level resolution. This ability sets it apart from STM, which was limited to analyzing only conductive or semiconducting surfaces [6].

As with STM, this instrument functions by scanning a sample's surface with a sharp tip. In AFM the tip is attached to a flexible silicon cantilever, maintaining contact or near contact with the surface. As the tip interacts with the sample, the cantilever deflects, and the tip-sample interaction is monitored using a laser beam focused on the back of the cantilever. The laser beam is reflected towards a four-quadrant photodetector (PD), which is divided into four photosensitive regions (A, B, C, and D) (Figure 1.1) [7]. The deflection of the cantilever causes the position of the reflected laser spot to shift, and the changes in the light intensity on each quadrant are used to measure the cantilever's deformation. Vertical and torsional deflections are tracked by calculating the difference in signals from the quadrants, providing information about the sample's mechanical and frictional properties. The sample is usually scanned by piezoelectric scanners, which enable precise movement at angstrom resolutions [8, 9].

A key component of AFM is the nanoprobe, a flexible cantilever with a sharp nanometric tip [10]. The nanoprobe is essential for interacting with the sample at the nanoscale, allowing precise measurements. Its high resolution and sensitivity enables the study of structures at atomic levels. Depending on the nature of the study, the nanoprobe can be coated with various materials, such as Au, Pt, other metals and even diamond, to customize its properties for specific applications [10]. These include analyzing nanostruc-

tures, studying molecular interactions and investigating biological systems, performing local electrical measurements, among others [10].

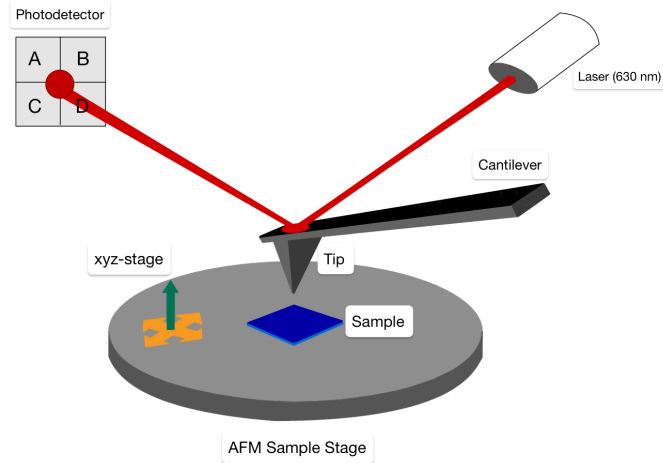


Figure 1.1: Diagram of the basic components of an AFM.

1.1.1 Conductive Atomic Force Microscopy

Atomic force microscopy has given rise to various modes of operation aimed at studying local properties beyond surface topography. Among these is conductive atomic force microscopy (C-AFM), a mode derived from conventional AFM that is typically operated in contact mode [11]. In this technique, in addition to the mechanical control of the tip–sample interaction, the measurement of local electrical current is incorporated through the use of conductive tips and the application of an electrical potential between the tip and the sample. This configuration allows the simultaneous mapping of a surface’s morphology and its local electrical conductivity with nanometric resolution.

The initial development of the C-AFM technique is documented in the work of Murrell *et al.* in 1993 [12].

Currently, the C-AFM configuration shown in Figure 1.2 is most commonly employed, which includes a piezoelectric tube scanner (piezo tube) for precise nanoscale positioning of the tip or sample. In addition to this mechanical component, three specific technical adaptations are required for electrical characterization, as highlighted by Mario Lanza [11]: the use of a conductive probe to act as a mobile nanoscale electrode, the integration of a voltage source to establish a potential difference between the tip and the sample holder, and the addition of a current-to-voltage preamplifier to convert the analog current

signals into digital voltages processable by the computer.

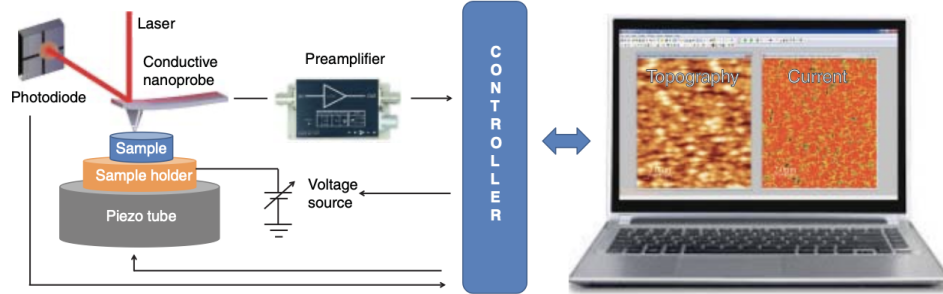


Figure 1.2: Diagram of the basic components of a Conductive Atomic Force Microscope, featuring the three additions for electrical characterization, a voltage source, a preamplifier, and a controller [11].

1.2 Graphene

Graphene (Gr) (Figure 1.3a), is a two-dimensional material and an allotrope of carbon, meaning it is composed exclusively of carbon atoms arranged in a specific crystal structure. In the case of graphene, each carbon atom is bonded to three other carbon atoms through covalent bonds, forming a flat two-dimensional honeycomb structure (Figure 1.3b). This material exhibits sp^2 hybridization, which consist of a single π orbital and three σ bonds oriented within the plane. The strong in-plane σ bonds provide structural rigidity by forming a stable hexagonal framework, while the out-of-plane π bonds enable electron delocalization, contributing to graphene's unique electronic properties and governing interactions between layers [13].

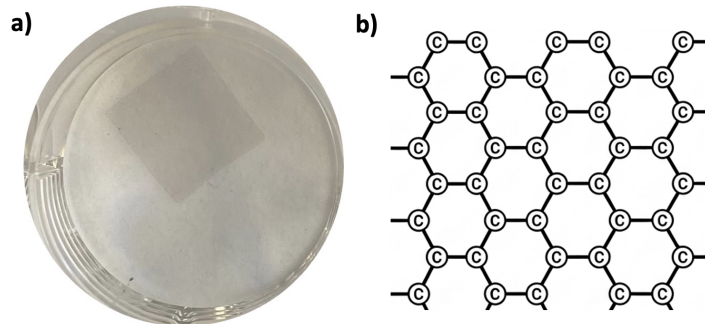


Figure 1.3: Structure and morphology of graphene. a) Large-area graphene sheet ($2 \times 2 \text{ cm}^2$) located at a water-air interface. b) Representation of the atomic honeycomb lattice model, where carbon atoms are organized through covalent bonds.

Graphene was first isolated in 2004 at the University of Manchester by physicists Konstantin Novoselov and Andre Geim using "Mechanical Exfoliation" commonly known as the "Scotch-tape method". As the name suggests, this method involves peeling off the top layers of a graphite sample to extract graphene flakes of varying thickness, from monolayer to few-layer systems, which are then transferred onto a substrate [14]. Their work earned them the Nobel Prize in Physics in 2010.

Table 1.1: Physical properties of monolayer and bilayer graphene.

Properties	Monolayer	Bilayer	References
Young's Modulus (TPa)	1.0 ± 0.1	0.8	[15, 16]
Optical Transparency (%)	97.7	95.0	[17, 18]
Elec. Conductivity ($\text{S} \cdot \text{m}^{-1}$)	$(1.46 \pm 0.82) \times 10^6$	–	[19]
Ther. Conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	3000–5000	2800	[20, 21]
Carrier Mobility ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)	2×10^5	4×10^4	[17, 22]

The physical properties of graphene (Table 1.1) make it a promising candidate to be incorporated as an additional coating material for AFM probes (Table 1.2), alongside materials such as Pt, Au, Ir, and even diamond, whose electrical behavior depends critically on crystal purity and specific doping conditions [23].

Table 1.2: Physical properties of conventional conductive coating materials used in AFM probes.

Property	Pt	Au	Ir	Diamond	References
Young's Modulus (GPa)	168	77.2	193	1050	[24–27]
Elec. Conductivity ($\text{S} \cdot \text{m}^{-1}$)	9.4×10^6	4.1×10^7	2.1×10^7	–	[24, 28, 29]
Ther. Conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	71	318	147	2000	[24, 30]

Graphene high Young's modulus provides notable mechanical strength, enhancing the structural durability of the tip. In addition, its good electrical conductivity enables efficient charge transport, while its thermal conductivity facilitates effective heat dissipation during electrical measurements. This latter property is particularly relevant in conductive scanning probe techniques such as C-AFM.

In the case of bilayer graphene, many of its physical properties remain comparable to those of monolayer graphene, maintaining high mechanical strength, thermal conductivity and carrier mobility which makes it also a promising material for this type of application. Regarding electrical conductivity, its value depends on external factors such as carrier density, temperature, and defect concentration, among others [21]. Con-

sequently, the reported conductivity can vary by several orders of magnitude depending on the experimental conditions or measurement methods.

1.3 Graphene-Coated Nanoprobes

To better understand the research topics addressed in this thesis, we will first examine relevant prior studies as a foundation for this work. In particular, we will focus on the review by Hui *et al.* (2017), titled "Graphene-Coated Nanoprobes: A Review" [10]. This article outlines several methods for coating AFM tips with graphene, aiming to extend the lifetime of conductive nanoprobes while maintaining high electrical conductivity and mechanical robustness.

Graphene has been proposed as a novel coating material, as conventional metals such as platinum (Pt), gold (Au), aluminum (Al), iridium (Ir), and even diamond present several drawbacks. One major issue is mechanical wear, since these coatings can degrade with repeated scanning, reducing tip sharpness and imaging resolution. Additionally, metallic coatings tend to increase the tip radius, which is < 25 nm, thereby lowering lateral resolution. Poor adhesion to the tip substrate is also common, particularly with gold and platinum, often requiring an intermediate adhesion layer such as chromium or titanium, respectively. Oxidation is another concern. Although diamond is mechanically robust, it can damage samples due to its high stiffness, which compromises both tip sharpness and electrical conductivity, and involves high production costs. Furthermore, some metals, such as iridium and platinum, are expensive and difficult to deposit uniformly, which limits their scalability in tip manufacturing.

In response to these limitations, the following sections presents five distinct graphene based coating methods designed to overcome the shortcomings of traditional metallic coatings. We will examine each of these methods in detail.

1.3.1 First Method: Direct Chemical Vapor Deposition of Graphene on AFM Nanoprobes

In the context of developing reproducible molecular junctions, Wen *et al.* (2012) [31] proposed the fabrication of silicon nanoprobes for AFM, coated with a layer of gold and subsequently covered with multilayer graphene (> 4 layers) via chemical vapor deposition (CVD). Ethanol was used as the carbon precursor, with the gold coating on the tips serving as the catalytic material in an H_2/Ar atmosphere at temperatures ranging from 750 to 850 $^{\circ}C$.

Characterization of the tip apex by scanning electron microscopy (SEM) (Figure 1.4a) revealed a lack of uniformity and homogeneity in the coating. The authors attributed these irregularities to the melting of gold during the graphene growth process. To confirm the formation of graphene on the tips, Raman spectra of the deposited material were obtained both from the tips and from gold electrodes subjected to the same CVD process (Figure 1.4b). This comparison was necessary because the curved and nanometric surface of the tips makes it difficult to obtain representative Raman spectra. Both spectra exhibit the G band at 1598 cm^{-1} and a pronounced D band, indicating the presence of structural defects in the material.

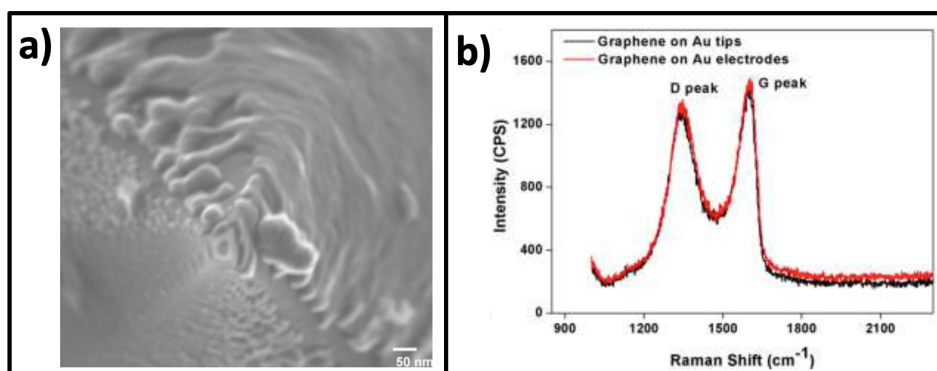


Figure 1.4: Graphene characterization. a) Top-view SEM image of the Au tip apex after CVD graphene deposition. b) Raman spectrum of graphene formed on the Au electrode (red line) and Au-coated AFM tip (black line). Adapted from Wen *et al.* [31].

After analyzing the carbon material, the authors implemented the experimental configuration shown in Figure 1.5a), in which the Gr-coated AFM tips were brought into controlled contact with self-assembled monolayers of alkanethiols or alkanedithiols of varying chain lengths, previously immobilized on a gold substrate. This configuration,

Gr-tip/monolayer/Au-substrate, was measured using C-AFM with an applied load at about 2 nN in contact mode, I–V curves were recorded to study charge transport through the molecular junctions (Figures 1.5b,c). In particular, for octanemonothiol junctions, the variability in conductance decreased significantly using Gr-coated tips as compared to Au-coated tips. Au-coated tips (Figure 1.5b) showed fluctuations of up to three orders of magnitude, while Gr-coated tips reduced this variability to a factor close to 2 (Figure 1.5c). The growth of graphene at high temperatures can successfully remove most or all of the contaminants on the different Au tips, which has a strong, exponential effect on the resistance.

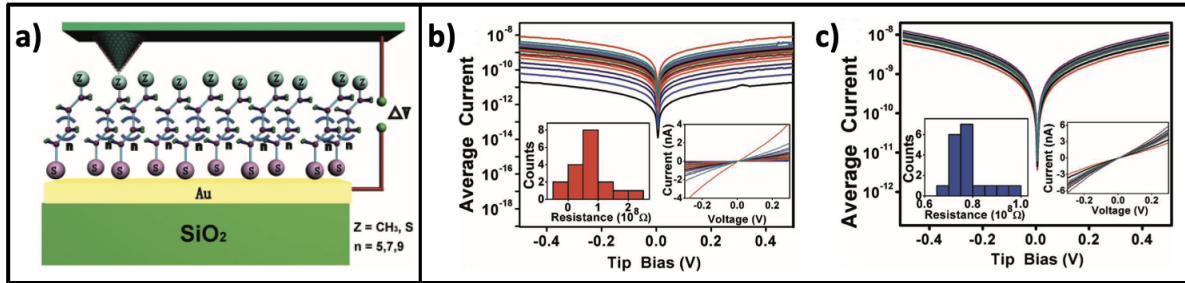


Figure 1.5: Results of Au AFM tips for molecular junction measurements with and without graphene. a) Diagram depicting a molecular tunnel junction constructed via C-AFM. b) Average I–V data for Au/octanemonothiol/Au junctions with the 18 different Au tips. c) Average I–V data for Au/octanemonothiol/Gr/Au junctions with the 18 different graphene tips. Adapted from Wen *et al.* [31].

1.3.2 Second Method: Transfer of CVD-Grown Graphene onto AFM Probes

Lanza *et al.* (2013) [32] proposed the development of Gr-coated AFM tips for C-AFM, with the main objective of enabling reliable nanoscale electrical characterization. This approach addresses the limitations of conventional metallic tips, which suffer from rapid degradation under high currents and friction, leading to inaccurate measurements.

To achieve this, similarly to the previous method, the authors employed a CVD process, differing in that the graphene was grown on copper foils. The growth was carried out in a tube furnace at 1000 °C, using methane as the carbon precursor in a hydrogen atmosphere. The synthesized material was subsequently characterized by Raman spectroscopy (Figure 1.6a), revealing that graphene growth occurred on both sides of the copper foil.

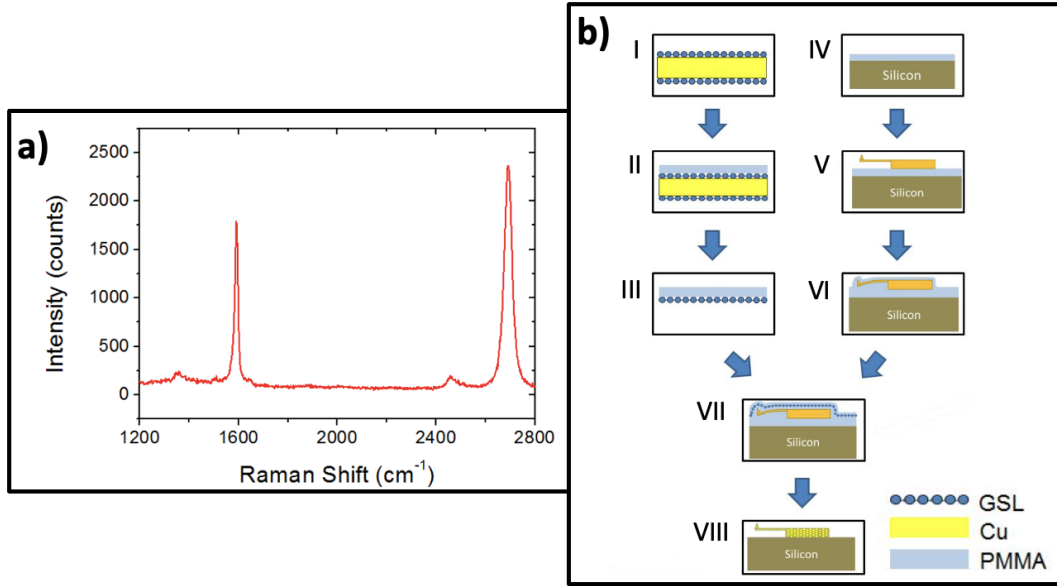


Figure 1.6: Graphene characterization and AFM tip transfer process. a) Raman spectrum of the graphene sample. b) AFM tip graphene transfer methodology. Adapted from Lanza *et al.* [32].

For the transfer process, a monolayer graphene sheet (GSL) grown on both sides of a Cu foil was used (Figure 1.6b.I). One side of this stack was coated with PMMA (Figure 1.6b.II); subsequently, the unprotected bottom GSL and the underlying copper foil were removed by chemical etching with FeCl_3 , leaving the GSL/PMMA film floating on the liquid surface (Figure 1.6b.III). In parallel, a silicon target substrate was spin-coated with ~ 200 nm of PMMA, and the AFM probe (a commercial silicon Pt/Ir nanoprobe) was positioned on top of this cold polymer layer (Figure 1.6b.IV). The structure was then baked on a hot plate at 170°C for 5 min to soften the PMMA, allowing the probe to sink slightly and become thermally immobilized upon cooling (Figure 1.6b.V). An additional film of the same polymer was subsequently applied over the assembly to ensure a secure mechanical encapsulation within the PMMA matrix (Figure 1.6b.VI). The floating GSL/PMMA film was then transferred onto the target structure, this aligns the graphene directly with the embedded tip (Figure 1.6b.VII). Finally, the multi-layered PMMA matrix was dissolved by immersion in boiling acetone for 30 min while maintaining the entire sample strictly horizontal (Figure 1.6b.VIII). This precise horizontal orientation is critical because the weight of the thick PMMA layers flexes the cantilever downward; keeping it horizontal prevents the tip from breaking against the substrate as the supporting polymer melts and removes its weight. As a result, the cantilever flexes back to its initial position, leaving the tip coated with graphene.

Ramp voltage stress (RVS) I–V measurements on $\text{HfO}_2/\text{SiO}_2$ stacks under identical high current density conditions ($\sim 10^8 \text{ A/cm}^2$) and high vacuum ($5 \times 10^{-7} \text{ Torr}$) for both non-coated tips and Gr-coated tips (performed in contact mode) show that Gr-coated tips maintain a stable and reproducible electrical response, even after multiple consecutive measurement cycles reaching out the current compliance level approximately at the same onset voltage without appreciable wearing (Figure 1.7b), in contrast to Pt/Ir tips, which rapidly degrade due to the high currents (Figure 1.7a). It is important to notice that tip is static, so that the degradation can not be attributed to the frictions.

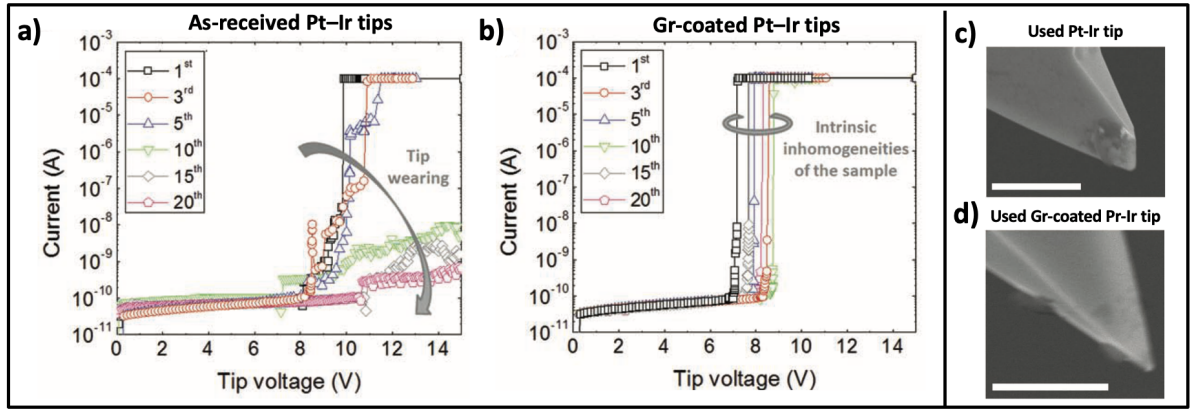


Figure 1.7: Electrical and morphological characterization of successive 1st, 3rd, 5th, 10th, 15th, and 20th I–V curves on $\text{HfO}_2/\text{SiO}_2$ using a) non Gr-coated Pt/Ir tips. b) Gr-coated Pt/Ir tips. c, d) SEM images of Pt/Ir tips after 20 I–V measurements: (c) Pt/Ir tips, (d) Gr-coated tip. Scale bars: $5 \mu\text{m}$ and $3 \mu\text{m}$ respectively. Adapted from Lanza *et al.* [32].

