UNIVERSIDAD POLITÉCNICA DE MADRID

ESCUELA TÉCNICA SUPERIOR DE INGENIEROS
DE TELECOMUNICACIÓN

**DEVELOPMENT AND CHARACTERIZATION
OF GRAPHENE-BASED ELECTRONIC
DEVICES**

TESIS DOCTORAL

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2017

TESIS DOCTORAL: Development and characterization of graphene-based electronic devices.

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A mi familia, mi novia, mis amigos y mis compañeros.

**"DON'T
PANIC"**

*Douglas Adams
The Hitchhiker's Guide to the Galaxy (1979)*

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Resumen

Esta tesis engloba un conjunto de estudios centrados en el grafeno, un material bidimensional de extraordinarias propiedades eléctricas, ópticas y mecánicas. Esta investigación ha sido llevada a cabo desde el punto de vista tecnológico, en el campo común que comparten la ciencia de materiales y la ingeniería electrónica, la física básica y sus aplicaciones. En el marco del presente trabajo de investigación, tanto la caracterización básica del material como las técnicas de micro y nanofabricación han sido incorporadas al estudio del grafeno.

Para entender la importancia de este material, es esclarecedor remontarse a su descubrimiento en 2004 por parte de Geim y Novoselov. La creencia más extendida en el momento, derivada de cálculos termodinámicos anteriores, era que los cristales bidimensionales no podían existir aislados de forma estable. Contrario a este prejuicio, desde el grupo investigador de Manchester fueron capaces de lograr el notable hito de aislar una monocapa de grafeno. Usando métodos rudimentarios para exfoliar una única capa de grafito, fueron capaces de medir las propiedades eléctricas del grafeno. Entre estas propiedades, se verificó que la dispersión energía-momento del material es lineal. Esta relación energía-momento les llevó a descubrir la extraordinariamente alta movilidad de portadores del material, la cual es indicativa de la existencia de transporte balístico de electrones. Esta última propiedad es ideal para aplicaciones electrónicas de alta frecuencia, y es una de las múltiples razones por las que el grafeno ha llamado la atención de la comunidad científica.

Desde su descubrimiento, la cantidad de grupos de investigación que han optado por su estudio se ha incrementado rápidamente, acelerando

el desarrollo del estado de la técnica del material. En su estado actual, varios obstáculos han aparecido en relación con su aplicación industrial. A largo plazo, el problema más importante al que se enfrenta la investigación en grafeno es encontrar el nicho de mercado en el que se pueda desarrollar todo el potencial del material. El grafeno ya ha demostrado ser una excelente solución en un gran abanico de aplicaciones, como la electrónica flexible, la obtención y almacenamiento de energía, o la electrónica de alta frecuencia, por citar algunas. Por ahora, parece que ninguna de estas tecnologías está lista para su introducción en el mercado, bien debido al coste asociado, o por el hecho de que las tecnologías preexistentes resultan ser una mejor opción. Para resolver esta dificultad, los medios de producción del material han de ser capaces de generar grafeno barato, en grandes cantidades, y de la mejor calidad posible. Por lo tanto, la **optimización de los métodos de crecimiento** es prioritaria a corto plazo. Entre las técnicas existentes, la deposición química de vapor (CVD) es una de las más extendidas, ya que es capaz de producir grandes áreas de material de buena calidad cristalina. En este método de crecimiento, los átomos de carbono provenientes de hidrocarburos gaseosos son depositados en una superficie catalítica metálica. No obstante, la densidad de nucleación y la velocidad de crecimiento del cristal necesitan ser optimizados. En esta tesis, se detalla un estudio preliminar de las condiciones de crecimiento en nuestro sistema CVD, en el que un tratamiento oxidativo de la superficie catalítica mejora parcialmente el crecimiento, en concordancia con otros estudios de la literatura.