The durability of the Gr-coated tips is further supported by SEM images, where significant wear and deterioration are observed in conventional Pt/Ir coatings after repeated use under the same conditions (Figure 1.7c), while the Gr-coated tip preserves its initial sharpness (Figure 1.7d).

As complementary evidence of their operational stability during prolonged scanning, topographic and current maps under high vacuum ($5 \times 10^{-7} \text{ Torr}$) were simultaneously obtained on conductive Gr-on-Cu samples using both as-received Pt/Ir tips and Gr-coated Pt/Ir tips (Figure 1.8).

The measurements were performed in contact mode with a controlled applied force, 5 nN for the as-received Pt/Ir tip and 50 nN for the Gr-coated tip, demonstrating the latter's ability to resist higher mechanical stress without degrading.

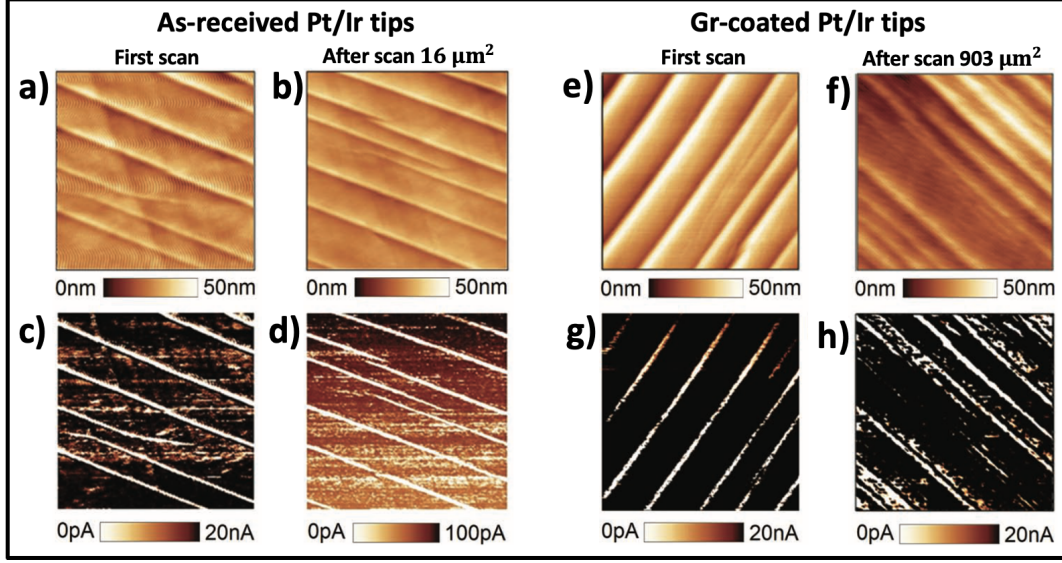


Figure 1.8: Comparison of topographic and current mapping performance between uncoated and Gr-coated Pt/Ir tips. a,b) Topographic images and c,d) current maps obtained with an as-received Pt/Ir tip (contact force: 5 nN). e,f) Topographic images and g,h) current maps obtained with a Gr-coated Pt/Ir tip (contact force: 50 nN). All images are $1 \times 1 \mu\text{m}^2$. Adapted from Lanza *et al.* [32].

A direct comparison of the current scales highlights the protective role of the graphene coating. For the as-received Pt/Ir tip, the current signal degrades substantially after scanning only $\sim 6 \mu\text{m}^2$ (six $1 \times 1 \mu\text{m}^2$ scans) under a low force of 5 nN. The first scan (Figure 1.8e) exhibits a current range of 0–20 nA, whereas Figure 1.8d shows that the signal drops to 0–100 pA, a decrease of two orders of magnitude, indicating severe loss of conductivity after moderate use. In stark contrast, the Gr-coated Pt/Ir tip maintains its original current sensitivity (0–20 nA) even after scanning an area over 150 times larger ($903 \mu\text{m}^2$, Figures 1.8g and 1.8h) under a tenfold higher force (50 nN), with no observable loss in signal amplitude. This demonstrates that the graphene layer effectively shields the underlying Pt/Ir coating from wear during continuous scanning, enabling long-duration nanoscale electrical imaging enhancing its lifetime on tip–sample interactions.

1.3.3 Third Method: Mold-assisted Transfer of CVD-Grown Graphene onto AFM Probes

In the context of microelectromechanical systems (MEMS) applied to AFM, the work of Martin-Olmos *et al.* (2013) [33] stands out, as they developed a fabrication process based

on pre-patterned silicon molds. In the first stage, inverted pyramids were defined by lithography and anisotropic KOH etching. Subsequently, the substrate was coated with a SiO_2 layer and a Cu film, on which graphene was grown by CVD. From Figure 1.9a), corresponding to Raman spectroscopy characterization, the formation of a monolayer graphene is observed, evidenced by a 2D band significantly more intense than the G band. Figure 1.9b) illustrates the step-by-step fabrication process. After creating the silicon tip molds and growing graphene on copper, two SU-8 layers were applied by spin-coating to first form the cantilever and then the probe body. Subsequently, the excess graphene was removed using an argon plasma, and finally the probes were released by dissolving the silicon and copper layers with chemical solutions.

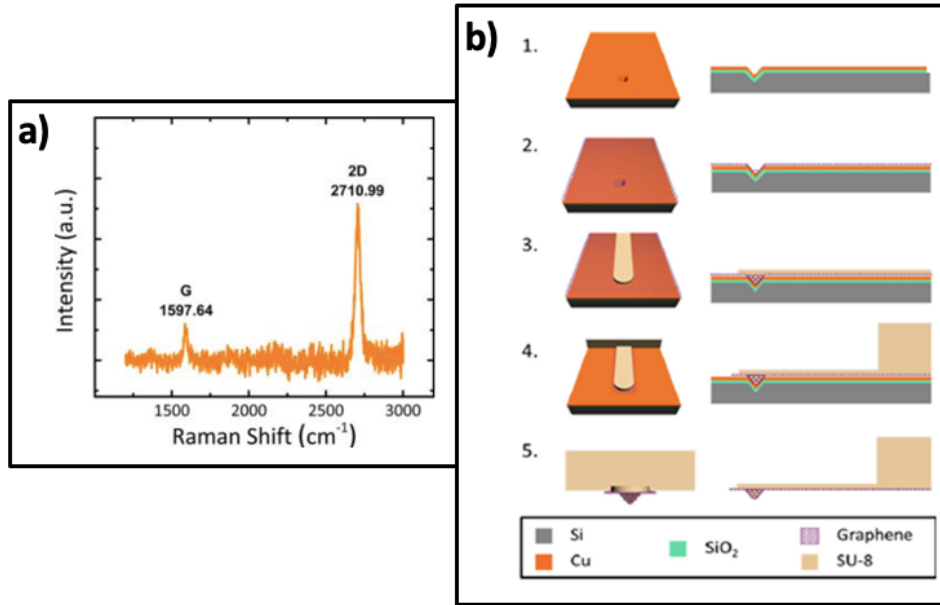


Figure 1.9: Graphene assessment and probe coating process. a) Raman spectrum of the graphene sample. b) Fabrication method for Gr-coated SU-8 AFM probes via transfer. Adapted from Martin-Olmos *et al.* [33]

The SEM images in Figures 1.10a,b) confirm the graphene coating of the AFM probes. The graphene layer is observed to continuously cover the entire surface of the cantilever and the SU-8 tip, conformally adapting to the pyramidal geometry. However, due to the thickness of the Cu layer used during CVD growth (500 nm), the tip exhibits a relatively large radius, resulting in a less sharp geometry. Nevertheless, the functional results demonstrate a significant improvement in the performance of the coated tips.

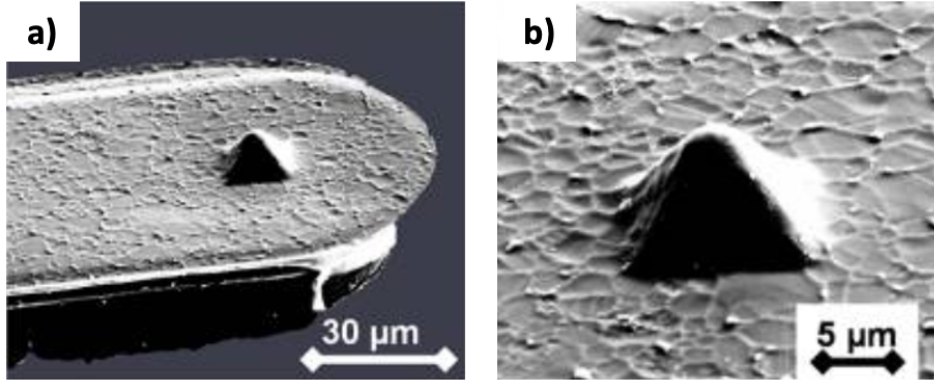


Figure 1.10: SEM micrographs from Gr-coated SU-8 probe. a) General view of the probe. b) High- magnification tip view. Adapted from Martin-Olmos *et al.* [33].

Conductivity measurements performed by C-AFM on a Pt substrate revealed a critical difference, the bare SU-8 probes, being a polymeric insulator, showed no measurable current (Figure 1.11a). In contrast, the Gr-coated SU-8 tips exhibited a clear electrical response with non-linear I-V curves (Figure 1.11b). These results confirm the electrical continuity of the graphene coating and demonstrate its effectiveness in transforming intrinsically insulating polymeric tips into conductive probes, thereby enabling their use in conductive AFM techniques.

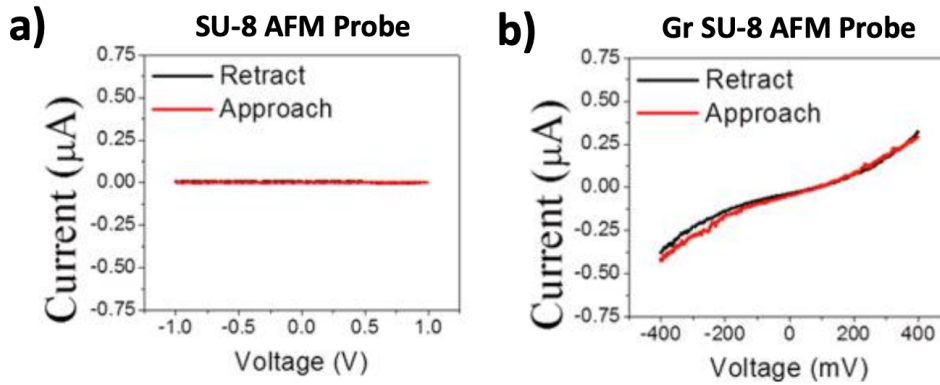


Figure 1.11: Current–voltage (I–V) curves for a) an uncoated SU-8 AFM tip and b) a Gr-coated SU-8 AFM tip. Adapted from Martin-Olmos *et al.* [33].

1.3.4 Fourth Method: Direct Graphite-like Thin Film Deposition on AFM Nanoprobes

An alternative approach was presented by Pacios *et al.* (2016) [34], who developed a method to coat AFM probe tips with ultrathin graphite (uG) without relying on CVD.

The technique is based on an *in-situ* synthesis via metal-catalyzed crystallization of an amorphous carbon layer, previously deposited together with the catalyst directly onto the cantilevers by sputtering. This approach enables the direct growth of ultrathin graphite on high aspect ratio nanometric structures at relatively low temperatures, close to 800 °C, under an argon atmosphere without transfer.

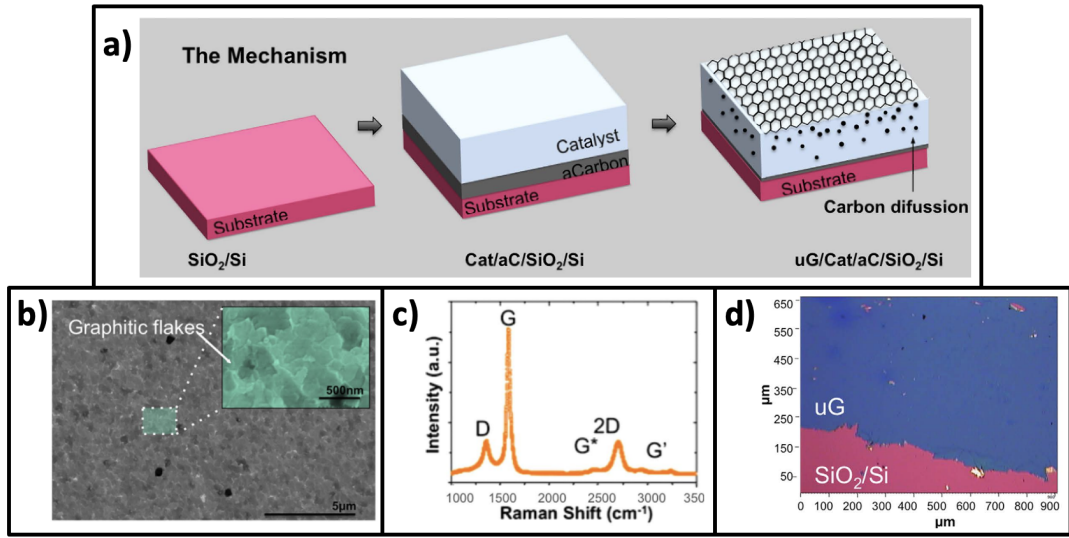


Figure 1.12: Growth results of ultrathin graphite on flat substrates. a) Growth mechanism of uG without transfer. b) SEM image of the homogeneous growth of graphene flakes on a flat SiO_2 substrate. c) Raman spectrum of uG on Pt catalyst. d) Optical microscope image of uG subsequently transferred on SiO_2/Si substrate using an electrolysis-based bubbling method in NaOH (1M) aqueous solution to detach PMMA-supported graphite from the catalyst, with the PMMA subsequently removed in acetone. Adapted from Pacios *et al.* [34].

To validate the viability of the method, the authors initially evaluated the growth of ultrathin graphite on flat substrates without transfer. The deposition process scheme is shown in Figure 1.12a), where amorphous carbon (aC) and the metal catalyst are deposited on SiO_2 by sputtering, then, the film is annealed and uG is precipitated on the surface. Once the growth technique has been carried out the samples are characterized using SEM and Raman. The SEM image in Figure 1.12b) confirms the homogeneous formation of uG coating over the entire substrate, with a polycrystalline morphology. Raman spectroscopy characterization (Figure 1.12c) reveals the characteristic peaks of graphitic materials. In particular, the $I(\text{G}) > I(2\text{D})$ ratio, together with the broadening and asymmetry of the 2D peak, allows the material to be identified as ultrathin graphite.

Although the proposed approach avoids transfer processes, the authors performed metrology on the ultrathin graphite, where they transferred this material onto a SiO_2/Si substrate using an electrolysis-based bubbling method. The imperfections attributable to the transfer itself are observed in the microscopical image (Figure 1.12d), highlighting the limitations of such steps when functionalizing nanometric structures such as AFM tips.

After validating the growth on flat substrates, the authors scaled the technique to 3D structures, using AFM tips. Spherical silicon/silicon dioxide tips with radii up to $2\ \mu\text{m}$ were employed, as well as rounded silicon tips with radii on the order of 90 nm/150 nm.

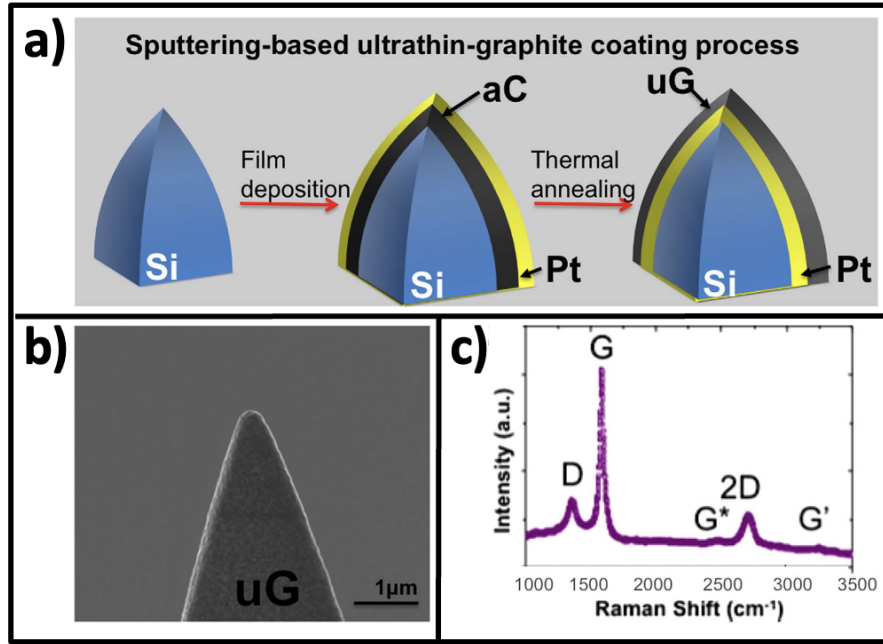


Figure 1.13: Growth results of ultrathin graphite on AFM silicon tips. a) Schematic of the growth process on a 3D shaped AFM nanoprobe. b) SEM image of the tip coated with uG. c) Raman spectrum of the tip showing the characteristic graphite peaks. Adapted from Pacios *et al.* [34].

As schematically shown in Figure 1.13a), the tips were initially coated by radio frequency sputtering with an amorphous carbon layer (30 nm) and a catalytic platinum layer (100 nm) annealed at $800\ ^\circ\text{C}$ under an argon flow (200 sccm, 9 Torr). The SEM image (Figure 1.13b) shows a continuous uG coating over the tip after annealing. To verify the nature of the material, Raman spectroscopy was performed directly on the

probe, confirming the presence of uG (Figure 1.13c), identical to that obtained on flat substrates.

On the other hand, to investigate the parameters influencing the coating quality, the authors analyzed samples processed under different pressure conditions by transmission electron microscopy (TEM). This was done to corroborate the coating at the tip apex. Even though the SEM and Raman resolution is sufficient to prove that graphite is present on the tip, this last being extremely small would introduce some error.

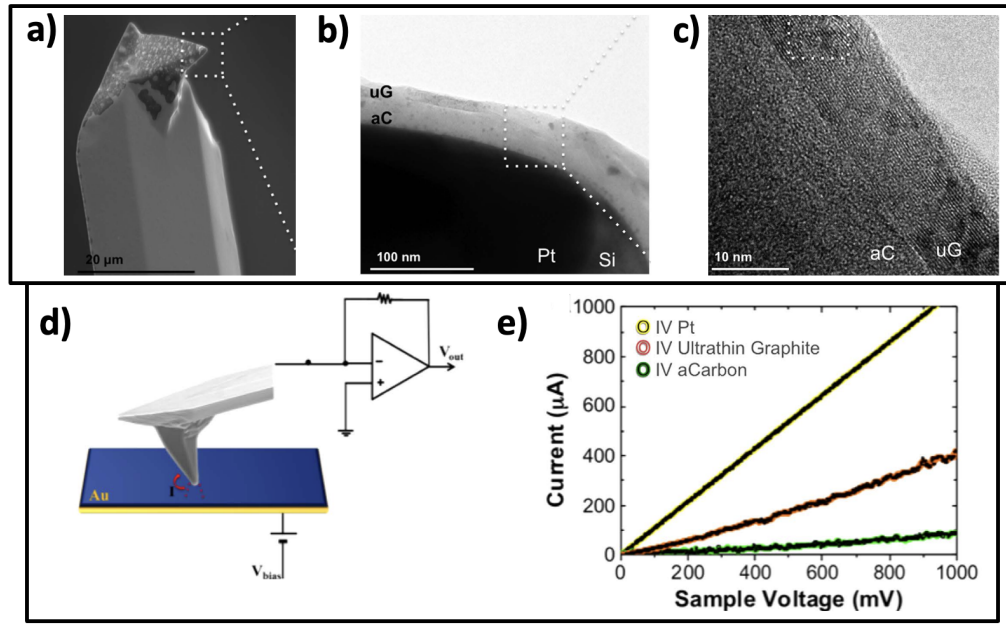


Figure 1.14: TEM and conductive characterization on different individual AFM tip-systems. The uG extends over the entire surface with thickness of ~ 10 nm. a, b, c) TEM images of the edges of distinct AFM tips after the growth process: (a) Full view of a tip. Cross-sectional view of a tip under low (b) and high (c) magnification. d) Schematic system for contact resistance measurements. e) I-V curves of the tips with different coatings on Au. Adapted from Pacios *et al.* [34].

In particular, the TEM images in Figures 1.14a-c), corresponding to processes carried out under high vacuum (10^{-3} to 10^{-7} Torr) for different tips, reveal defective growth, characterized by agglomeration of the platinum catalyst and the formation of a thick amorphous carbon layer covered by a thin graphite layer.

To evaluate the functional performance of the coating, electrical conductivity of uG-coated AFM tips was characterized in the context of applications in nanoelectromechanical systems (NEMS) switches and transistors.

The experimental configuration shown in Figure 1.14d) enabled the acquisition of I-V

curves for tips with different coatings. In the case of uG, the results in Figure 1.14e) indicate a linear ohmic behavior and high conductivity, exceeding that of amorphous carbon.

1.3.5 Fifth Method: Liquid Phase Graphene Flakes Coated AFM Probes

Hui *et al.* (2016) [35] identified that the previously mentioned graphene coating methods are too complex for large-scale industrial production. For this reason, they proposed a simple, fast, and low-cost approach based on solution-processed reduced graphene oxide (rGO). This material is obtained from graphite powder through redox reactions based on the Hummers–Offeman method, which produce graphene oxide, followed by a chemical reduction that yields graphene sheets with a thickness of approximately 0.7 nm and a lateral size below 1 μm .

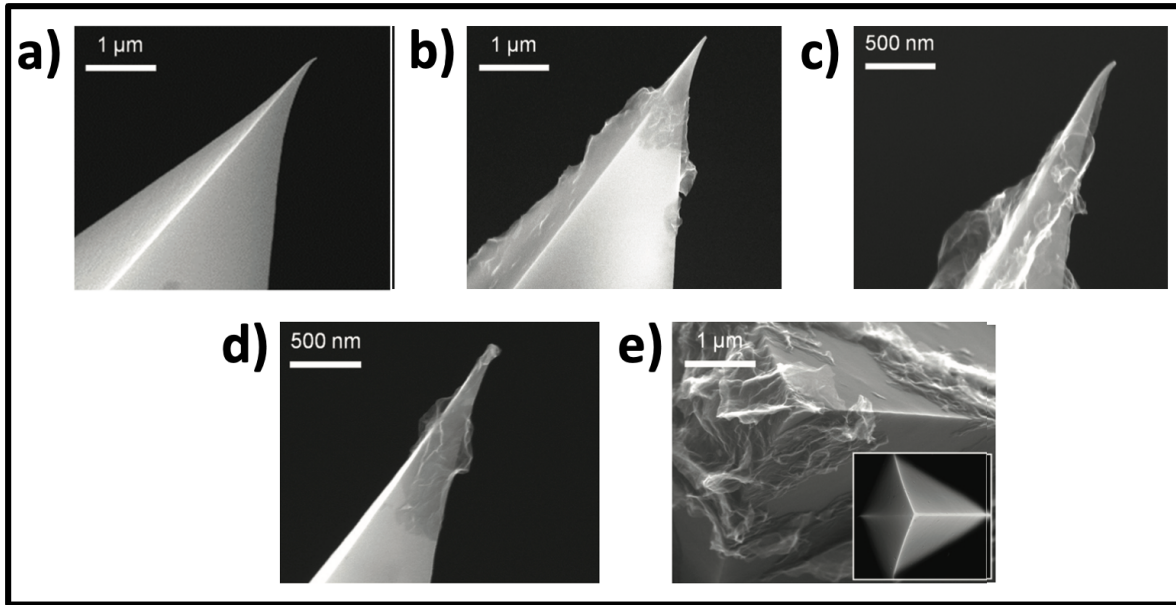


Figure 1.15: SEM images of different Pt-varnished silicon tips before and after Gr coating. a) As-received OMCL-AC240 nanoprobe. b,c) OMCL-AC240 nanoprobe coated with low and high density of Gr layers (respectively). d,e) OSCM-PT and SCM-PIC nanoprobe coated with low density of graphene sheets (respectively). Adapted from Hui *et al.* [35].

The simplicity of this method lies in the coating process itself: by immersing standard tips into the solution, the two-dimensional graphene flakes spontaneously adhere to the tip surface due to strong van der Waals. This allows the graphene to conform perfectly to the sharp profile of the probe, forming a uniform layer even on tips with diverse geometries. Consequently, the authors demonstrated a cost-effective route for the fabrication of

Gr-coated nanotips with enhanced performance and low cost, paving the way for their potential industrial production.

Using SEM images, the authors verified the effectiveness of the coating on different Pt-varnished silicon tip models (Figure 1.15 b-e). These images show that graphene adheres to the apex of the tip via van der Waals forces. This region constitutes the main focus of the study, as it is the part that comes into direct contact with the sample during experiments. Although an excess of graphene on the backside of the cantilever could affect the reflection of the AFM laser toward the photodiode, the experimental results show that this reduction is below 20%, allowing effective deflection detection.

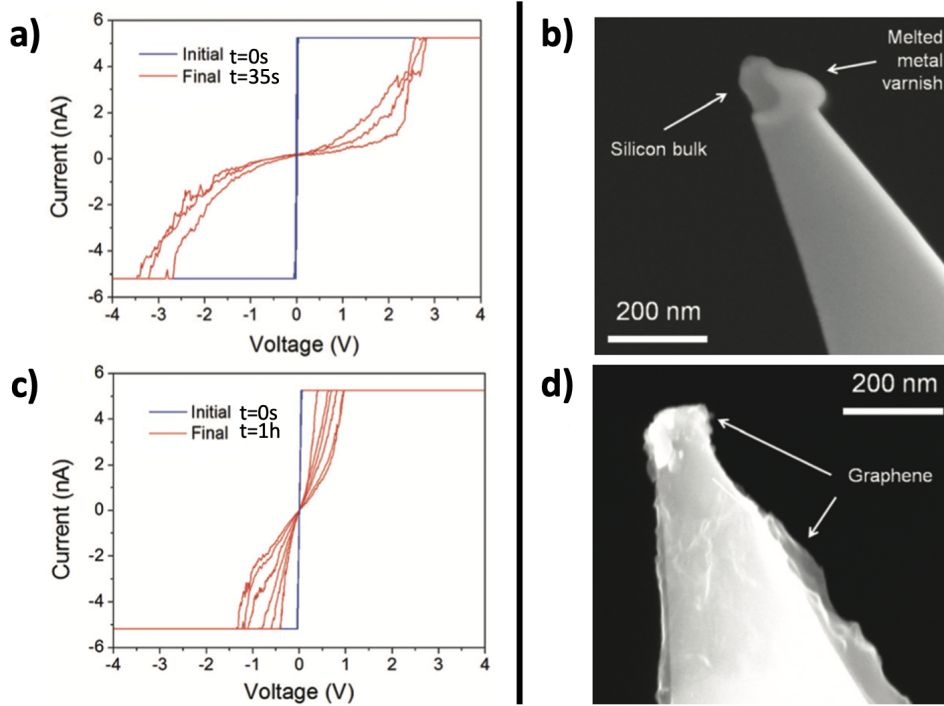


Figure 1.16: a) Durability evaluation of graphene-coated nanoprobe. I–V curves, and SEM images b) acquired with a standard metal-coated nanoprobe. Under identical experimental conditions, Gr-coated tips maintain stable performance even after 92 scans c,d). Adapted from Hui *et al.* [35]

After analyzing the morphology of the tips, their durability was evaluated through C-AFM measurements, including continuous current maps and I–V curves (Figure 1.16). These experiments compared standard Pt-coated nanoprobe against the Gr-coated ones under identical conditions, using a deflection setpoint of 4 V and a bias voltage of 1 V.

Both the electrical measurements and the SEM images reveal significant degradation

in the as-received commercial tips. In these Pt-coated probes, rapid wear is observed after approximately 35 scans, causing the current in the maps to drop to noise levels and causing a severe loss of conductivity in the I–V curves (Figure 1.16a,b). In contrast, the nanoprobe coated with graphene maintain stable currents and high conductivity over extended periods (up to 92 scans or approximately one hour of continuous operation), demonstrating a longer lifetime without morphological degradation (Figure 1.16c,d).

1.4 Objectives and Scope

Based on the previous sections, it is clear that graphene is a great coating material for conductive AFM probes because of its properties. However, current fabrication methods still have some drawbacks.

In the case of direct graphene growth on Au-coated probes, the high temperatures required during the CVD process may induce partial melting and redistribution of the catalytic gold layer, leading to non-uniform graphene growth and poor coating homogeneity at the tip apex [31]. Because the performance of conductive AFM probes is heavily dependent on the quality and structure of the coating, these uneven areas can ruin the accuracy and reproducibility of the data.

While the PMMA-assisted transfer proposed by Lanza *et al.* [32] successfully increases the durability of Gr-coated probes in high-current C-AFM, it complicates the fabrication process. Repetition of the deposition and removal steps of the polymer not only adds complexity but also increases the chances of polymer contamination, mechanical stress, or structural damage during transfer.

Similarly, even with the success of the mold-assisted SU-8 approach in fabricating conductive Gr-coated probes [33], these structures differ substantially from the conventional Si-based AFM probes commonly employed in conductive AFM applications. A major drawback of this method is the resulting large tip radius, which significantly degrades the lateral resolution during topographic mapping.

An alternative approach proposed by Pacios *et al.* [34] involves the direct deposition of uG onto AFM probes. Despite avoiding transfer-related issues, this method yields a multi-layered stack known as ultrathin graphite. Regardless of both being carbon-based materials with the same atomic arrangement, their structural thickness and electronic

properties differ significantly, since graphite exhibits stronger interlayer coupling and a markedly different electronic band structure compared to single-layer graphene [36]

While the solution-processed coating approach proposed by Hui *et al.* [35] successfully avoids polymer contamination and enables large-scale fabrication, it presents some limitations. First, it relies on reduced graphene oxide (rGO) rather than high-quality CVD graphene, resulting in a material with a higher defect density and lower electrical performance. In addition, the quality and uniformity of the coating depend on processing parameters such as the concentration of the suspension, the size of the graphene flakes, and the geometry of the AFM tip, making the coating process more difficult to control and reproduce.

All this highlights the necessity of developing methods capable of transferring high-quality graphene without polymer assistance to preserve electrical paths at the tip apex. That's why our method focuses on transferring graphene directly and evenly using a polymer-free approach. Instead, we grow graphene on copper via CVD and transfer it using a polymer-free wet solution, simply by immersing the silicon tip (using a three-axis hydraulic micromanipulator) onto the graphene suspended over a water-air interface. To achieve this, our main goals are to synthesize the graphene on copper and analyze its defects and layer count using Raman spectroscopy. We then aim to successfully transfer the film and characterize it through SEM, Raman, and optical microscopy to evaluate its viability for electrical AFM modes, such as C-AFM.

EXPERIMENTAL SETUPS AND PROTOCOL

In this chapter, the experimental setup used to carry out the graphene growth process will be discussed, which includes the stages of synthesis, characterization and transfer of the material under investigation.

2.1 Synthesis

The synthesis of graphene refers to the process of manufacturing graphene sheets from base materials. One of the most widely used approaches for graphene synthesis is chemical vapor deposition (CVD). The CVD furnace enables the controlled and uniform deposition of materials onto substrates through chemical reactions of precursor gases. Depending on the process conditions, the resulting products may take the form of thin films, powders, or crystalline structures.

For this CVD process, copper sheets are selected as the substrate for graphene growth. Copper is chosen due to its intrinsic properties, such as its low carbon solubility (~ 7 ppm at 1050°C) and high catalytic activity. Furthermore, copper does not require extensive polishing to achieve adequate surface planarity and allows better control over the number of graphene layers, since methane decomposition is predominantly restricted to the surface [37].

The precursor gases employed in this process are molecular hydrogen (H_2), argon (Ar), and methane (CH_4), with methane serving as the primary carbon source. Methane

is selected over other hydrocarbons due to its simple molecular structure and balanced carbon-to-hydrogen ratio, which facilitates controlled carbon incorporation and promotes the formation of high-quality graphene layers.

2.1.1 Growth, heating and cooling process

A quartz tube is introduced into the furnace, inside which there is a cylindrical copper sheet. At one end of the tube, a copper sheet cover with a hole in the center is placed to allow gas flow within the tube (Figure 2.1).

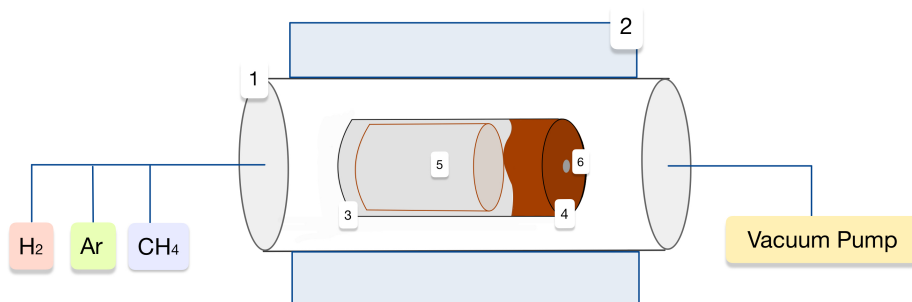


Figure 2.1: Illustration depicting the graphene synthesis configuration via CVD. 1. Main quartz tube, into which the smaller quartz tube is inserted. 2. Furnace. 3. The smaller quartz tube, used for graphene deposition. 4. Copper rear cover, which seals one end of the tube. 5. Cylindrical copper sheet inside the tube. 6. Central hole in the cover that allows the turbulent flow of gases within the tube.

The process is carried out under vacuum conditions at pressures on the order of 0.0075 Torr. Such low-pressure conditions are achieved using a turbomolecular vacuum pump (Pfeiffer Vacuum), which ensures a controlled gaseous environment, minimizes contamination, and promotes uniform graphene growth.

The furnace gradually increases its temperature until reaching 970 °C. During this time an atmosphere of H₂ is introduced to clean and reduce the substrate. The methane then interacts with the hydrogen to facilitate material deposition onto the substrate.

This reaction is described by:



The carbon produced is deposited onto the copper surface, resulting in the formation of graphene layers.

Before removing the sample, it is necessary to cool the system. This ensures that the temperature decreases sufficiently before extracting the Gr-coated copper sample.

If removed at high temperatures under ambient conditions, the sample may undergo oxidation, leading to degradation of both the copper substrate and the graphene layer.

2.2 Characterization: Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a characterization technique that provides detailed information about surface morphology and elemental composition [38]. It enables the analysis of both organic and inorganic materials at the nanometer to micrometer scale [39]. In this work, a Zeiss EVO MA10 scanning electron microscope (Figure 2.2a) was used to evaluate the graphene coating on the nanoprobes, with special focus on the coverage at the tip apex.

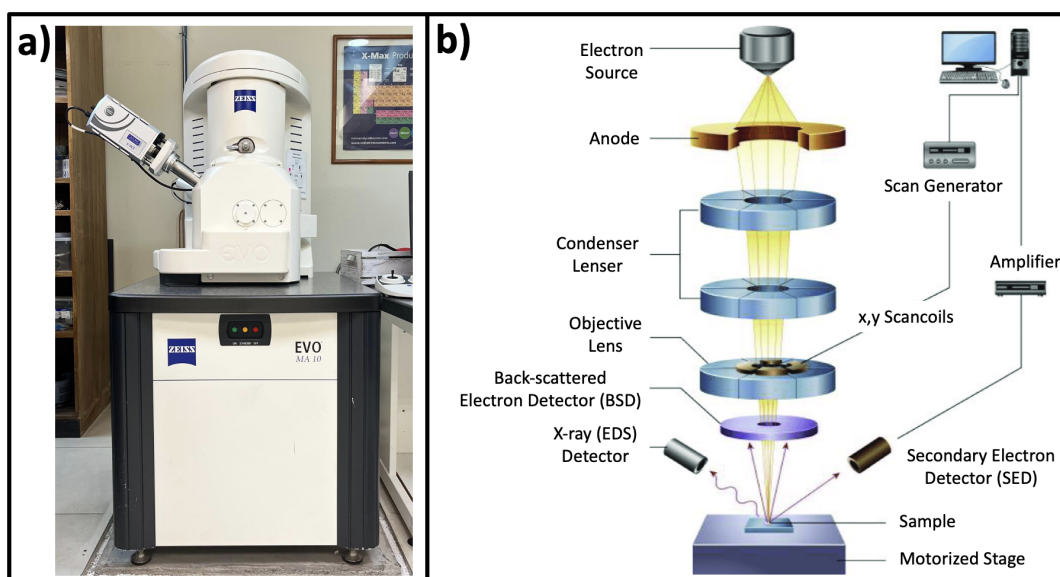


Figure 2.2: a) Scanning electron microscope (Zeiss EVO MA10) used to perform morphological imaging and energy-dispersive X-ray spectroscopy (EDS) analysis of the samples. b) Schematic illustration of the SEM system [40].

The entire measurement process (Figure 2.2b) is performed under vacuum conditions (between 10^{-5} and 10^{-7} Torr) in order to prevent interactions between gas molecules and the electrons emitted from the electron source. These electrons are then accelerated toward the anode due to its positive potential, forming a focused electron beam. Two types of electromagnetic lenses are involved in the beam control. First, the condenser lenses regulate the diameter of the electron beam, which directly influences the resolution of the obtained image. The scan coils then deflect the beam in the x - y plane, allowing a raster scan across the sample surface [41].

The objective lens focuses the electron beam onto a very small spot on the sample surface. When the beam interacts with the sample, different signals are generated. Among the most important are secondary electrons (SE) and backscattered electrons (BSE). Secondary electrons originate from the surface or near-surface regions and are detected by the secondary electron detector (SED); these are mainly used to obtain high-resolution images of the sample's surface topography. On the other hand, BSE are a result of elastic collisions between the beam electrons and the sample atoms, which alters the electrons' trajectory. These are collected by the backscattered electron detector (BSD) and provide compositional contrast, as their intensity directly depends on the atomic number of the elements present in the sample. The detected signals are then processed by an electronic amplifier, which increases their intensity. Finally, the scan generator (Figure 2.2b), together with an external computer, synchronizes the position of the electron beam with this amplified signal intensity at each moment. By correlating the beam coordinates with the detected signal, a grayscale image is reconstructed and displayed in real time on a pixel-by-pixel basis [41].

Energy-dispersive X-ray spectroscopy (EDS) enables the analysis of a sample's chemical composition by detecting the X-rays generated during electron beam irradiation. Specifically, in this work, this technique allows the identification and verification of carbon presence on Gr-coated silicon tips.

2.3 Characterization: Raman Spectroscopy

Raman spectroscopy is a high-resolution photonic technique, known for rapidly providing chemical and structural information. It can be applied to virtually any material or compound, whether organic or inorganic, enabling easy identification. This analytical method relies on studying the light scattered by a material when exposed to a monochromatic light beam [42].

Raman scattering involves an exchange of energy between the incident photon and vibrational modes of the material (phonons) or vibrational states of chemical bonds, resulting in the scattered photon having a different energy from the incident photon. This energy difference is known as the Raman shift [43]. More specifically, the scattered photon may either lose or gain energy through the creation or annihilation of a phonon in the material.

In this study, a Raman spectrometer (inVia, Renishaw) equipped with a monochromatic laser source at a wavelength of 532 nm is used (Figure 2.3a).

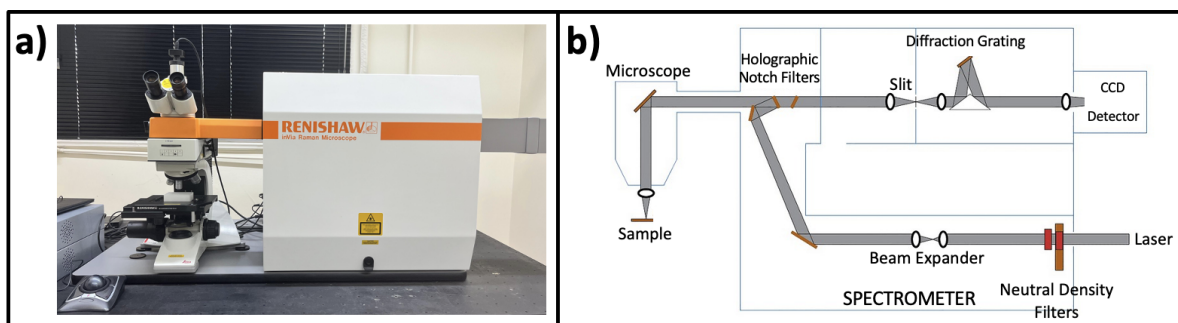


Figure 2.3: a) Raman spectrometer (inVia, Renishaw) used to characterize graphene samples. b) Schematic illustration of a Raman spectrometer [44].