Un problema ligado al uso de grafeno crecido mediante CVD es la necesidad de transferir el material desde el sustrato catalítico a uno más adecuado, normalmente un dieléctrico. A pesar de estar sujeto a una mejora continua, este proceso tecnológico es realizado comúnmente de forma manual. Solo grandes compañías, como Sony o Samsung, han sido capaces de desarrollar un método automático de transferencia. Incluso en estos casos, la elección del sustrato final está limitada a sustratos flexibles, ya que estos métodos están basados en técnicas *roll-to-roll*. Entre los resultados de esta tesis, **se ha diseñado y evaluado un sistema automático de transferencia**, el cual permite el uso de sustratos rígidos como soporte final del grafeno. En comparación con el método manual, se demuestra que el método automático desarrollado mejora el rendimiento del proceso, dando lugar a muestras más limpias y con menor tensión mecánica. Para llegar a estos resultados, **se ha implementado una metodología de procesado** de dispositivos en el Instituto de Sistemas Optoelectrónicos y Microtecnología (ISOM-UPM), donde se han fabricado y caracterizado transistores de efecto campo ba-

sados en grafeno (GFETs). Este tipo de dispositivo resulta muy versátil en el caso del grafeno, puesto que sus características eléctricas de salida están íntimamente relacionadas con la calidad cristalina del material y sus propiedades físicas. Entre estas propiedades, son destacables la movilidad de electrones y huecos, o incluso la posibilidad de controlar el tipo de portador eléctrico dominante en el material mediante efecto campo.

Por último, esta tesis también se enfrenta al problema de cómo **estandarizar la caracterización de dispositivos** basados en grafeno, necesaria para cuantificar sus propiedades. Esta actividad es esencial en la industria de la electrónica, donde pequeños problemas de calidad durante el procesamiento pueden reducir de forma drástica el rendimiento de la producción. Por lo tanto, la competitividad de cualquier compañía depende de evitar estos fallos. Con la ayuda de métodos de caracterización fiables y capaces de detectar dichos fallos, se pueden resolver estos problemas. Con este propósito, en esta tesis se han diseñado **métodos de caracterización óptica y eléctrica**. En ellos, una conexión a modelos físicos teóricos nos permite extraer información cuantitativa de los dispositivos fabricados en el laboratorio. En el caso del método de caracterización eléctrica desarrollado, es destacable que la información correspondiente a los dos tipos de portadores en grafeno se puede obtener de forma simultánea e independiente. Para llevar a cabo la caracterización óptica, se ha realizado espectroscopía Raman en el canal de dispositivos GFET. Mediante una transformación algebraica, se han logrado desacoplar los efectos en el espectro debidos a la tensión y al dopado del material, pudiendo cuantificarse ambos.

Una vez estos métodos de caracterización han sido desarrollados, nuestro primer paso ha sido comprobar que los resultados que generan son correctos, usando para ello datos de la literatura. Una vez su efectividad ha sido asegurada, se han caracterizado dispositivos de muestras transferidas de forma manual y automática. El resultado de esta caracterización, ya mencionado anteriormente, es que los dispositivos fabricados utilizando el sistema automático desarrollado durante esta tesis exhiben mejores propiedades que los fabricados de forma manual.

Por último, es importante destacar que el desarrollo de las tecnologías asociadas al grafeno se encuentra en un estado inicial, ya que su incorporación a la industria está fuera del alcance a corto plazo. No obstante, debido a la velocidad del progreso en el estado de la técnica, el campo de investigación del grafeno tiene un futuro prometedor.

Abstract

This thesis encloses a set of studies centered in graphene, a two-dimensional material with extraordinary electrical, optical and mechanical properties. The research has been conducted from the technological point of view, on the boundary between material science and electrical engineering, basic physics and its applications. In the framework of the present research work, both basic material characterization, and micro- and nano-fabrication techniques have been adopted for the study of graphene.