The main components of the Raman spectrometer are schematically illustrated in Figure 2.3b). The system includes a monochromatic laser source whose beam passes through a set of neutral density (ND) filters, which attenuate the laser power to prevent sample damage or detector saturation. The beam is then expanded through a beam expander, an optical device that increases the diameter of the laser beam and reduces its divergence, thereby improving focusing conditions at the sample surface [42]. The laser is directed onto the sample through an optical microscope. The scattered light is collected by the same objective and passes through holographic notch filters, which suppress the intense elastically scattered light (Rayleigh scattering) while transmitting the much weaker inelastically scattered Raman signal [42]. The filtered light then passes through a slit, which controls the amount of scattered light entering the system and defines the spectral resolution [42]. Subsequently, a diffraction grating disperses the Raman-scattered light by angularly separating its different wavelengths in space before they reach the CCD detector, enabling spectral resolution and accurate intensity measurement as a function of wavelength [45]. Finally, the dispersed light is detected by a charge-coupled device (CCD) detector, where the Raman spectrum is recorded.

In the context of graphene, Raman spectroscopy is used to characterize vibration and excitation modes. The peaks observed in the Raman spectrum arise from the inelastic scattering of incident light by electrons and phonons in the structure, Figure 2.4. Raman techniques are particularly useful for graphene because the absence of a bandgap makes all wavelengths of incident radiation resonant. As a result, the Raman spectrum provides information not only about the atomic structure but also electronic properties of graphene [46].

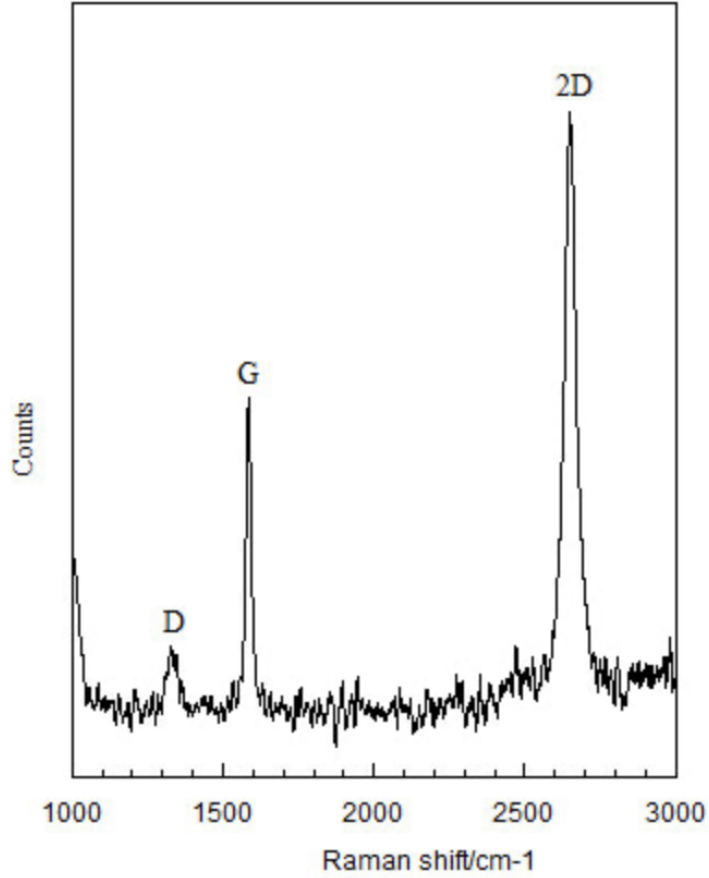


Figure 2.4: Characteristic bands of the Raman spectrum of graphene [47].

The D-peak, known as the defect peak, is located at approximately 1355 cm^{-1} and is associated with structural disorder in graphene, such as point defects, grain boundaries, edges, or chemical functionalization. It corresponds to a breathing mode of A_{1g} symmetry (Figure 2.5) involving phonons near the K point at the edge of the Brillouin zone, which means it is a symmetric vibration where carbon atoms move in and out together. This mode is normally inactive in perfect graphene, but becomes Raman active when defects or edges are present because they break the crystal symmetry and enable the double resonance scattering process. Additionally, the D mode is dispersive, its frequency position depends on the excitation laser energy [43].

The G-peak appears at 1580 cm^{-1} , it reflects the in-plane vibration of carbon atoms bonded in an sp^2 configuration, and originates from a double degenerate optical phonon mode (transverse optical (TO) and longitudinal optical (LO)) with E_{2g} symmetry (Figure 2.5) located at the center of the Brillouin zone [48], this means that this vibrational mode involves symmetrical stretching of carbon-carbon bonds within the plane of the

graphene lattice, where two equivalent phonon modes vibrate perpendicular and parallel to the direction of propagation, preserving the lattice symmetry.

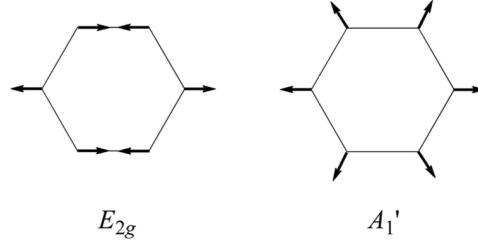


Figure 2.5: Graphite E_{2g} and A_{1g} vibrational modes [49].

The 2D-peak appears at approximately 2670 cm^{-1} [48]. This peak corresponds to the second-order overtone of the D-peak and originates from a two-phonon double-resonance scattering process in which momentum conservation is satisfied by two phonons with opposite wave vectors. Unlike the D-peak, the activation of the 2D-peak does not require the presence of defects, and it is therefore always observed in graphene samples [46]. In addition, because the 2D process is fully resonant, the 2D-peak can exhibit a much higher intensity than the D-peak, especially in high-quality graphene with low defect density. This characteristic makes the 2D-peak a reliable feature for assessing graphene quality, layer number, and stacking order.

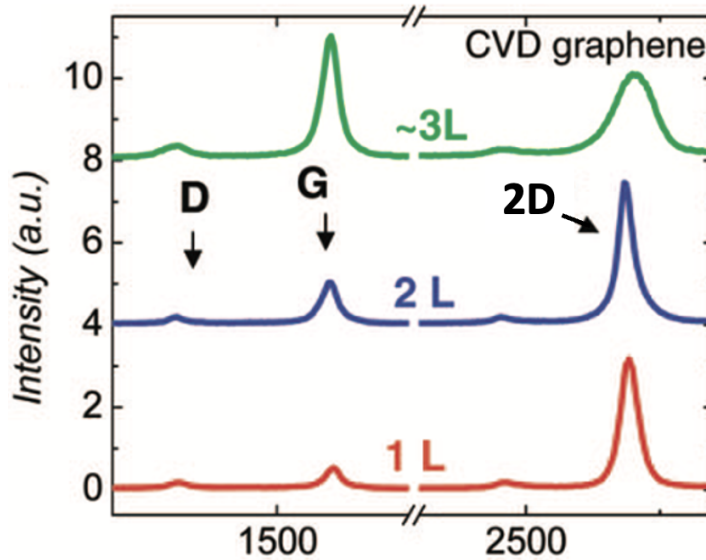


Figure 2.6: Raman spectroscopy of CVD-grown graphene films on SiO_2/Si . Raman spectra of 1 (red), 2 (blue), and ~ 3 (green) graphene layers from a CVD graphene film [50].

It is well-established that the intensity ratio between the 2D and G bands (I_{2D}/I_G) in

Raman spectroscopy serves as a reliable indicator for estimating the number of graphene layers as shown in Figure 2.6. This criterion is generally applicable to graphene synthesized on various substrates. A ratio of $I_{2D}/I_G \sim 2\text{--}3$ is characteristic of monolayer graphene. A ratio in the range of $1 < I_{2D}/I_G < 2$ typically indicates bilayer graphene. Finally, a ratio of $I_{2D}/I_G < 1$ is associated with multilayer graphene (three or more layers) [50–52].

Regarding defects in the lattice, the intensity ratio I_D/I_G is commonly used as a parameter to estimate the degree of graphitization in carbonaceous materials [53]. The evolution of this ratio follows a two-stage behavior: Stage 1, corresponding to low-defect graphene, and Stage 2, corresponding to highly disordered graphene. The transition between Stage 1 and Stage 2 occurs at I_D/I_G values of approximately 3.5 for an excitation energy of 2.41 eV [43], which corresponds to a green laser similar to the one used in the present work.

2.4 Characterization: Optical Microscopy

In order to further analyze the morphology of the nanoprobe, particularly the graphene coverage on the AFM chips, optical microscopy was employed. In this work, a Zeiss Primotech optical microscope was used for this purpose, Figure 2.7a). This technique allows the identification of the coated regions on the chip, which is essential for evaluating their suitability for establishing electrical contacts during C-AFM measurements. Additionally, optical microscopy enables the assessment of the surface uniformity of the sample and the detection of macroscopic defects such as cracks or discontinuities in the graphene layer.

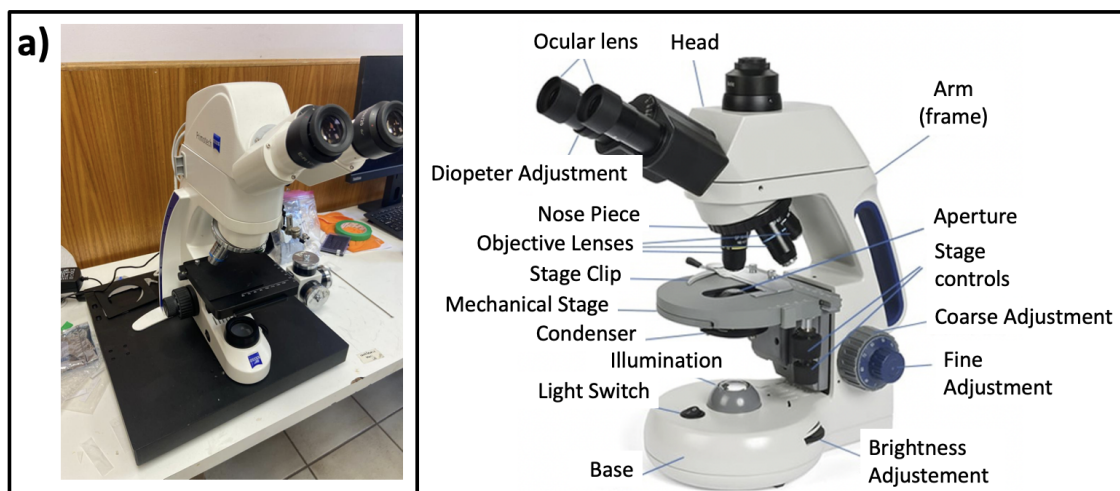


Figure 2.7: a) Optical microscope (Zeiss Primotech) used to analyze de chip of the Gr-coated samples. b) Schematic illustration of optical microscope.

The components of the optical microscope are schematically illustrated in Figure 2.7b).

The sample is placed on the mechanical stage, where it is illuminated by the microscope light source. The image of the sample is then collected by the objective lens, which determines the magnification of the image, and subsequently observed through the eyepiece lenses. Different objective lenses can be selected depending on the desired magnification. The position of the sample relative to the objective lens is adjusted using the coarse adjustment knob, which moves the mechanical stage up and down to obtain an initial focus. For finer and more precise focusing, the fine adjustment knob is used [54].

2.5 Characterization: Conductive Atomic Force Microscopy

To analyze the topography and electrical conductivity of the tips, conductive atomic force microscopy (C-AFM) was employed using a floppy disk as a test sample. The floppy disk consists of Fe_2O_3 particles mixed with carbon black embedded in a polyurethane matrix, providing a well-defined contrast between insulating and conductive regions that is suitable for evaluating the electrical performance of conductive AFM probes. Electrical contact to the AFM sample bias was established using silver paste.

All C-AFM measurements were carried out using a Bruker Dimension Icon system, Figure 2.8. A PPP-EFM Pt/Ir-coated silicon probe by Nano and More was used as a reference, featuring a nominal tip radius of < 25 nm, a resonance frequency of 75 kHz, a force constant of 2.8 N/m, and a length of 225 μm .

All measurements were performed under ambient conditions using a bias voltage of 500 mV. This value was chosen as a standard initial bias, higher voltages can lead to tip degradation or damage due to strong local electric fields (arising from the small tip radius), while lower voltages may result in currents below the detection limit of the system.

The operation of the instrument is described in Section 1.1.1.



Figure 2.8: C-AFM system (Bruker Dimension Icon) used for topography and current measurements [55].

2.6 Graphene Transfer Process

After completing the growth and characterization stages, the graphene transfer process will be carried out using a polymer-free wet solution method. For greater clarity, the steps of the transfer process are illustrated in Figure 2.9.

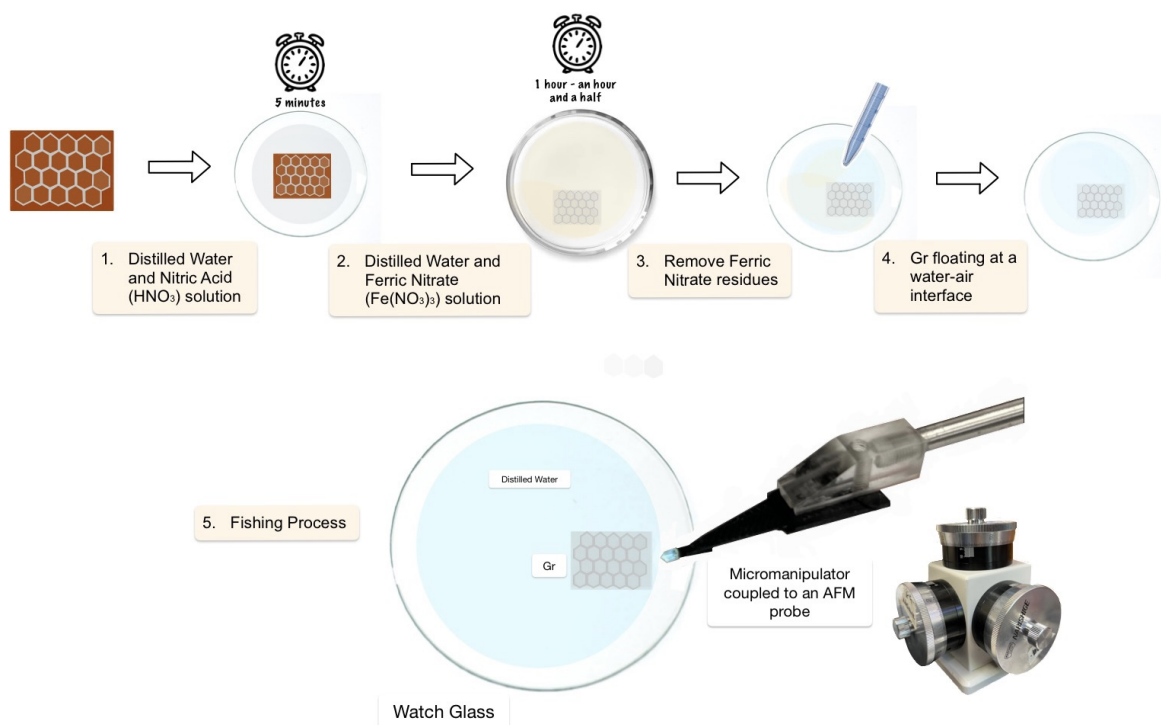


Figure 2.9: Graphene transfer process from a copper catalyst material to a water-air interface.

In the first step, squares of graphene-on-copper samples are cut, each with sides of approximately 3 cm, to facilitate subsequent handling. These squares float in a solution composed of 20 mL of desionized water (H_2O) and 4 mL of nitric acid (HNO_3) at 69-70% concentration, placed in a watch glass for 5 minutes. This homogeneous mixture serves to remove carbon residues that may be present on the backside of the graphene deposited on the copper foil.

Subsequently, the sample is removed and placed in a solution of 50 g of ferric nitrate $\text{Fe}(\text{NO}_3)_3$ in 300 mL of H_2O . This step aims to fully dissolve any remaining copper residues, thereby revealing the graphene film. The sample is kept suspended in the solution for 1 hour, or until no visible copper residue remains.

Next, the sample is transferred to a watch glass containing distilled water. The transfer between solutions is performed manually, by scooping the floating film from below

using a 9 cm diameter watch glass attached to a metallic arm. Using a pipette, ferric nitrate residues are carefully removed and replaced with fresh H_2O , taking extreme care not to damage the integrity of the graphene structure. It is essential to ensure that no visible traces of $\text{Fe}(\text{NO}_3)_3$ remain. Once this final step is completed, a graphene film floating at the water–air interface is obtained.

For the coating process, the PPP-FMR SiO_2 AFM probe or an EFM-10 Pt/Ir-coated silicon probe is mounted on a three-axis hydraulic micromanipulator (Narishige MMO-203), allowing for precise movements when approaching the graphene. Both probes have a resonance frequency of 75 kHz, a force constant of 2.8 N/m and length of 225 μm . The first probe has a tip radius of < 20 nm, and the second probe has a tip radius of < 25 nm. The coating is carried out by carefully immersing the tip into the sample, ensuring gentle and uniform contact. Once immersed, the tip is slowly lifted using the micromanipulator, allowing the graphene to adhere to its surface.

The graphene samples were categorized as "MSF" for the ones that follow the synthesis and transferring process describe previously. In contrast, the samples labeled "MM" were produced using a prolonged annealing process, particularly with respect to the initial hydrogen atmosphere, and an extended cooling stage was also implemented. Additionally, for these samples, an extra step was introduced during the transfer process: prior to reaching the final water–air interface, residual ferric nitrate was removed using an HCl solution.

RESULTS AND ANALYSIS

The results presented in this work include structural and morphological characterization by Raman spectroscopy, SEM, optical microscopy and C-AFM. The samples used correspond to commercially available PPP-FMR silicon probes, originally uncoated at the tip and EFM-10 silicon Pt/Ir coated probes. The synthesized graphene was transferred onto these probes prior to their evaluation using the aforementioned techniques.

3.1 Graphene Sample MSF04

For this process, the MSF04 sample, consisting of a graphene film initially grown on a copper substrate, was selected. Raman spectroscopy was employed to characterize the sample (Figure 3.1) and to evaluate its subsequent transfer onto a silicon PPP-FMR tips (Figure 3.2).

The corresponding Raman spectrum (Figure 3.1a) reveals the absence of the D band, indicating a negligible defect density in the film. The G band is observed at $\sim 1580 \text{ cm}^{-1}$, while the 2D band appears at $\sim 2700 \text{ cm}^{-1}$. At first glance, the G peak exhibits a higher intensity compared to the 2D peak. To obtain a reliable quantification of these parameters, the fluorescence background must be removed, as it artificially raises the baseline, and each peak is fitted with a Lorentzian profile. This procedure enables the accurate determination of peak positions, widths, and intensities. Nevertheless, the fluorescence originating from the copper substrate alters the true intensities of the

intrinsic graphene vibrational modes, thereby distorting their relative ratios. As a result, the I_{2D}/I_G ratio of Gr/Cu can only be regarded as an approximate indicator of the number of graphene layers.

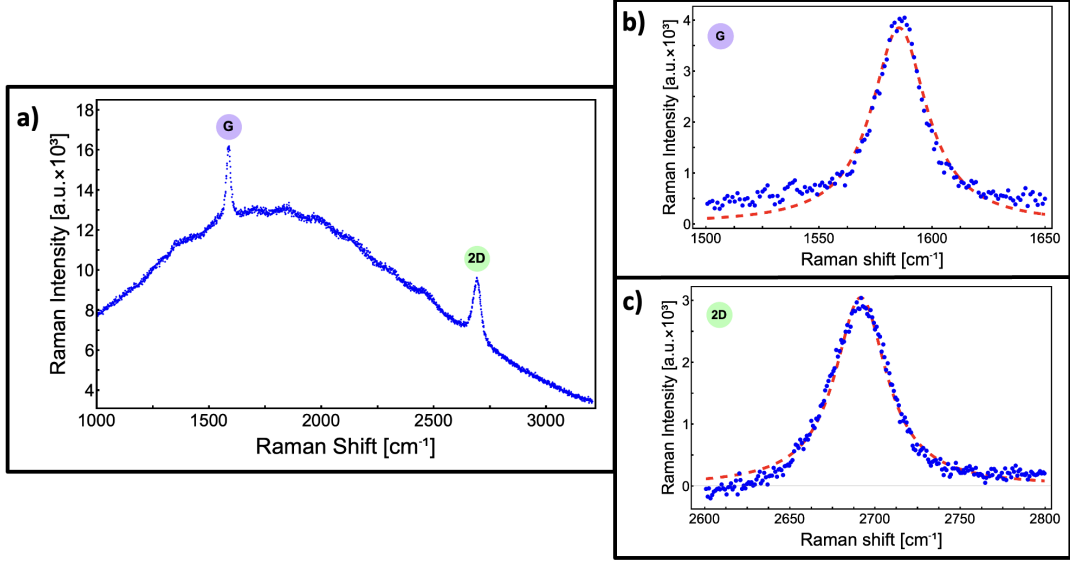


Figure 3.1: a) Raman spectrum of sample MSF04 on Cu. b,c) Lorentzian fit curves for b) G peak and c) 2D peak.

Once the background is removed, the Lorentzian fits applied to the G and 2D peaks of the Raman spectrum shown in Figure 3.1b,c) are obtained. The fits accurately reproduce the symmetric shape of both peaks, with no signs of extra or overlapping peaks, indicating that the graphene film has a good structural quality, this can be attributed to the absence of the D peak in the spectrum.

Table 3.1: Lorentzian fit parameters of the Raman G and 2D peaks of the graphene sample MSF04 on Cu after removing the background.

Peak	Center [cm ⁻¹]	FWHM [cm ⁻¹]	Height [a.u.]
G	1585.32 ± 0.29	29.64 ± 0.84	3853.6 ± 76.5
2D	2691.52 ± 0.20	36.99 ± 0.58	3049.1 ± 33.3

The corresponding fitting parameters are summarized in Table 3.1, where it can be observed that the full width at half maximums (FWHM) are 29.64 ± 0.84 cm⁻¹ for the G peak and 36.99 ± 0.58 cm⁻¹ for the 2D peak. For a monolayer graphene, the literature typically reports a 2D peak FWHM in the range of ~ 25 – 30 cm⁻¹ [51]. In our case we are differing by approximately 7 cm⁻¹ and the 2D is less intense than the G peak, suggesting that the sample does not correspond to monolayer graphene.

To estimate the amount of layers we will use the intensity ratio I_{2D}/I_G method, obtaining $\approx 0.79 \pm 0.02$, value which is consistent with a multilayer graphene [52].

Subsequently the graphene sample is transferred to a Si-based receiver substrate, a PPP-FMR cantilever, using the water–air interface method described in Section 2.6. Several immersion steps were performed during the transfer process. After completing the transfer, the tip was re-examined using Raman spectroscopy in order to verify the quality of the graphene layer.

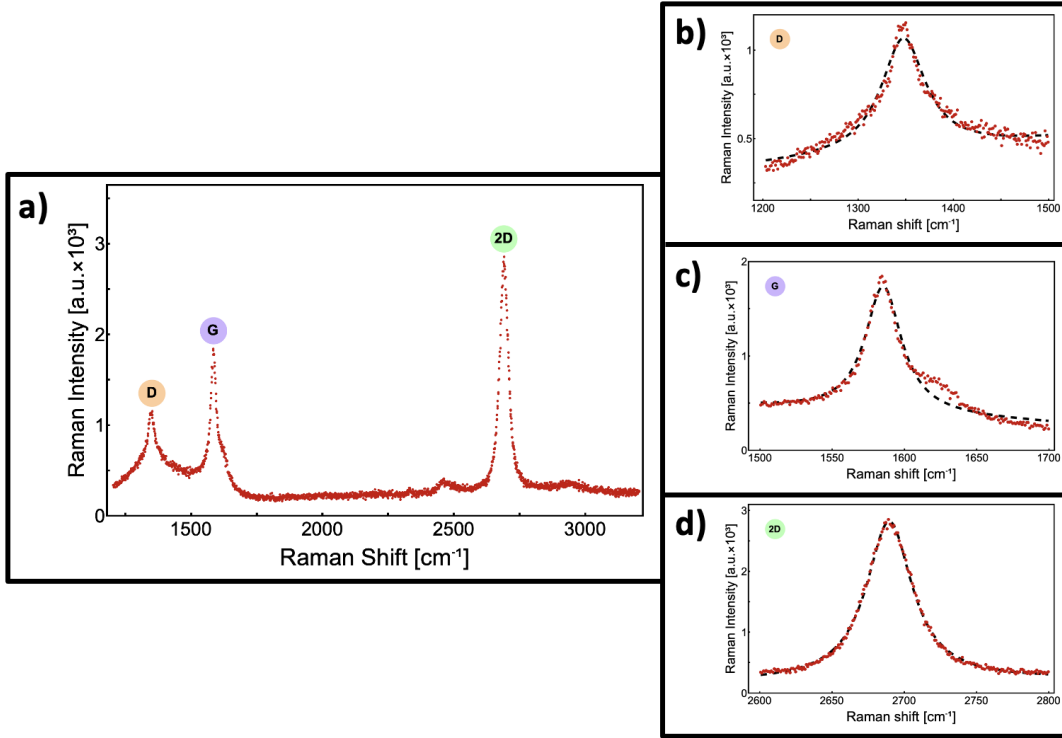


Figure 3.2: Raman spectrum of Gr (sample MSF04) transferred to a PPP-FMR SiO₂ cantilever. b-d) Lorentzian fit curves for b) D peak, c) G peak d) 2D peak.

The successful coating of the AFM tip with graphene is evident in Figure 3.2a). Unlike the spectrum on copper, fluorescence is absent on the SiO₂ substrate, resulting in a flat baseline that allows the graphene Raman bands to be observed clearly. The D and G peaks are visible but do not exhibit symmetric intensities, with the D peak remaining less intense than the G peak; this asymmetry indicates that the sample is not graphene oxide [53]. The appearance of the D peak after the transfer indicates the introduction of defects, likely associated with wrinkles formed during the transfer on the water-air interface.

Additionally, the 2D peak exhibits a higher intensity than the G peak, possible indicating

the presence of a monolayer-bilayer system. For a more precise analysis of each band, Lorentzian fitting of the main peaks will be performed (Figures 3.2b-d).

Table 3.2: Lorentzian fit parameters of the Raman D, G and 2D peaks of the Gr-coated nanoprobe corresponding to sample MSF04.

Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
D	1347.26 ± 0.40	56.89 ± 1.55	643.9 ± 9.0
G	1585.19 ± 0.25	30.72 ± 0.93	1350.1 ± 21.9
2D	2689.46 ± 0.07	38.62 ± 0.29	2619.0 ± 9.9

From Table 3.2, it can be observed that all peaks are positioned within the ranges reported in the literature [51], showing only minimal differences with respect to the reference values. This confirms that the analyzed material corresponds to graphene. On the other hand, it is necessary to further investigate its structural properties. Although the sample does not correspond to graphene oxide, it presents defects that are evidenced by the presence of the D peak (Figure 3.2b), which exhibits an intensity of 643.9 a.u. It should be recalled that this peak becomes active when the contributions from different defects add up independently [46]. These defects may be associated with wrinkle formation during the contact process between the probe and the graphene, which is initially floating at the water–air interface. Additionally, this transfer process may introduce external defects, such as oxygen adsorption. This interpretation is further supported by the broadening of the D band ($\text{FWHM} = 56.89 \text{ cm}^{-1}$) which is larger than the values typically reported for high-quality graphene in the literature [46], and by its intensity ratio with respect to the G band, $I_D/I_G = 0.48 \pm 0.01$, which present low defect degrees, or stage 1 [53].

When analyzing the number of layers in the sample, an intensity ratio of $I_{2D}/I_G = 1.94 \pm 0.03$ is obtained, which is characteristic of bilayer graphene. This assignment is further supported by the broadening of the 2D peak, which exhibits a FWHM larger than 30 cm^{-1} , which is inconsistent with monolayer graphene.

3.2 Graphene Sample MSF06

For the following case, we will use sample MSF06, which again consists of graphene initially synthesized on copper (Figure 3.3). This sample will be characterized after its transfer on the nanoprobe using scanning electron microscopy (SEM), Raman spec-

troscopy, and optical microscopy. Regarding the transfer process, several immersions were done in order to transfer the graphene onto the tip apex.

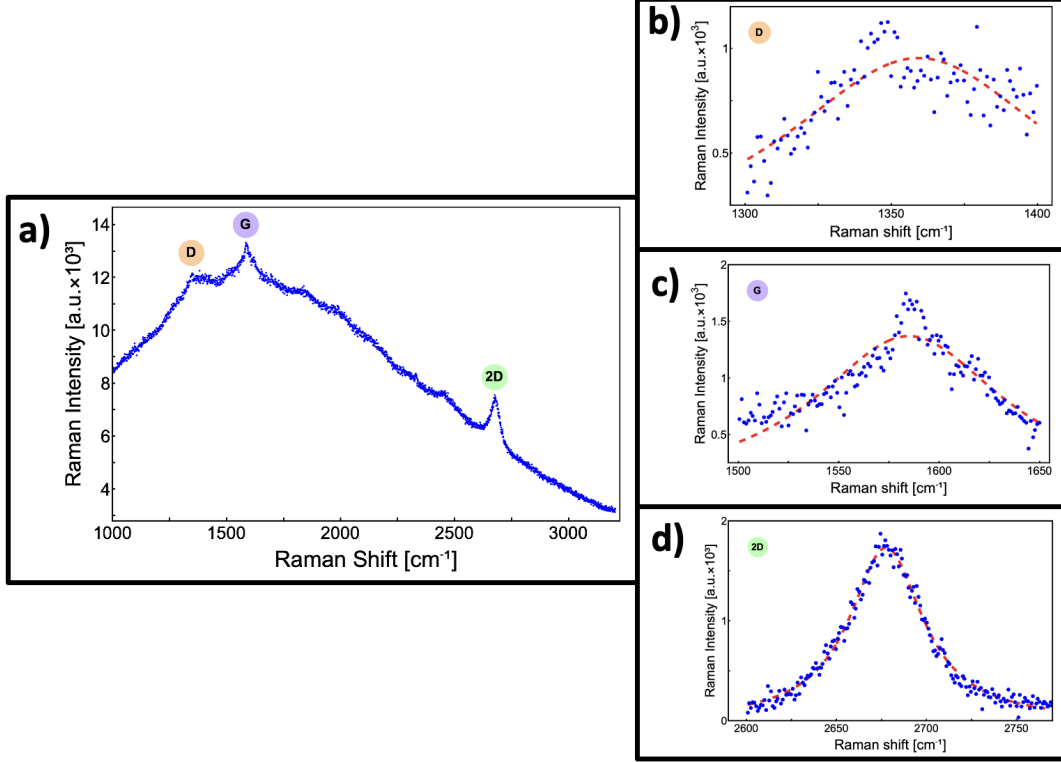


Figure 3.3: a) Raman spectrum of sample MSF06 on Cu. b-d) Lorentzian fit curves for b) D peak, c) G peak and d) 2D peak.

Although the Raman spectrum shown in Figure 3.3a) reveals a higher data dispersion than the previous sample in both the D peak (Figure 3.3b) and the G peak (Figure 3.3c), the coefficient of determination obtained for each fit ($R^2 = 0.98$) indicates that the Lorentzian model appropriately describes the spectral features. The presence of defects is not inferred from the fitting quality but rather from the presence of the D band. In particular, the appearance of the D peak intensity suggests the presence of structural defects and possible strain fluctuations in the graphene lattice.

Table 3.3: Lorentzian fit parameters of the Raman D, G and 2D peaks of the graphene sample MSF06 on Cu after removing the background.

Peak	Center [cm ⁻¹]	FWHM [cm ⁻¹]	Height [a.u.]
D	1359.29 ± 1.48	115.44 ± 7.16	954.70 ± 21.10
G	1584.78 ± 1.04	115.56 ± 4.03	1371.1 ± 24.4
2D	2677.45 ± 0.26	49.50 ± 0.76	1735.9 ± 18.3

The intensity ratio $I_D/I_G = 0.70 \pm 0.02$ indicates that the graphene remains within stage 1 but with a higher defect density compared to sample MSF04. Additionally, the large FWHM values of the D and G bands ($\sim 115 \text{ cm}^{-1}$) suggest significant structural disorder, likely associated with polycrystalline graphene domains or lattice defects.

Regarding the number of layers, the ratio $I_{2D}/I_G = 1.27 \pm 0.03$ indicates that the material corresponds to bilayer graphene. After confirming the presence of defective yet still crystalline graphene, the material was transferred onto the nanoprobe, followed by an initial structural characterization based on SEM imaging (Figure 3.4).

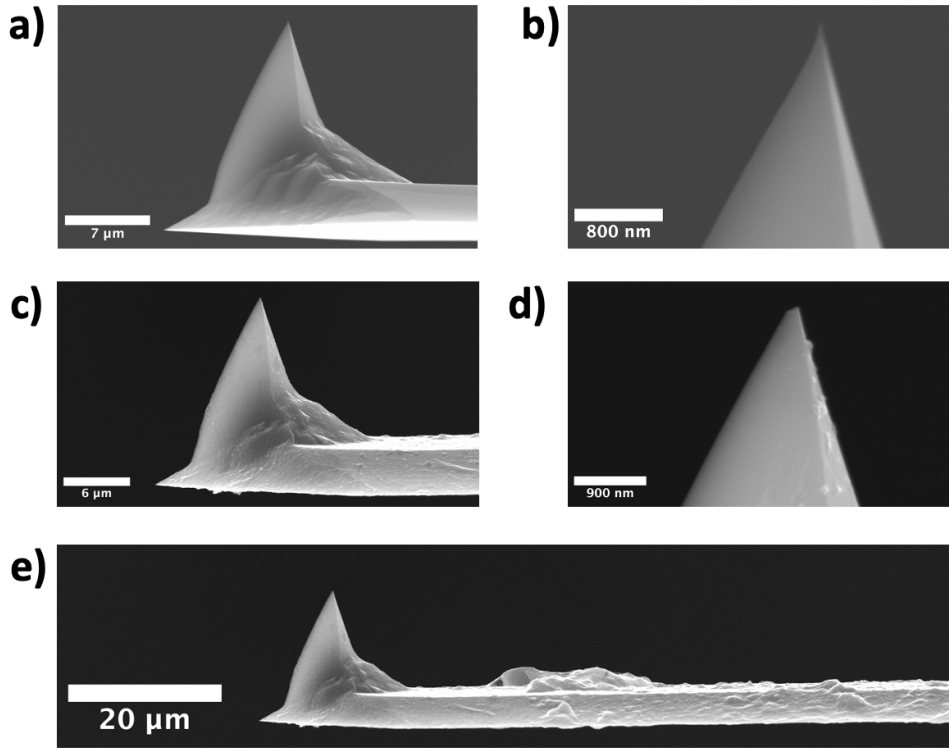


Figure 3.4: SEM images of the Gr-coated nanoprobe corresponding to sample MSF06. a) Lateral view of an uncoated silicon tip (magnification of 7.00 kX.) b) Magnified view (50.00 kX) of the apex of the uncoated tip. c) Lateral view of the silicon Gr-coated (MSF06) tip after the transfer process (magnification of 7.00 kX). d) Magnified view (50.00 kX) of the coated tip apex. e) Side view of both the tip and the cantilever coated (magnification of 2.00 kX). All images were acquired using an EHT of 25.00 kV.

In Figure 3.4a), an uncoated silicon tip is shown, which is used as a reference to analyze the initial morphology of the nanoprobe prior to the transfer process. After the graphene transfer, characteristic wrinkles and an increase in surface roughness covering

the tip are observed (Figure 3.4c), which were not present in the original tip. Although the coating extends over the entire probe, it is not uniform. When the field of view is increased, the cantilever (Figure 3.4e) is also observed to be coated; however, it exhibits larger and inhomogeneous agglomerations of carbon material. These agglomerations may modify the elastic constant of the probe, leading to a reduction in its resonance frequency, and alter its mechanical response. The agglomerations can be attributed to mechanical stresses or local accumulation of the material associated with the use of a water–air interface during the transfer process.

Focusing on the tip apex (Figure 3.4d), a reduction in sharpness is observed compared to the uncoated tip (Figure 3.4b), suggesting an increase in the effective tip radius. To quantitatively analyze this morphological feature, the software *ImageJ* was employed, yielding an apex radius of curvature of approximately 89.9 nm. This increase in radius, compared to the original value (17.17 nm), implies a potential reduction in lateral resolution in topographic AFM modes; however, it does not directly affect the ability to perform conductivity measurements using C-AFM, which may even benefit from an increased contact area between the tip and the substrate [33].

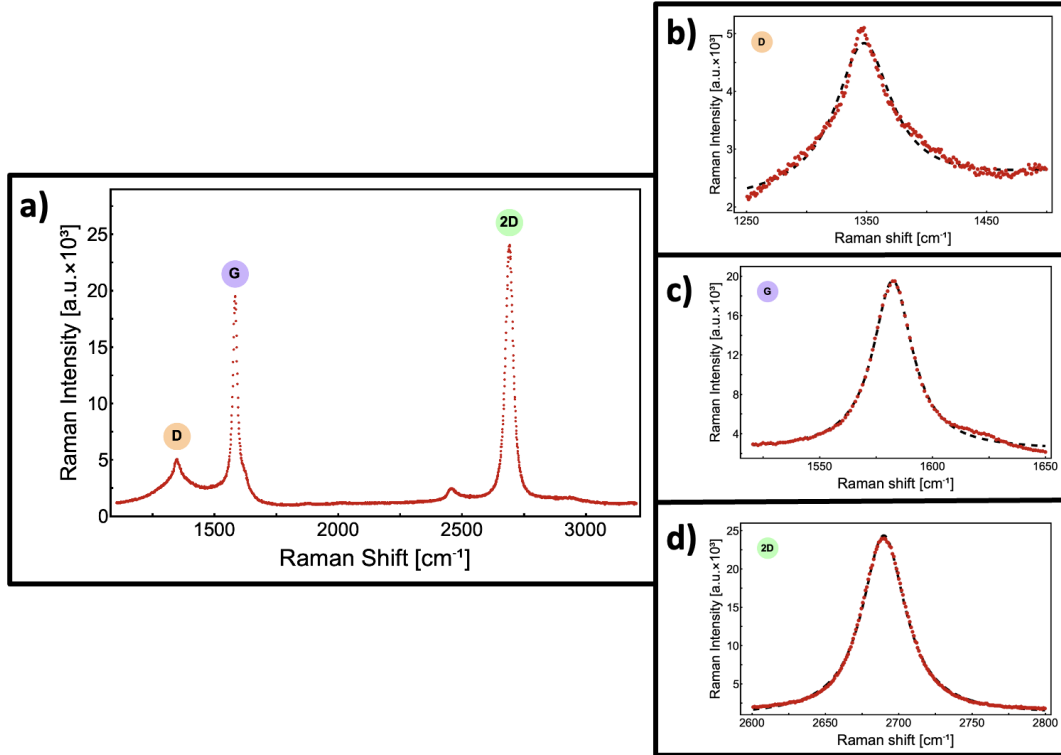


Figure 3.5: Raman spectrum of Gr (sample MSF06) on a PPP-FMR SiO₂ cantilever. b-d) Lorentzian fit curves for b) D peak, c) G peak and d) 2D peak.

Once the morphological characteristics of the Gr coating have been established by SEM, Raman spectroscopy is employed to further assess its structural composition.

From Figure 3.5, the characteristic graphene peaks can be observed on the silicon tip. The relatively low intensity of the D band compared to the G and 2D bands indicates a limited concentration of structural defects. Such defects are expected as a consequence of the transfer process.

Table 3.4: Lorentzian fit parameters of the Raman D, G and 2D peaks of the Gr-coated nanoprobe corresponding to sample MSF06.

Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
D	1347.42 ± 0.28	56.70 ± 1.17	2538.2 ± 25.3
G	1582.27 ± 0.06	21.22 ± 0.22	17204.4 ± 95.1
2D	2689.62 ± 0.04	35.78 ± 0.16	23517.2 ± 55.5

Although the presence of defects is supported by the relatively broad D peak (FWHM $\sim 56 \text{ cm}^{-1}$), the intensity ratio $I_D/I_G = 0.15$ indicates a very low defect density within the graphene lattice and remains in stage 1.

On the other hand, the 2D peak is more prominent than the G peak, ruling out the presence of thick multilayer graphene. The intensity ratio $I_{2D}/I_G = 1.37 \pm 0.01$ indicates a bilayer graphene at the apex of the silicon nanoprobe.

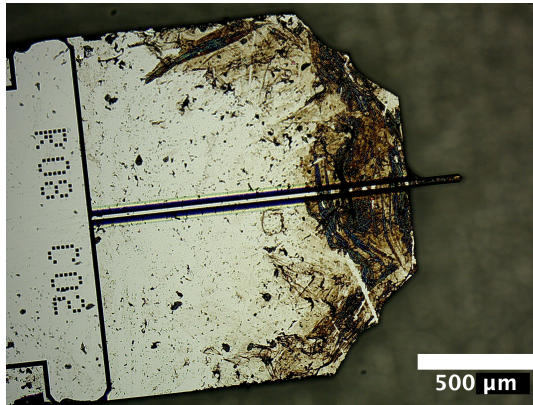


Figure 3.6: Optical microscope image of the back of the nanoprobe using sample MSF06 at $5\times$ magnification, revealing regions of graphene on the chip.

Optical images allow assessment of the nanoprobe chip coverage, which is critical to ensure electrical conductivity during via C-AFM. In Figure 3.6, the coating is confined to the top of the chip and is not uniform enough to form a conductive path for C-AFM.

3.3 Graphene Sample MSF14

In this section three transfer processes were performed using the graphene sample designated as MSF14. Initially, the graphene synthesized on copper was analyzed (Figure 3.7). Subsequently, three independent transfers (done with several immersions) were carried out, each onto a different uncoated PPP-FMR silicon nanoprobe. The resulting Gr-coated probes were then characterized by scanning electron microscopy (SEM), Raman spectroscopy, optical microscopy and C-AFM.