To understand the importance of this material, it is inviting to go back to its discovery in 2004 by Geim and Novoselov. The general belief at the time, derived from previous thermodynamical calculations, was that two-dimensional crystals could not exist isolated in a stable way. Against this prejudgment, the research group from Manchester was able to achieve the remarkable goal of isolating graphene. Using rudimentary methods to exfoliate a single layer from graphite, they were capable to measure the electronic properties of graphene, in which they verified a linear energy-momentum dispersion. This dispersion relation lead them to discover its extraordinarily high charge carrier mobility, which indicates that electrons in graphene travel in a ballistic regime. Such a high mobility is a desirable attribute for electronic applications where high frequency is required, and it has been one of the reasons why graphene has drawn the attention of the scientific community.

Since this discovery, the amount of research groups focused on this material has increased rapidly, pushing forward the state of the art in the field very quickly. In the current stage of the field, several issues have aroused regarding this material. On the long-term, the most important is-

sue is to find the niche application where the material excels. Graphene has proved to be an excellent solution for a variety of subjects, such as flexible electronics, energy harvesting and storage, and high speed electronics, to cite some. For now, it seems that none of them are ready for the market, either due to the cost, or to the fact that the existing solutions exhibit better characteristics than graphene. In order to solve this first issue, the production means need to be capable of fabricating cheaper graphene, in large quantities and of the best quality. Therefore, the **optimization of the growth methods** is a short term priority. Among the existing techniques, chemical vapor deposition (CVD) is one of the most spread ones, as highly ordered material in large quantities can be obtained. In this growth method, carbon is deposited on the surface of a metallic catalyst from a gaseous carbon source. Nevertheless, both the nucleation density and the growth rate need to be further improved. In this thesis, a preliminary study of the growth conditions is detailed, where an oxygen treatment of the catalytic substrate is proved to overcome these issues, in agreement with results published elsewhere.

A problem derived from the CVD growth method is the need to transfer the material from the catalytic substrate to a more suitable one, typically a dielectric. Even being continuously optimized, this technological process is commonly performed manually. Only big companies, such as Sony or Samsung, have been capable of developing an automatized version of the process. Even for these cases, the choice of substrate is limited, as these methods are based in roll-to-roll processing, and hence its application is restricted to only flexible substrates. In this thesis, an alternative **automatic transfer method** that accepts rigid target substrates has been designed and tested. When compared to the common manual method, it has been demonstrated that the developed transfer method improves the yield of the process, resulting in cleaner samples with less tensile strain. For reaching these conclusions, a complete **processing methodology** has been implemented at Instituto de Sistemas Optoelectrónicos y Microtecnología (ISOM-UPM), where graphene field-effect transistors (GFETs) have been fabricated and characterized. This device structure is quite versatile in the case of graphene, as its electrical output characteristics are closely related to the material quality and its intrinsic physical properties, such as the electron and hole mobilities, or even the possibility to select the charge carrier type through a controlled electrical field.

Finally, the last high-priority problem faced in this thesis is how to **standardize and ensure the quality of the graphene-based devices**. This activity is essential for the electronics industry, where small quality

issues during the processing steps or on the final products can drastically reduce the production yield, which may affect badly to competitiveness of any company from the sector. With help of precise, sensitive characterization methods, this issue can be overcome. For this purpose, **electrical and optical characterization methods** have been adapted and developed during this thesis. In them, a deep connection with physical models allows to extract quantitative information from the fabricated GFET devices. As a remarkable property of the electrical method, information from each carrier type can be obtained at once. Regarding the optical method, Raman spectroscopy mapping has been assessed on the GFET channel. By means of an algebraic transformation, a separation between doping and strain effects on the material allows to quantify both effects.

Once these characterization methods have been developed, our first step has been to test the results that they provide against data from the literature, with successful results. As the effectiveness of the methods has been ensured, devices from manually and automatically transferred samples have been characterized. The outcome of this characterization, as mentioned earlier, is that devices fabricated using the in-house automatic transfer method exhibit higher quality when compared to devices fabricated with the manual method.