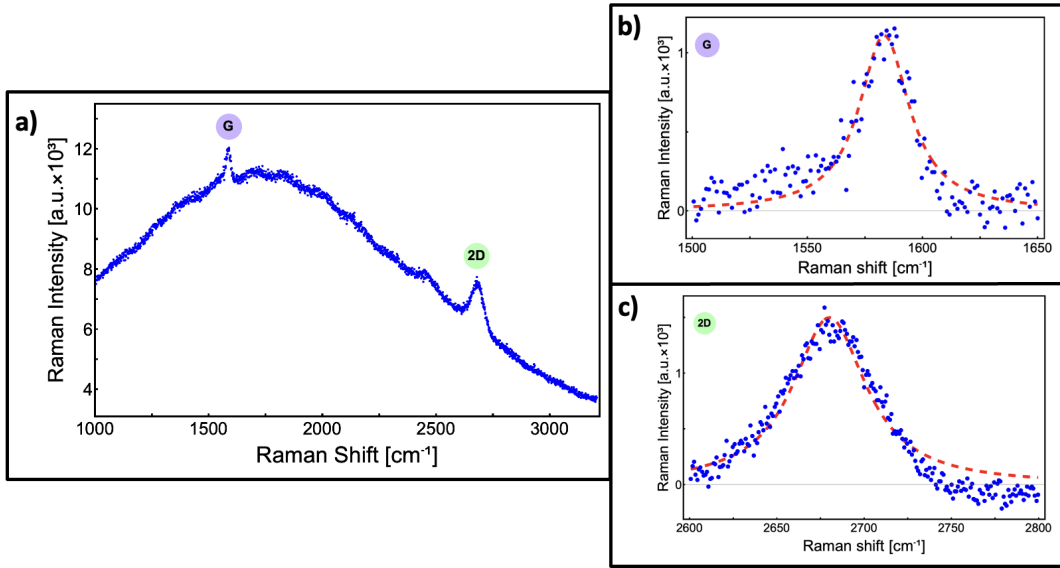


Figure 3.7: a) Raman spectrum of sample MSF14 on Cu. b,c) Lorentzian fit curves for G peak (b) and 2D peak (c).

Based on Figure 3.7a), the presence of graphene on copper is confirmed by the characteristic peaks observed in the Raman spectrum, the G band at $\sim 1580 \text{ cm}^{-1}$ and the 2D band $\sim 2700 \text{ cm}^{-1}$. In addition, the absence of the D band indicates that the sample has a low density of structural defects.

From Figure 3.7a), the sample does not exhibit evident defects. The higher intensity of the 2D peak relative to the G peak suggests that the sample corresponds approximately to monolayer or bilayer graphene. To confirm this interpretation, the Lorentzian fits of each peak are analyzed (Figures 3.7b,c).

Table 3.5: Lorentzian fit parameters of the Raman G and 2D peaks of the graphene sample MSF14 on Cu after removing the background.

Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
G	1583.24 ± 0.44	25.58 ± 1.26	1111.2 ± 37.0
2D	2679.97 ± 0.49	51.09 ± 1.44	1499.3 ± 29.1

The value FWHM $\sim 51 \text{ cm}^{-1}$ for the 2D peak is consistent with the presence of bilayer graphene. Likewise, the ratio $I_{2D}/I_G = 1.35 \pm 0.05$ supports this interpretation, indicating that the obtained graphene corresponds to a bilayer.

Once the presence of graphene was confirmed, the copper substrate was chemically etched, allowing the bilayer graphene film to remain suspended at the water–air interface. When the graphene is left over this interface, the silicon tips were individually submerged, enabling them to become fully coated.

The morphology of the tips was analyzed by scanning electron microscopy (SEM). Figure 3.8 presents a comparison between the three coated samples and an uncoated silicon tip (as-received SiO_2 tips).

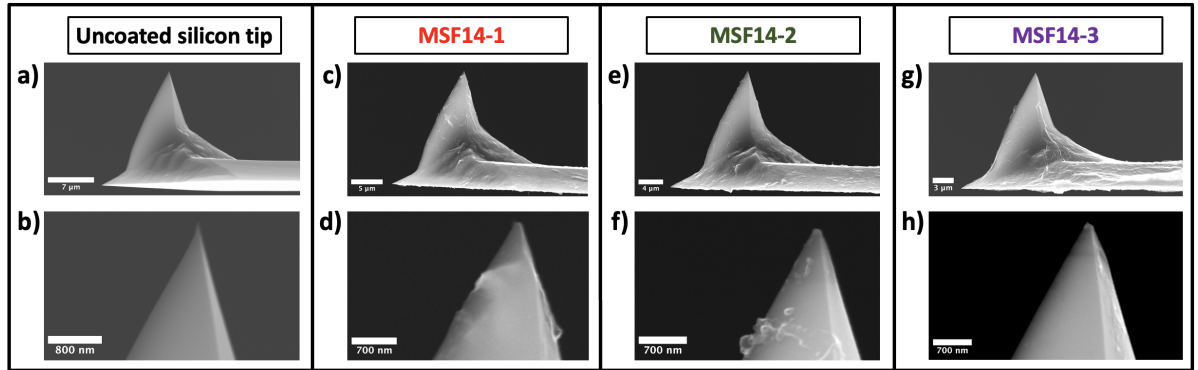


Figure 3.8: SEM images of the Gr-coated nanoprobe tips corresponding to sample MSF14. a) Lateral view of an uncoated silicon tip (magnification of 7.00 kX.) b) Magnified view (50.00 kX) of the apex of the uncoated tip. c,e,g) Lateral views of the Gr-coated samples MSF14–1, MSF14–2, and MSF14–3, respectively (magnification of 7.00 kX.). d,f,h) Magnified views (50.00 kX) of the apex of the Gr-coated tips corresponding to samples MSF14–1, MSF14–2, and MSF14–3. All images were acquired using an EHT of 25.00 kV.

From Figure 3.8, it can be observed that the three tips exhibit a graphene coating with increased roughness on both the cantilever and the apex. In the latter region, a slight flattening is observed compared to the uncoated silicon tip (Figures 3.8a,b), which may be attributed to the successive immersions at the water–air interface. For these

samples, more than two immersion steps were performed, which could have influenced the modification of the apex radius.

Furthermore, for the first two tips (Figures 3.8c,d,e,f), the coating is not completely uniform, and graphene agglomerations can be observed. In contrast, the third tip (Figure 3.8h) does not exhibit this behavior, showing a more homogeneous coating at the tip.

Using *ImageJ* once again, the apex radius was determined for each sample. For MSF14–1 (Figure 3.8d), the radius is 74.08 nm; for MSF14–2 (Figure 3.8f), 73.58 nm; and for the third tip, MSF14–3, a radius of 79.26 nm was obtained. Although the obtained values are relatively high and may affect the lateral resolution of the topographic images, it is important to note that, as long as the electrical contact remains stable and reproducible, small variations in the radius do not significantly alter the analysis of the C-AFM measurements.

Following the SEM confirmation of the graphene coating on the tips, Raman spectroscopy was performed to further characterize each sample (Figure 3.9 and Figure 3.10).

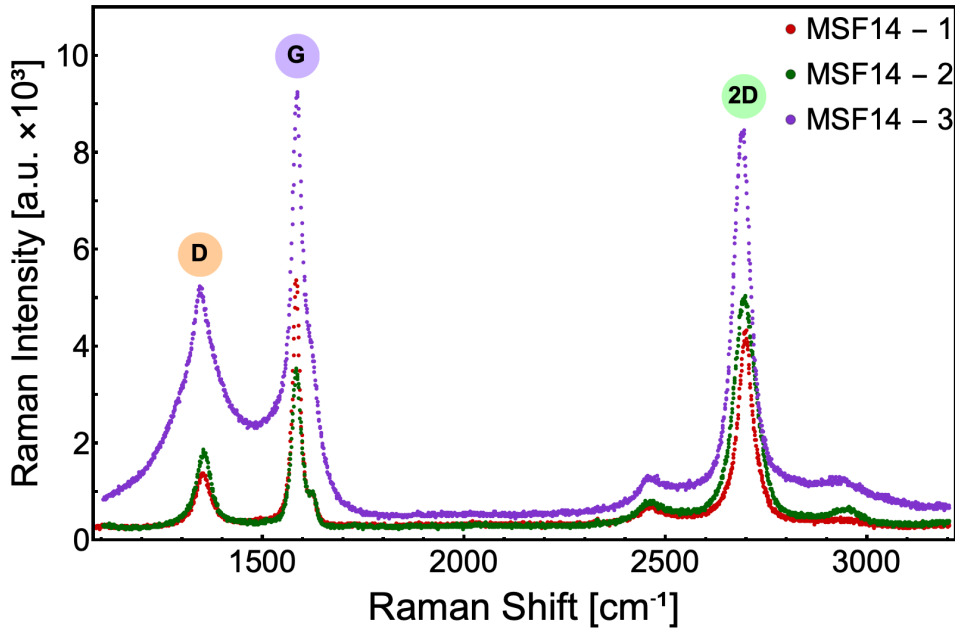


Figure 3.9: Raman spectrum of Gr (samples MSF14–1,2,3) transferred to a PPP-FMR SiO₂ cantilever.

The Raman spectra of the first two tips are nearly identical (Figure 3.9). Although

slight differences in peak intensities are observed, the spectral positions remain unchanged. In the case of sample MSF14–2, the 2D peak exhibits a higher intensity than the G peak, which rules out the presence of multilayer graphene and suggests a behavior characteristic of monolayer or bilayer graphene.

In contrast, for samples MSF14–1 and MSF14–3, the 2D peak is less intense than the G peak, indicating the presence of multilayer graphene. Additionally, in the third sample, a broadening of the D peak is observed, suggesting an increased level of structural disorder. This increase in defect density may be associated with mechanical strain induced during the transfer process, the formation of grain boundaries, or potential oxidation of the material. The possibility that the three samples correspond to graphene oxide can be ruled out due to the pronounced presence of the 2D peaks; however, the broadening of the Raman bands (D and G) in sample MSF14–3 may be associated with the presence of OH bonds introduced during the transfer process.

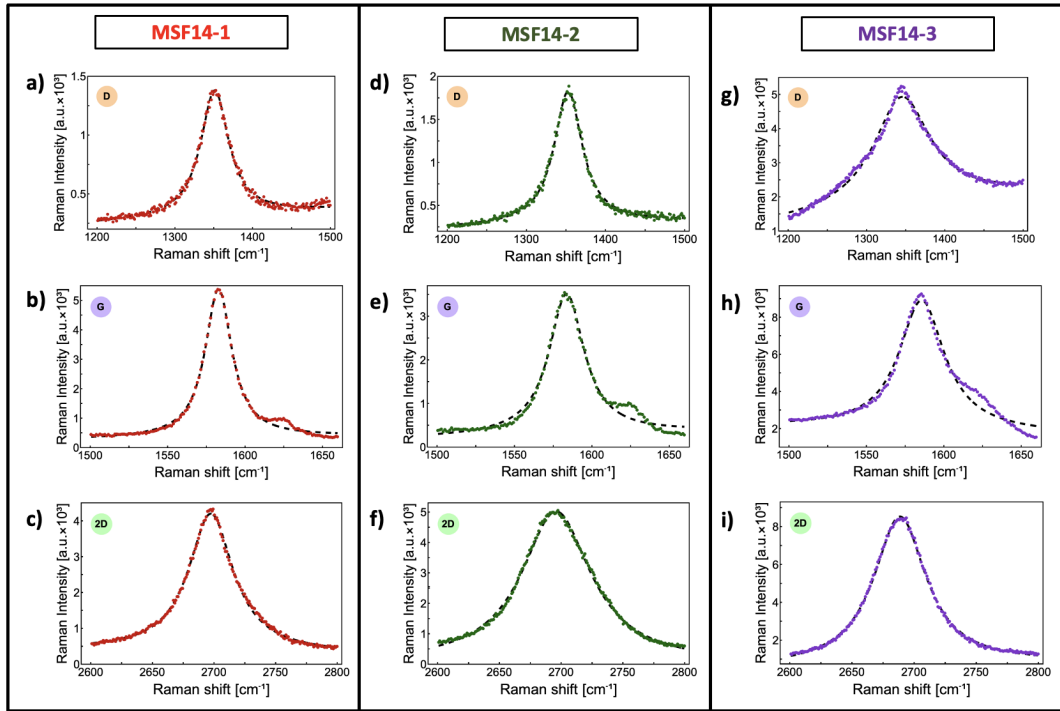


Figure 3.10: Lorentzian fits of the Raman spectra of graphene (samples MSF14–1, MSF14–2, and MSF14–3) transferred to a PPP-FMR SiO₂ cantilever. Figures a,d,g) show the Lorentzian fits of the D peak; b,e,h) correspond to the G peak; and c,f,i) to the 2D peak.

In order to analyze in greater detail the defects and the number of layers associated

with each peak, we performed a Lorentzian fit for each of the spectra (Figure 3.10). The fitted peaks are similar among the three samples, with the exception of the D peak in the third sample (Figure 3.10g). A more detailed analysis reveals the presence of a small peak adjacent to the G peak in all three, Figures 3.10b,e,h). This feature corresponds to the D' peak, which originates from an intravalley scattering process ($K \rightarrow K$) [56]. The D' peak is activated by structural defects, which provide the necessary momentum to conserve total momentum during the Raman process, allowing the observation of this vibrational mode at approximately 1620cm^{-1} . Its presence indicates the existence of local-scale disorder, implying that the graphene crystalline lattice is not perfectly ideal [56].

On the other hand, the D peak originates from an intervalley scattering process ($K \rightarrow K'$) [56], in which the electron is scattered between two distinct valleys of the reciprocal space.

Figure 3.10 shows the Lorentzian fits of the Raman spectra of the MSF14 graphene sample on the silicon probe. The extracted parameters are summarized in Table 3.6.

Table 3.6: Lorentzian fit parameters of the Raman D, G and 2D peaks of the Gr-coated nanoprobe corresponding to sample MSF14.

MSF14-1			
Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
D	1350.93 ± 0.13	43.67 ± 0.46	1071.31 ± 6.30
G	1582.70 ± 0.07	20.94 ± 0.26	5042.07 ± 35.4
2D	2697.26 ± 0.08	44.26 ± 0.32	3852.30 ± 13.8
MSF14-2			
Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
D	1352.48 ± 0.11	43.38 ± 0.40	1545.93 ± 7.81
G	1583.53 ± 0.17	27.71 ± 0.62	3220.47 ± 38.3
2D	2695.73 ± 0.12	68.14 ± 0.57	4983.75 ± 19.2
MSF14-3			
Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
D	1344.89 ± 0.29	89.45 ± 1.29	3244.93 ± 21.56
G	1585.58 ± 0.25	35.54 ± 1.00	6992.01 ± 95.87
2D	2688.38 ± 0.06	51.17 ± 0.27	7859.59 ± 19.37

From these results, it can be observed that all three measurements show the presence of structural defects in the graphene lattice, as evidenced by the intensity of the D peaks (Figures 3.10a,d,g). The widths varies significantly between measurements, with

FMHW increasing from $\sim 43 \text{ cm}^{-1}$ for MSF14–1 and MSF14–2 to $\sim 89 \text{ cm}^{-1}$ for MSF14–3, suggesting a higher level of disorder and oxygenation at this location.

For the three samples, a D' peak is observed on the left side of the G peak (Figures 3.10b,e,h), located around 1625 cm^{-1} . The presence of this peak is typically associated, as said before, with defect-activated intravalley scattering and may originate from strain, grain boundaries, impurities, among other structural imperfections in the graphene lattice. The observed variation in the FMHW of peaks G, ranging from ~ 21 to $\sim 36 \text{ cm}^{-1}$, may be related to local variations in strain or charge doping induced by the silicon substrate.

For the 2D band (Figures 3.10c,f,i), the widths ranges from ~ 44 to $\sim 68 \text{ cm}^{-1}$, with the largest value observed for MSF14–2. This suggests that the samples do not correspond to monolayer graphene.

Table 3.7: Intensity ratio values for each of the MSF14 samples.

Sample	I_D/I_G	I_{2D}/I_G
MSF14–1	0.21	0.76
MSF14–2	0.48	1.55
MSF14–3	0.46	1.12

From the intensity ratios reported in Table 3.7, it can be inferred that the three samples are in stage 1 of disorder and correspond to multilayer graphene for MSF14–1 and bilayer graphene for samples MSF14–2 and MSF14–3.

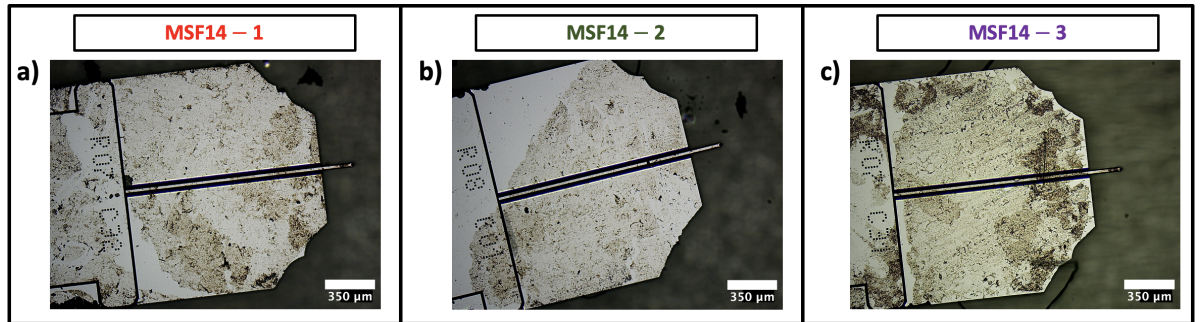


Figure 3.11: Optical microscope images of the back of the nanoprobe chips, MSF14–1, MSF14–2 and MSF14–3 respectively at $5\times$ magnification, revealing regions of graphene on the chips

The nanoprobe chips do not present a homogeneous coating, as seen in Figures 3.11a,c). There are regions with a higher concentration of carbon material. However, the coating extends over the entire chip, making these samples suitable for generating contacts for

conductivity measurements. On the other hand, the chip of sample MSF14–2 (Figure 3.11b) presents a region without graphene coverage; nevertheless, the coated area is sufficient to establish electrical contacts.

Conductive atomic force microscopy was used to acquire topography and current maps, providing information on the spatial distribution of conductivity. Both maps were obtained using the MSF14–1 tip.

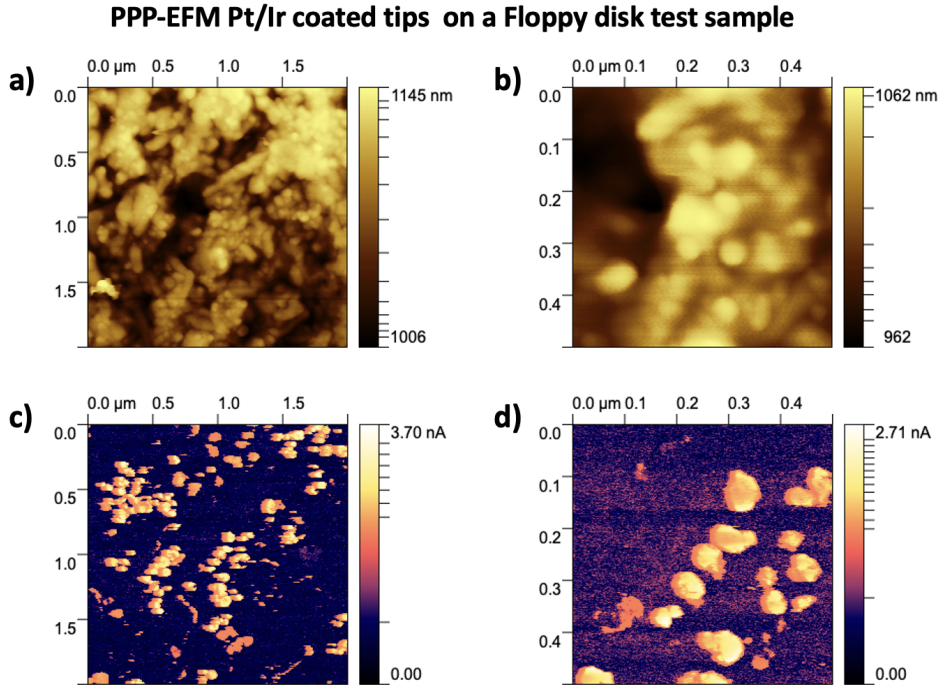


Figure 3.12: Topography images and current maps obtained by C-AFM using a reference PPP-EFM tip coated with Pt/Ir on a floppy disk test sample. a,b) Topography images and (c,d) current maps acquired at an applied bias of 500 mV. The scanned areas correspond to $2 \mu\text{m} \times 2 \mu\text{m}$ for a,c) and $0.5 \mu\text{m} \times 0.5 \mu\text{m}$ for b,d), respectively. The color scale in the topography images represents height (nm), while in the current maps it represents the measured current (nA).

To establish a reference for comparison for C-AFM, a PPP-EFM tip coated with Pt/Ir, with a radius of $\sim 25 \text{ nm}$, was used on a floppy disk at a bias of 500 mV (Figure 3.12). The topography image reveals a granular surface morphology with a relatively homogeneous distribution of domains (Figure 3.12a), which is consistent with the nature of the floppy disk, whose layer is composed of magnetic nano-particles dispersed within a matrix.

In the magnified image (Figure 3.12b), corresponding to an area of $\sim 0.5 \mu\text{m} \times 0.5 \mu\text{m}$, the surface morphology can be observed more clearly, revealing well-defined grains with

sizes on the order of nanometers.

Regarding the electrical response, the current maps (Figures 3.12c,d) show a heterogeneous distribution of conductivity, with localized regions of relatively high current, 0–3.70 nA, while other areas remain close to the noise level. The presence of conductive pathways in the sample is evidenced in the nA range.

Topography and conductivity measurements of the sample, performed by C-AFM using a Gr-coated MSF14–1 tip, are presented in the following images, Figure 3.13.

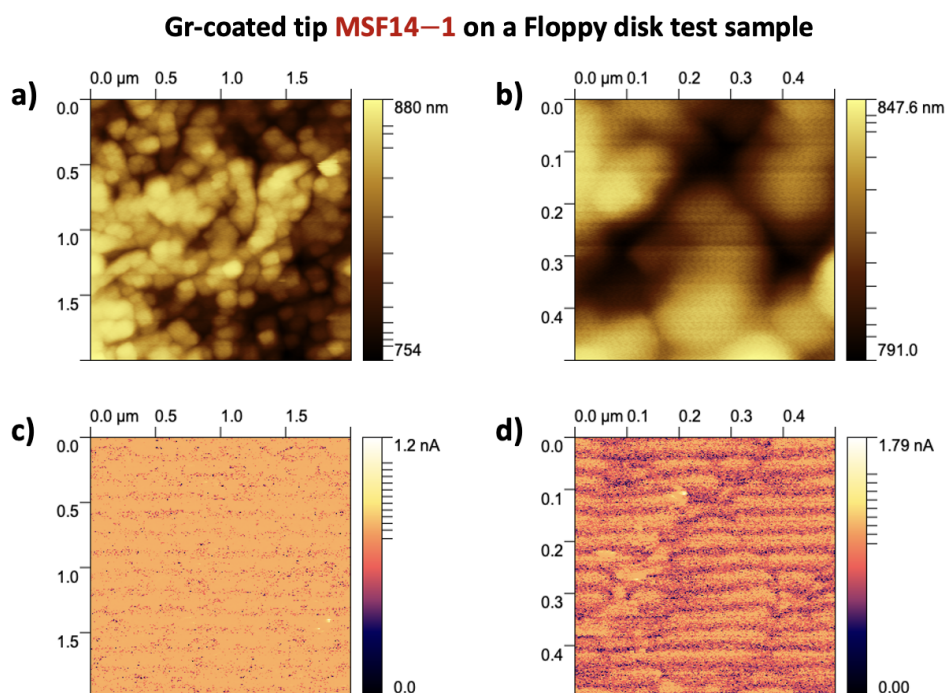


Figure 3.13: Topography images and current maps obtained by C-AFM using sample MSF14–1 on a floppy disk test sample. a,b) Topography images and c,d) current maps acquired at an applied bias of 500 mV. The scanned areas correspond to $2\ \mu\text{m} \times 2\ \mu\text{m}$ for a,c) and $0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$ for b,d), respectively. The color scale in the topography images represents height (nm), while in the current maps it represents the measured current (nA).

From the topography images, it is consistent to state that the tip resolution remains comparable to the Pt/Ir-coated silicon tip, as the granular surface structures can be clearly observed. Regarding the conductivity measurements (Figures c,d), we observe a significant level of noise. This behavior is also observed in the magnified current map (Figures 3.13d). Overall, these results indicate that the MSF14–1 tip doesn't exhibit conductivity properties.

3.4 Graphene Sample MM1

The graphene probe MM1 was fabricated using a PPP-FMR silicon probe by transferring graphene through a single immersion of the probe into the graphene film and was characterized using all the previously described methods. The morphological features were examined by SEM and optical microscopy. The structural quality and defect density were evaluated by Raman spectroscopy. Finally, the electrical conductivity of the sample was measured by C-AFM.

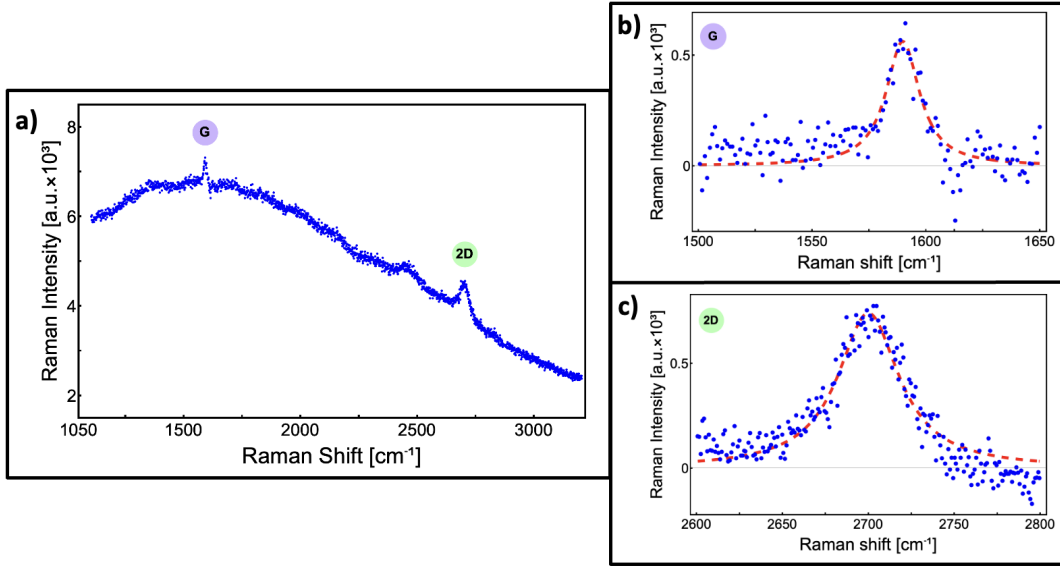


Figure 3.14: a) Raman spectrum of sample MM1 on Cu. Lorentzian fit curves for b) G peak and c) 2D peak.

The MM1 sample synthesized on copper (Figure 3.14a) does not exhibit a noticeable D band, indicating a low density of structural defects in the graphene lattice. Furthermore, the characteristic G and 2D bands display comparable intensities, which suggests the possible presence of bilayer or multilayer graphene.

Table 3.8: Lorentzian fit parameters of the Raman G and 2D peaks of the graphene sample MM1 on Cu after removing the background.

Peak	Center [cm ⁻¹]	FWHM [cm ⁻¹]	Height [a.u.]
G	1589.74 ± 0.53	17.89 ± 1.49	526.57 ± 33.13
2D	2699.90 ± 0.54	43.35 ± 1.55	740.06 ± 18.43

Once the Lorentzian fits for each peak were established (Table 3.8), an intensity ratio of $I_{2D}/I_G \sim 1.41 \pm 0.10$ was obtained, which is consistent with bilayer graphene with a

low defect density.

Subsequently, the transfer process is carried out.

Then, the morphology of the sample was analyzed by SEM (Figure 3.15).

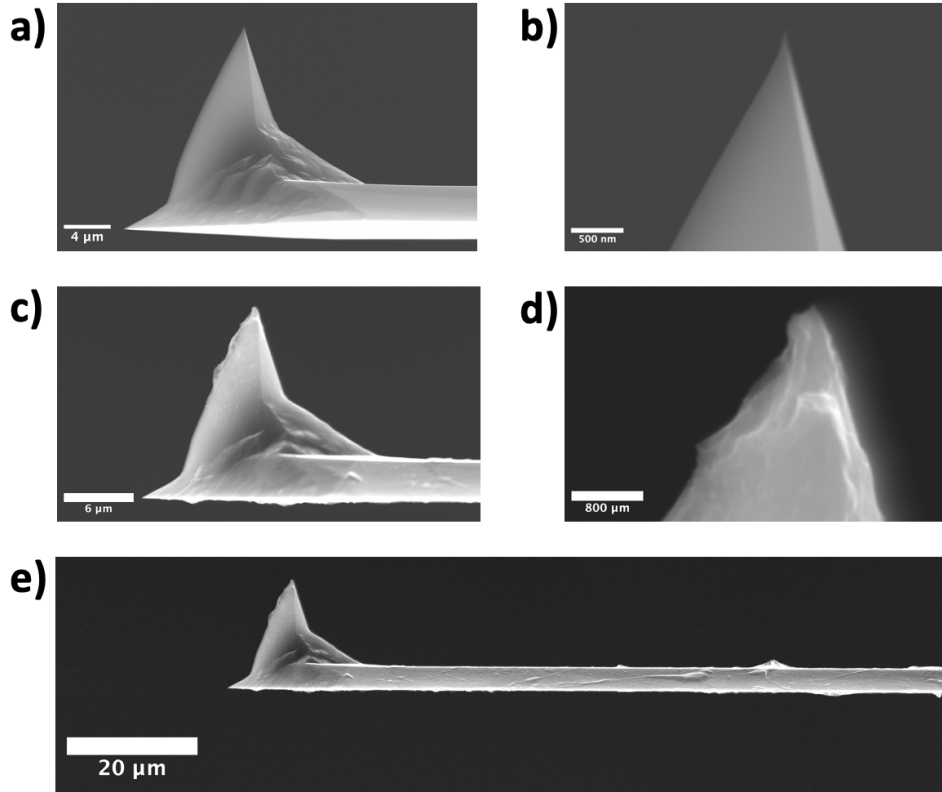


Figure 3.15: SEM images of the Gr-coated nanoprobe corresponding to sample MM1. a) Lateral view of an uncoated silicon tip (magnification of 7.00 kX). b) Magnified view (50.00 kX) of the apex of the uncoated tip. c) Lateral view of the silicon Gr-coated (MM1) tip after the transfer process (magnification of 7.00 kX). d) Magnified view (50.00 kX) of the coated tip apex. e) Side view of both the tip and the cantilever coated (magnification of 2.00 kX). All images were acquired using an EHT of 25.00 kV

By comparing the obtained tip with an uncoated one, it can be established that although the coating covers both the cantilever (Figure 3.15c,e) and the tip (Figures 3.15d), its distribution is not uniform. Carbon agglomerations are observed both at the apex and along the tip geometry. A closer inspection of the tip (Figure 3.15d) shows that the apex has not flattened in comparison with the previous cases. This may be a consequence of the transfer process, since in this case only a single immersion of the nanoprobe at the water–air interface was performed. Using *ImageJ*, a tip radius of 24.73 nm was obtained. The tip radius of the uncoated sample is 17.17 nm, the sample MM1 is approximately 8 nm larger than the expected original radius.

In order to evaluate the structural quality of the nanoprobe, a Raman spectroscopy analysis was performed (Figure 3.16).

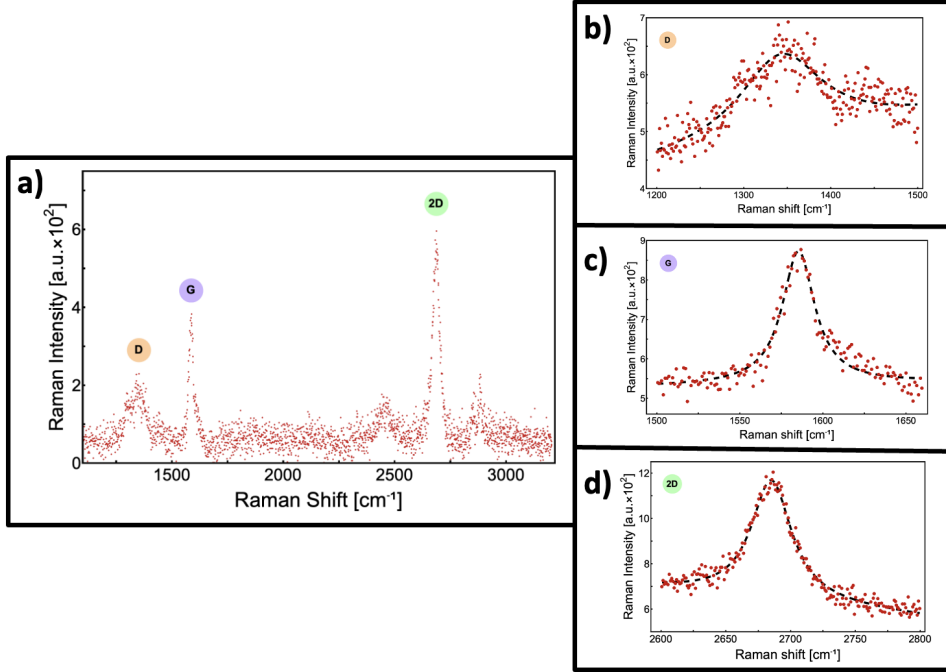


Figure 3.16: Raman spectrum of Gr (sample MM1) on a PPP-FMR SiO₂ cantilever.

From Figure 3.16, it can be observed that the D peak (Figure 3.16b) shows a larger dispersion of the data and a broader bandwidth, suggesting that the graphene structure contains defects after the transfer onto the silicon substrate. On the other hand, the intensity of the 2D peak (Figure 3.16d) is higher than that of the G peak (Figure 3.16c), indicating that the sample corresponds to monolayer or bilayer graphene.

Table 3.9: Lorentzian fit parameters of the Raman D, G and 2D peaks of the Gr-coated nanoprobe corresponding to sample MM1.

Peak	Center [cm ⁻¹]	FWHM [cm ⁻¹]	Height [a.u.]
D	1342.64 ± 1.99	118.95 ± 10.22	150.94 ± 6.27
G	1585.20 ± 0.31	23.77 ± 1.13	336.16 ± 8.74
2D	2684.99 ± 0.25	38.01 ± 0.99	528.55 ± 7.01

From Table 3.9, it can be observed that the D peak, associated with structural defects, exhibits a relatively large width of $\sim 118 \text{ cm}^{-1}$. This can be attributed to the graphene transfer process, which increases the defect density in the sample, as reflected in both the peak broadening (FWHM) and its intensity ($\sim 150 \text{ a.u.}$).

Regarding the G and 2D bands, their widths ($\sim 24 \text{ cm}^{-1}$ and $\sim 38 \text{ cm}^{-1}$, respectively) fall within typical ranges reported in literature [46, 51], suggesting that despite the presence of defects, the graphene retains a relatively well-defined crystalline structure.

From the Lorentzian fit intensities, the ratios I_D/I_G and I_{2D}/I_G were calculated, yielding values of $\sim 0.45 \pm 0.02$ and $\sim 1.57 \pm 0.05$, respectively. The I_D/I_G ratio indicates the presence of defects in stage 1, while $I_{2D}/I_G > 1$ suggests the presence of bilayer graphene.

We now proceed to perform C-AFM measurements with this tip. The same sample is used.

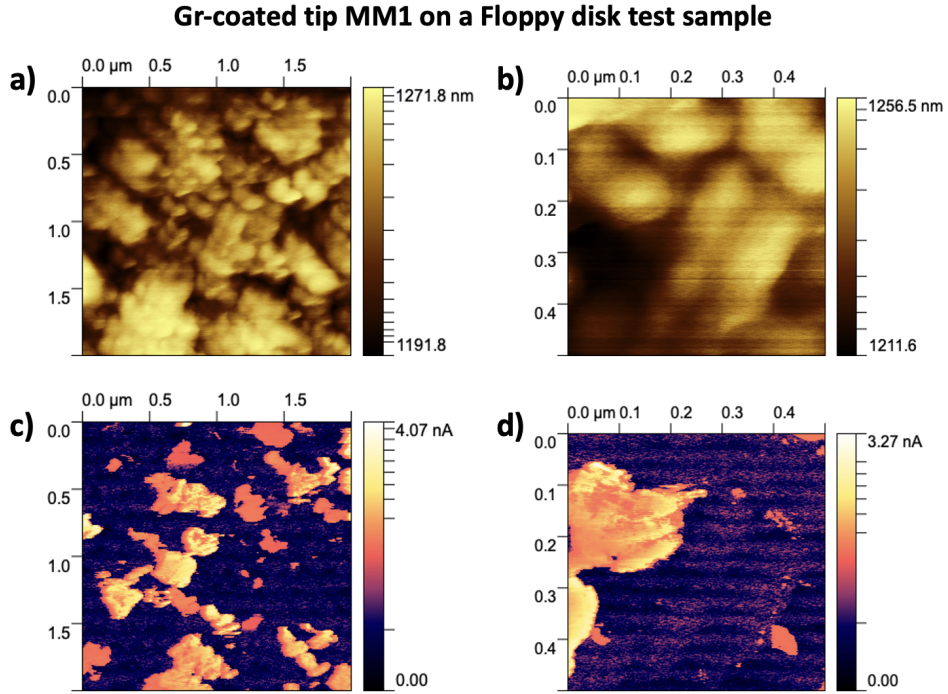


Figure 3.17: Topography images and current maps obtained by C-AFM using sample MM1 on a floppy disk test sample. a,b) Topography images and c,d) current maps acquired at an applied bias of 500 mV. The scanned areas correspond to $2 \mu\text{m} \times 2 \mu\text{m}$ for a,c) and $0.5 \mu\text{m} \times 0.5 \mu\text{m}$ for b,d), respectively. The color scale in the topography images represents height (nm), while in the current maps it represents the measured current (nA).

For this sample, a granular morphology is again observed in the topography images (Figures 3.17a,b), similar to that of the reference sample. However, a noticeable loss of image resolution is evident, together with the appearance of repetitive surface features. These repeated structures suggest the presence of a tip artifact, where the measured topography becomes distorted due to the convolution of the sample morphology with

the geometry of the probe apex. As a result, surface features may appear broadened or replicated, leading to a reduction in the accuracy with which fine details are resolved.

Regarding the conductivity, the current maps (Figures 3.17c,d) reveal the presence of localized conductive regions that are larger in size than those observed with the reference tip. These regions are heterogeneously distributed, with some areas exhibiting high current intensity. In this case, the measured current remains in the nA range, indicating that the tip still exhibits significant conductivity.

3.5 Graphene Sample MM2

For the following case, a conductive silicon probe coated with platinum/iridium (Pt/Ir) was used. Two AFM tips coated with Graphene were fabricated by performing two transfer steps using a single immersion at the air/graphene/water interface. SEM images of the tips are presented after the conductivity measurements. First, the graphene grown on copper is analyzed, as shown in Figure 3.18.

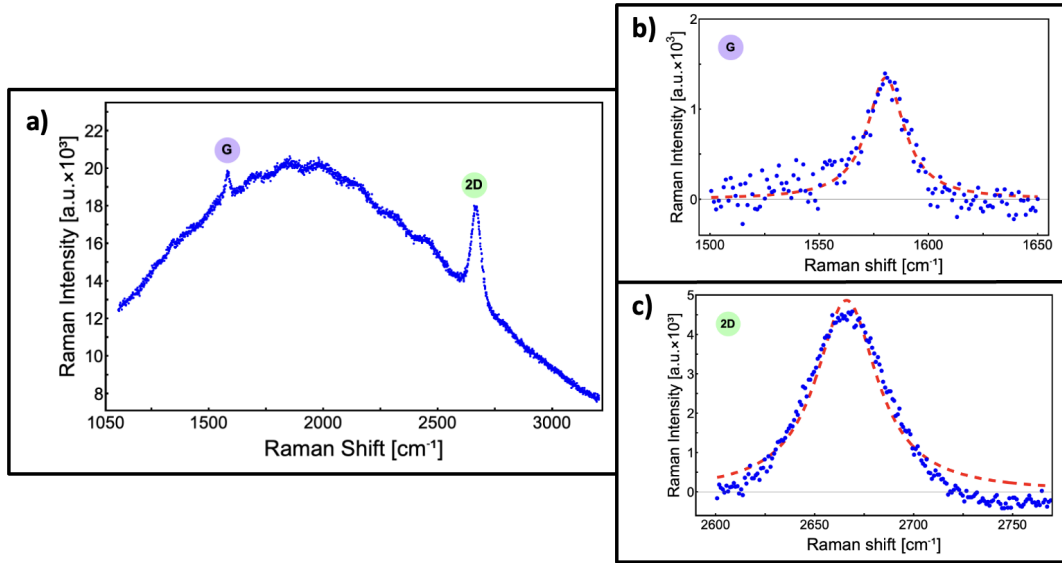


Figure 3.18: Raman spectrum of sample MM2 on Cu. b,c) Lorentzian fit curves for G peak (b) and 2D peak (c).

First, the most relevant feature of this spectrum (Figure 3.18a) is the prominent intensity of the 2D peak. Its intensity relative to the G peak indicates, in addition to the low defect density, that the analyzed sample corresponds to monolayer graphene. To further confirm this, Lorentzian fittings were performed for each of the peaks after removing the fluorescence background (Figures 3.18b,c).

Table 3.10: Lorentzian fit parameters of the Raman G and 2D peaks of the graphene sample MM2 on Cu after removing the background.

Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
G	1580.32 ± 0.41	20.65 ± 1.16	1350.3 ± 53.2
2D	2665.98 ± 0.36	37.67 ± 1.05	4870.6 ± 94.5

From the parameters obtained in Table 3.10, an intensity ratio $I_{2D}/I_G = 3.61 \pm 0.16$ is obtained, which is characteristic of monolayer graphene. This result is consistent with the bandwidth of the 2D peak, whose FWHM is approximately 37 cm^{-1} . Although this value differs by about 7 cm^{-1} from the value typically reported for monolayer graphene, this variation may be attributed to strain or interactions with the copper substrate. Taken together, these results indicate that the sample corresponds to monolayer graphene grown on copper.