The development of the technologies associated with graphene is still in its early stage, as its incorporation to the existing industrial applications is out of reach in the short term. Nevertheless, with the state of the art evolving on a daily basis, it has become a very promising and exciting research field.

Acknowledgements

En este apartado me gustaría dar las gracias a todas las personas que han estado involucradas en esta tesis, en especial a mi novia Susana y a mis padres, ya que sin su apoyo, este periodo de aprendizaje no hubiese sido tan gratificante como considero que ha sido. He de agradecer a mi director de tesis, Fernando Calle, el haberme ofrecido la oportunidad de empezar la carrera investigadora, y su plena disponibilidad para enriquecer con su punto de vista el desarrollo de mi trabajo. A Javier Martínez, también mi director de tesis, le agradezco su pragmatismo, que espero haber adoptado en parte. A Jorge Pedrós, le agradezco que haya tenido la paciencia de transmitirme su visión de la investigación, así como su capacidad para agitar mis inquietudes científicas. También, me gustaría agradecer la hospitalidad de Tomás Palacios y José Antonio Garrido, en cuyos grupos realicé las estancias durante mi doctorado.

Gracias a mis antiguos compañeros de despacho Sara, Tommaso, Mariajo, Alejandro, Gema, Manu, Ana y Juan por permitirme compartir tantos buenos momentos con ellos; y a los técnicos del ISOM Maika, David, Alicia, Óscar y Fernando, por ofrecerme cantidad de ideas para resolver los problemas a los que me he enfrentado. Gracias a todos los compañeros y colaboradores que he tenido a lo largo de estos años por su apoyo, al haber sido tan generosos de compartir su conocimiento técnico conmigo, especialmente los del ISOM-UPM y del Departamento de Ingeniería Electrónica. Del ICMM-CSIC, José María y Violeta, por presentarme el apasionante mundo de la electroquímica de los supercondensadores. También a Susana, Esteban y Alicia por enseñarme las bondades de la espectroscopía Raman, y a Laura, Amadeo y Ricardo del CIEMAT por permitirme disponer de dicha técnica.

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Acronyms

AFM atomic force microscopy. 13, 17, 18

APS ammonium peroxydisulfate. 33

APTES 3-aminopropyltriethoxysilane. 32, 48

BOE buffered oxide etch. 45

CIEMAT Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas. 14

CNT carbon nanotubes. 2, 43

CSIC Consejo Superior de Investigaciones Científicas. xii, 14, 68

CVD chemical vapor deposition. 2, 6, 7, 10, 11, 13–17, 21, 28, 30, 43, 45, 46, 59–61, 63, 64, 69, 71, 75

DIC differential interference contrast. 16, 17

DIW deionized water. 7, 24, 33–37, 39, 40

DOE density of states. 3, 4

EBL electron beam lithography. 5, 13, 45, 46

FET field-effect transistors. 8, 52, 53, 60, 62, 63

FETs field-effect transistors. 4, 51, 55

- FWHM** full width at half maximum. 20, 26
- GFET** graphene field-effect transistor. 8, 12, 52–54, 59, 61, 63, 69, 74, 76
- GFETs** graphene field-effect transistors. 8, 9, 12, 14, 34, 43, 45, 46, 60, 61, 64, 68–73, 76
- HOPG** highly oriented pyrolytic graphite. 15
- ICP** inductively-coupled plasma. 13, 33, 59
- ICV-CSIC** Instituto de Cerámica y Vidrio. 14, 68
- IPA** isopropyl alcohol. 32, 42
- ISOM-UPM** Instituto de Sistemas Optoelectrónicos y Microtecnología. 1, 10, 13, 14, 16, 22, 51, 76
- MIT** Massachusetts Institute of Technology. 42, 76
- NA** numerical aperture. 68
- NIST** National Institute of Standards and Technology. 28
- NMP** n-methyl-2-pyrrolidone. 41
- PDDA** polydiallyldimethylammonium chloride. 36
- PET** polyethylene terephthalate. 32
- PID** proportional-integral-derivative. 38
- PLA** polylactate acid. 36
- PMMA** polymethyl methacrylate. 7, 17, 33, 34, 37, 39–41, 47, 63, 72
- PSS** polystyrene sodium sulfonate. 36
- PTFE** polytetrafluoroethylene. 24, 35, 36, 38, 69, 77
- PVA** polyvinyl alcohol. 42
- RF** radio frequency. 17, 50
- RIE** reactive ion etching. 13, 17, 21, 47, 59