Once the sample on copper was initially characterized, the transfer process on two different cantilevers was carried out. These samples are labeled as "MM2–Gr/Pt/Ir (1)" and "MM2–Gr/Pt/Ir (2)". To characterize the composition of these tips, Raman spectroscopy was performed (Figure 3.19).

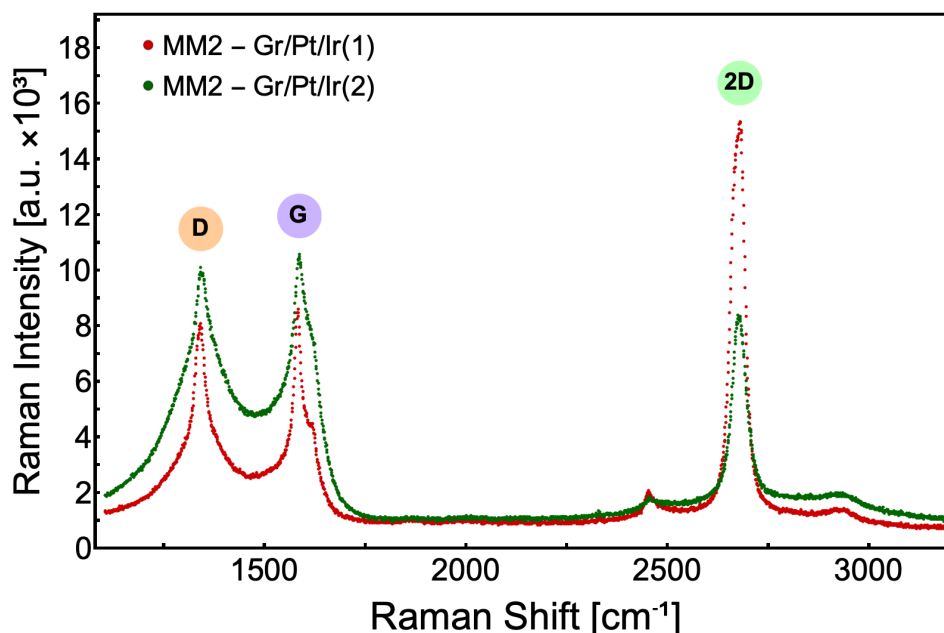


Figure 3.19: Raman spectrum of Gr (samples MM2–Gr/Pt/Ir (1), (2)) on a conductive cantilever.

From Figure 3.19 it is possible to observe the presence of defects in the sample. However, a prominent 2D peak is also visible in both sample (1) (red) and sample (2)

(green). In the first case, the intensity of the 2D peak is significantly higher than that of the G peak, indicating the presence of monolayer graphene. In contrast, in the second sample the 2D peak exhibits a lower intensity than the G peak, which is characteristic of multilayer graphene. Additionally, a broadening of the D and G peaks can be observed in both samples. This effect can be attributed to the presence of OH bonds introduced during the transfer process. Although the intensities of the D and G peaks are similar, the possibility that the samples correspond to graphene oxide can be ruled out due to the pronounced presence of the 2D peak in the spectra.

To further analyze the system, Lorentzian curves will be fitted to the peaks of both samples (Figure 3.20).

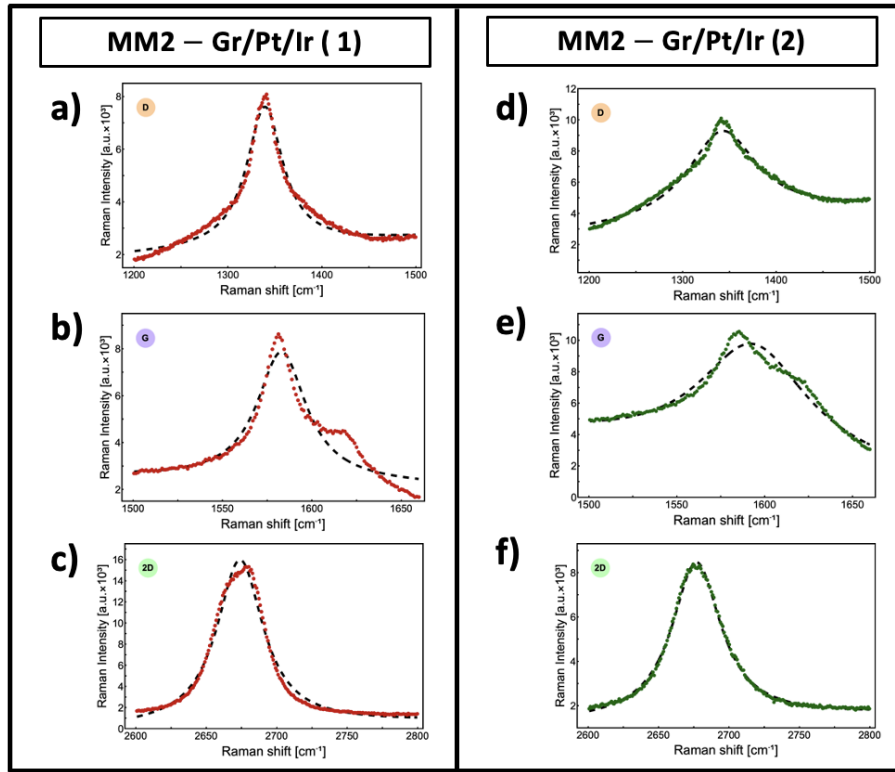


Figure 3.20: Lorentzian fit curves of Raman spectrums of Gr (samples MM2– Gr/Pt/Ir (1), (2)) on a conductive (Pt/Ir-SiO₂) cantilever.

By comparing the peaks of both spectra (Figure 3.20), it is possible to observe that the second sample exhibits a higher defect density, which is reflected in the increased intensity and broader width of the three characteristic peaks of graphene. For sample (1), the presence of the D' peak can be observed in Figure 3.20b). This feature is again attributed to the presence of structural defects introduced during the transfer process.

Table 3.11: Lorentzian fit parameters of the Raman D, G and 2D peaks of the Gr-coated nanoprobe corresponding to sample MM2.

MM2 – Gr/Pt/Ir (1)			
Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
D	1339.04 ± 0.24	47.08 ± 0.88	5320.49 ± 53.91
G	1582.92 ± 0.43	33.57 ± 1.71	5500.14 ± 140.0
2D	2673.79 ± 0.17	40.05 ± 0.69	15702.50 ± 132.20
MM2 – Gr/Pt/Ir (2)			
Peak	Center [cm^{-1}]	FWHM [cm^{-1}]	Height [a.u.]
D	1342.32 ± 0.39	90.60 ± 1.79	5723.77 ± 52.14
G	1593.53 ± 0.56	75.74 ± 3.15	7258.44 ± 174.60
2D	2676.71 ± 0.08	42.34 ± 0.33	7076.87 ± 26.73

From the Lorentzian fitting parameters obtained for each case, it can be confirmed that the 2D peak of sample (1) exhibits a high intensity of approximately 15700 a.u., compared to the G peak with an intensity of about 5500 a.u. However, the presence of defects in the sample is evidenced by the broadening of the Raman bands, with FWHM values exceeding 40 cm^{-1} for both the D and 2D peaks. Additionally, the small difference in intensity between the G and D peaks (~ 180) indicates a noticeable defect density in the graphene layer.

Regarding sample (2), a higher density of structural defects in the lattice is observed. This is reflected in the width of the D band, which reaches approximately 90 cm^{-1} . Such broadening can also be associated with the presence of oxygen-related groups in the sample. Overall, both samples correspond to graphene with structural defects.

To further analyze the defect density and the number of graphene layers, the intensity ratios I_D/I_G and I_{2D}/I_G are evaluated (Table 3.12).

Table 3.12: Intensity ratio values for each of the MM2 samples.

Sample	I_D/I_G	I_{2D}/I_G
MSF14–1	0.97 ± 0.03	2.86 ± 0.08
MSF14–2	0.79 ± 0.02	0.98 ± 0.02

For sample (1) (Table 3.12 red), although defects corresponding to stage 1 are present, the sample can be identified as monolayer graphene. In contrast, sample (2) (Table 3.12 green) also exhibits stage 1 defects but corresponds to multilayer graphene.

We now examine the topography and conductivity measurements for each sample using C-AFM, Figure 3.21 and Figure 3.22.

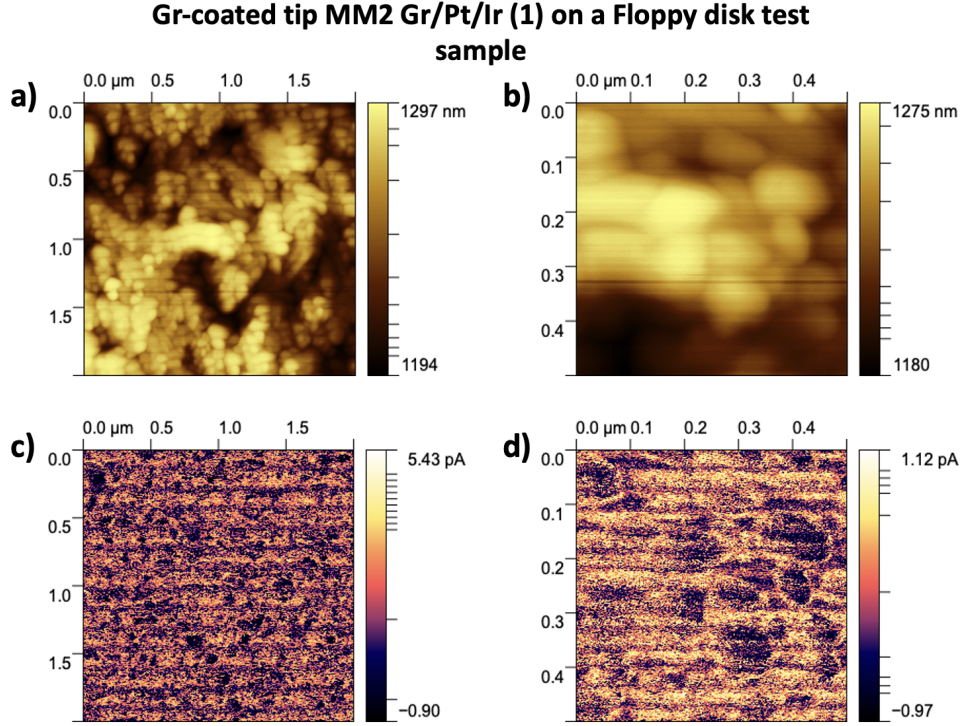


Figure 3.21: Topography images and current maps obtained by C-AFM using sample MM2 Gr/Pt/Ir (1) on a floppy disk test sample. a,b) Topography images and c,d) current maps acquired at an applied bias of 500 mV. The scanned areas correspond to $2\ \mu\text{m} \times 2\ \mu\text{m}$ for a,c) and $0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$ for b,d), respectively. The color scale in the topography images represents height (nm), while in the current maps it represents the measured current (pA).

For sample (MM2 Gr/Pt/Ir (1)), the granular structure of the surface can still be observed in the larger-scale image ($2\ \mu\text{m} \times 2\ \mu\text{m}$, Figure 3.21a). However, the image appears blurrier compared to the reference, suggesting a loss of spatial resolution. The height scale ranges from 0 to 120 nm, indicating that the overall topographical variations are preserved. In the smaller-scale image (Figure 3.21b), a significant loss in image quality and definition is observed, further indicating a limitation in the lateral resolution of the tip.

Regarding conductivity, no current signal is detected in the corresponding maps (Figures 3.21c,d), as evidenced by a homogeneous noise level across the entire scanned area. This indicates the absence of electrical conduction between the tip and the sample. This behavior can be attributed to a loss of tip conductivity, possibly associated with defects, or damage to the graphene conductive coating. Furthermore, the absence of a measurable current may also be related to the nature of charge transport through a

graphene monolayer. Although graphene exhibits excellent in-plane electrical conductivity, charge transport perpendicular to the graphene plane is fundamentally different and is strongly influenced by interfacial coupling and electron tunneling mechanisms. Therefore, the absence of a measurable current may also be related to the inherently more challenging out-of-plane charge transport in a graphene monolayer [57, 58].

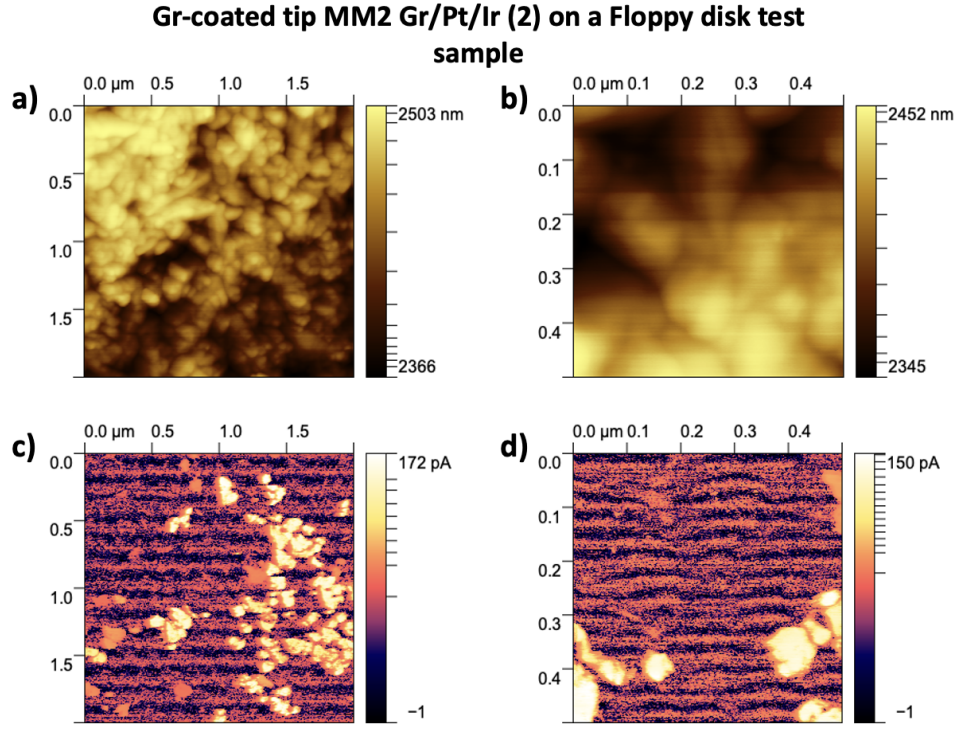


Figure 3.22: Topography images and current maps obtained by C-AFM using sample MM2 Gr/Pt/Ir (2) on a floppy disk test sample. a,b) Topography images and c,d) current maps acquired at an applied bias of 500 mV. The scanned areas correspond to $2\ \mu\text{m} \times 2\ \mu\text{m}$ for a,c) and $0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$ for b,d), respectively. The color scale in the topography images represents height (nm), while in the current maps it represents the measured current (pA).

For sample (MM2 Gr/Pt/Ir (2)), the topography images (Figures 3.22a,b) show a well-defined granular surface morphology. In the larger-scale image ($2\ \mu\text{m} \times 2\ \mu\text{m}$, Figure 3.22a), the surface features are clearly resolved, with height variations in the range of 2366–2503 nm, indicating that the tip maintains good spatial resolution at this scale. However, in the smaller-scale image, a loss of lateral resolution is observed.

Regarding conductivity, when the current scale is adjusted to the pA range, measurable signals in the range of -1–172 pA become evident. This behavior is observed in both the larger-scale image ($2\ \mu\text{m} \times 2\ \mu\text{m}$, Figures 3.22e,g) and the smaller-scale

image ($0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$, Figures 3.22f,h). In both cases, the current distribution is heterogeneous, with localized conductive regions over a background close to the noise level.

These results demonstrate that it is possible to synthesize graphene and transfer it onto nanoprobe without the use of polymer-assisted transfer methods. Although most of the probes exhibit an increase in tip radius relative to the original value (17.17 nm for the PPP-FMR silicon tips), which leads to a reduction in lateral resolution, the Gr-coated probes remain electrically conductive. Conductivity was successfully demonstrated on a floppy disk test sample using both originally non-conductive silicon probes coated with graphene and conductive Pt/Ir probes subsequently coated with graphene. In particular, probes coated with bilayer and multilayer graphene through a single immersion into the graphene film exhibited measurable current signals in the nA and pA ranges, respectively.

Overall, these findings confirm that both the graphene transfer procedure and the subsequent structural and electrical characterizations were successful, demonstrating the feasibility of fabricating Gr-coated nanoprobe suitable for conductive AFM measurements.

CONCLUSIONS AND FUTURE OUTLOOKS

This research focused on the fabrication and characterization of graphene-coated nanoprobe and their application in conductive atomic force microscopy measurements.

Throughout this thesis, AFM tips were successfully coated with graphene using a polymer-free wet transfer method, as confirmed by SEM images acquired in both side and apex views. The graphene coating was found to be heterogeneous, exhibiting surface roughness across the tip. This process resulted in an increase in the tip radius to values ranging from 24 to 89 nm, exceeding the original radius of 17.17 nm for PPP-FMR silicon probes.

Regarding the structural composition, Raman spectra of each sample confirm the presence of graphene through its characteristic peaks. Furthermore, the intensity ratio I_{2D}/I_G indicates the formation of monolayer, bilayer, and multilayer graphene on the AFM tips. Structural defects are also observed, as evidenced by the presence and relative intensity of the D peak and its ratio to the G peak, which can be attributed to grain boundaries and transfer-related processes occurring at the water-air interface and during deposition onto the tip. All samples remain within stage 1 of the defect regime.

Optical microscopy further confirmed the presence of graphene over a significant area of the nanoprobe chips, enabling subsequent topographic and conductivity via C-AFM over a floppy disk test sample.

C-AFM measurements revealed that the coated probes are capable of resolving topographic features while providing measurable conductivity signals in the nA and pA range. For comparison, a Pt/Ir-coated PPP-EFM probe was used as a reference during the C-AFM measurements. No measurable current was observed for the monolayer-coated probe, whereas the bilayer- and multilayer-coated probes exhibited measurable electrical conduction. Although charge transport perpendicular to the graphene plane is fundamentally different from its in-plane transport [57, 58], the improved electrical response observed for the bilayer and multilayer coatings suggests that increasing the number of graphene layers may enhance interfacial coupling and provide a more efficient pathway for vertical charge transport. Furthermore, measurable conductivity was obtained for probes fabricated using a single immersion into the graphene film, whereas probes subjected to multiple immersion steps did not exhibit measurable current under the experimental conditions of this work. This observation suggests that the transfer process itself plays a key role in determining the electrical performance of the graphene-coated probes.

Future work should focus on improving the uniformity of the graphene coating, reducing tip radius enlargement, and optimizing the transfer process to minimize defects. In particular, future fabrication will employ a single immersion of the AFM probe into the graphene film, as this approach provided the best electrical performance in the present work. The fabricated probes will be tested in electrical AFM modes such as Kelvin probe force microscopy (KPFM) and piezoresponse force microscopy (PFM) to obtain nanoscale maps of properties such as work function and piezoelectric response. We also plan to investigate potential applications in Twistronics by measuring the electrical response between the graphene-coated nanoprobe and a rotated graphene sample.

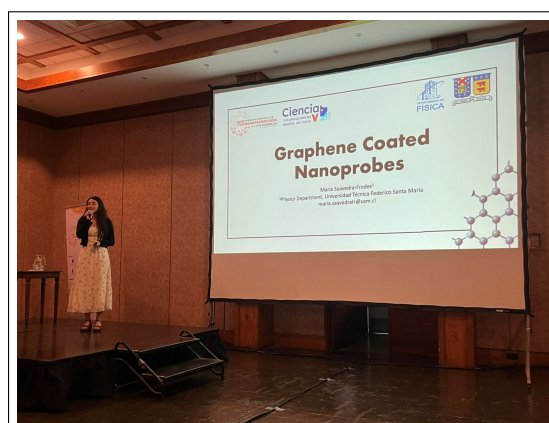
Overall the results highlight the potential of Gr-coated probes for nanoscale electrical measurements, particularly in applications requiring conductive and mechanically robust tips.

MASTER'S PRODUCTS

5.1 Congress and Conferences



XIII School on Nanostructures
 "Nanopuntas de silicio recubiertas de óxido de
 grafeno como sensores para campos
 magnéticos"
 Poster presentation
 2025



VIII National Congress on Nanotechnology
 "Graphene Coated Nanoprobes"
 Talk presentation
 2025

5.2 Papers

1. "Blending Salmon Gelatin with Polyvinylidene Fluoride Using Coaxial Electrospinning"
Martin Chavarria-Vidal, Dragica Bezjak, Maria Saavedra-Fredes, Benjamin Schleyer-Thiers, Javier Enrione, Cristian Acevedo, Jorge Tapia, Tomas P. Corrales.
BBA Advances.
2025
(<https://doi.org/10.1016/j.bbadv.2025.100168>)
2. "Boron-doped nanocrystalline silicon: understanding a tricky material for high performance heterojunction solar cells"
Amanda Merino, Patricia Martinez-Rojas, Maria Saavedra-Fredes, Patricio Häberle, Tristan Gageot, José Alvarez, Jean-Paul Kleider, Valeria del Campo, Delfina Muñoz
Proceedings of the IEEE 52nd Photovoltaic Specialists Conference (PVSC 52).
2025
doi=10.1109/PVSC59419.2025.11132544

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