RT room temperature. 8, 38, 41, 52

RTA rapid thermal annealing. 17, 19

SAMs self-assembled monolayers. 15, 35–37

SEM scanning electron microscopy. 11, 13, 20, 25, 26

TLM transmission line model. 46

UPM Universidad Politécnica de Madrid. xii, 1, 10, 13, 14, 16, 22, 52, 76

UV ultraviolet. 13, 46

Introduction

This thesis comprehends most of the research in properties and applications of a novel material, graphene, performed at *Instituto de Sistemas Optoelectrónicos y Microtecnología* (ISOM-UPM). Consequently, graphene is compelled to be the overarching topic of the whole text. At ISOM-UPM, a research institution from the Technical University of Madrid, the activity is focused in micro- and nano-fabrication, optoelectronics, and the applications of the former ones. Therefore, either in material growth, layer transfer, device processing or standardization procedures, a combination of the scientific approach and the engineering strategies has been accomplished, in order to maximize the potential of the pursued goals.

Graphene, whose potential was discovered in 2004 by Novoselov and Geim [1], is a two-dimensional crystal consisting of carbon atoms linked with coplanar, sp^2 covalent bonds. Although this material was theoretically studied long time ago as the constitutive element of graphite [2], which is just a special stacking of graphene layers, only recently, attention has been given to its structure. As each carbon atom shares one electron with each of the three neighbor carbon atoms, the 120° between bonds generates an hexagonal pattern, typically referred as *honeycomb lattice* in the literature. As carbon has four electrons available in the last uncomplete electronic level (i.e. valence 4), one electron from each carbon atom will contribute to form an electronic band, which provides the material with exceptional electronic properties, a discovery that led to the Nobel prize in 2010 [3]. When this property is combined with others, such as its atomic thickness, or its mechanical strength for its size, the application field of such material is broadened even more.

Although graphene is a unique material in several aspects, there exist several open problems that are hindering its implementation into the industry. The first of these problems is the material growth, where the obtention of single crystal material in a scalable, viable way is turning out to be a complicated task. Nowadays, the research in this topic is focused on using catalytic substrates for graphene growth, in detriment of the initial obtention method, which was based on mechanical exfoliation from graphite.

Closely related with the previous issue, the second problem faced by the industrial and research community regarding this material is its processing. Despite the available processing techniques for the electronic industry are an excellent starting point for developing a two-dimensional material such as graphene (as opposed to the deeper, intrinsic problems of other promising materials such as carbon nanotubes (CNT)), some issues are still present. The most ubiquitous of these issues is a technological process typically referred to as *graphene transfer*. This is a mandatory step with the leading graphene growth techniques, where the material has to be deposited on top of catalytic substrates that are not adequate for almost any final application. Therefore, to develop a transfer procedure reliable and scalable has become a crucial issue to solve in this exciting research field.

The third high-priority problem is how to standardize and ensure the quality of the graphene-based devices. This activity is essential for the electronics industry, where small quality issues during the processing steps or on the final products can drastically reduce the production yield, which may affect badly to competitiveness of any company from the sector. With help of precise, sensitive characterization methods, this third issue can be overcome.

In this thesis, the previous issues will be addressed with several approaches. Related to the material growth issues, our efforts will be directed to understand and improve graphene growth using chemical vapor deposition (CVD), where we will focus on the catalytic substrate pretreatment to improve the crystalline quality of graphene. Related to the graphene processing issues, a scalable automatic transfer system will be developed to improve the yield and efficiency of the transfer process. Finally, the standardization issue will be solved by means of developing the available characterization methods (electrical and optical), where a deep connection with physical models will allow to extract quantitative information from fabricated graphene devices.

In the next section, a general background of the state of the art in graphene research is provided.

1.1 State of the art

Graphene, whose extraordinary properties have just started to be discovered, is a novel material with a wide range of applications. To cite some examples, flexible electronics [4–11], optical devices [12–16], sensors [17–21] or energy applications such as supercapacitors [22–30] and batteries [31–34] are several of the most remarkable application fields for graphene.

The reason that makes graphene an excellent material for such amount of unrelated topics is its unique properties. As it consists of an atomically thin carbon layer, its specific surface is extremely high (theoretically 2630 m g^{-1} [35]). Also, its carbon-carbon sp^2 bonds, which bestow the material its hexagonal crystalline structure, also provide mechanical robustness and flexibility [36], as well as good chemical stability. The free electrons from the π orbitals of the individual carbon atoms are the responsible of its unique band structure [2, 37], commonly denominated as *semimetal* due to the absence of a bandgap. Using the tight-binding model as well as numerical calculations, it has been found that the energy-momentum dispersion relation for the electrons in the material is linear where the π and π^* bands meet (called K and K' points in the Brillouin zone, which correspond to $\kappa = K$ in Fig. 1.1a). These bands are equivalent to the conduction and valence bands in classical semiconductors although, in this case, there are not forbidden energy states for the charge carriers between them.

The linear relation between energy and momentum at the point where the two bands contact, called *Dirac point* in the literature, implies that, from the classical point of view, the cyclotron mass depends on the square root of the carrier concentration, which is close to zero at the Dirac point. The outcome of this singularly low effective mass for low carrier concentrations is an extremely high carrier mobility, attainable even at room temperature, a remarkable feature difficult to find in any other material. Also, linear dispersion in graphene implies that the electronic density of states (DOE) is linear with energy (Fig. 1.1a left). The direct implication of this fact is that the carrier concentration in the material can be selected, either by doping or by capacitive coupling. Classical substitutional doping in graphene is typically avoided, as the electronic properties of the material are degraded using this method. Therefore, doping in graphene is understood as a fixed surface charge density attached to the graphene surface in a relatively stable way. The other method to select carrier concentration in graphene is applying a controlled electrical field between the graphene channel and an external charged plate, allowing to select even

Figure 1.1: a) Schematic of the linear dependence of the density of states and electron momentum with energy near the points K (or K') of the Brillouin zone. The green dashed line represents the Dirac point energy, and matches the Fermi energy for neutral, undoped graphene. b) An schematic showing the Dirac cone for electron and hole-doped graphene, respectively, where filled electronic states are represented in color and the displaced Fermi energy is represented with a black line.

the type of carrier (holes or electrons) by electrical means. This working principle is similar to the one present in classical field-effect transistors (FETs) devices. As an example on how the carrier concentration can be selected, while in Fig. 1.1a right the Fermi energy in graphene matches the Dirac point energy, in Fig. 1.1b, the Fermi energy is either raised or lowered when referred to the Dirac point. The further the Fermi energy is displaced from the Dirac point, the higher the induced carrier concentration, as can be seen in the DOE diagram. When the Fermi energy of the material is displaced into the band equivalent to a classic valence band, holes become the majority carriers. When the displacement is into the equivalent conduction band, the electrons are then the majority carriers. This type of conduction is typically referred as *ambipolar*, and is also one of the surprising properties found in graphene.

Although all these properties together in the same material forecast an optimistic future for graphene, there exist issues inherent to these same properties that must be accounted for. The most noteworthy of these inconveniences is the lack of bandgap (semimetal), which impedes its direct application in digital electronics due to the achievable on/off ratio, which is orders of magnitude smaller than the one achieved in semiconductor electronic materials, such as silicon. Another property that may turn out to be an inconvenience is its high specific surface, which may be problematic in terms of surface contamination or substrate inter-

actions. As a comment, another issue in the current development stage of the field is that graphene cannot substitute any commercial product in a viable way, mainly due to its cost, difficult mass production and low quality.

Even considering that the most advantageous application for graphene is yet to come, the amount of research papers and industrial property that is being produced each year is enormous and under acceleration. This situation makes graphene an exciting topic for research, where the understanding of the topic deepens on a daily basis.

Graphene fabrication

There exist several fabrication methods for graphene, and each of them is more suitable for a certain range of applications than the others. The interest in graphene started with *exfoliated graphene*, a material obtained from highly-crystalline graphite using the *Scotch Tape method* [1]. As graphene can be visualized as a single layer of graphite, this method is based on mechanical delamination from this mineral and on the insulation of a single layer. This material obtained through this method is virtually defect-free and, nowadays, isolated flakes with areas of thousands of μm^2 can be obtained. The main uses of this kind of material have been to prove physics phenomena, typically derived from the quantum mechanics theory [38, 39] and to fabricate proof-of-concept devices [40], which generally requires the use of electron beam lithography (EBL) technique, which increases even more the cost of its possible industrial applications.

Another type of graphene is the commonly-denominated *epitaxial graphene* [41], which is obtained applying high temperatures in a controlled environment to a crystalline SiC wafer, a common and well-known semiconductor. This way, the sublimation of Si creates several stacked graphene layers in both surfaces of the wafer, allowing the obtention of graphene areas in the order of cm^2 . This fabrication method was, during the first years of graphene research, the preferred one for device production in a conventional, scalable way, allowing the use of well established processes from the semiconductor industry [42]. The strong interaction between graphene and the substrate dangling bonds, the formation of *terraces* during growth, or the difficulty to select the number of layers are some of the weaknesses of this method. Although this method is still under development by several groups, most of the research effort is now focused on alternative methods.

On the opposite side of the previous methods (in terms of quality, scalability and price), chemically-derived graphene can be found. This material, which is cheap, with an elevated defect concentration, and can be produced easily in the kg regime, is obtained applying Hummers method [43]. In this chemical method, the constitutive layers that form graphite are separated *via* chemical oxidation. After this process, a mixture of oxidative liquid chemicals and solved graphene oxide is obtained. In the succeeding processes, this material is reduced, partially decreasing the amount of defects and oxygenated functional groups. As an example, chemical sensors based on this material have proved outstanding sensitivity, but its use in electronics away from these niche applications is limited, as the material electronic properties are deteriorated by the oxidative process.

Finally, graphene can be fabricated using the CVD method, in which a compromise between material quality, production size and cost concur. In this method, using metallic catalysts such as nickel [44, 45] or copper [46], carbon can be deposited from gaseous precursors, such as bubbled ethylene, methane or other hydrocarbons. One of the advantages of this method when copper is selected as catalyst is the possibility to obtain single-layer graphene in a self-limited way. Another advantage is the attainable maximum sample size, which is bigger than in the rest of the existing methods that produce electronic-grade graphene (up to 30 inch diameter samples [10]). Regarding the material quality, single crystal material with a diameter up to 5.9 mm [47] or bigger have been produced with this method just by varying the growth conditions. A large single-crystal size is the main desirable property in order to obtain the best electrical characteristics of the material. As it was presented before, the main issue associated with this production method is the necessity to transfer the graphene layer to a pertinent target substrate. This necessity depends of the desired target application as, for most of them, it is impossible to use graphene while it lays on top of the catalyst substrate, typically a metal.

Nowadays, this last production method is the most fitted one for developing devices using planar technology while keeping a high electronic quality. To point out some of the drawbacks of this method that need to be addressed, apart from the requirement of a transfer process, are the following. The first drawback is the current crystal domain size and quality, that is clearly subpar when compared to other mature technological materials. The second drawback, intimately connected with the first one, is the lack of knowledge of the nucleation processes. Solving these two drawbacks is a necessary step that ought to be fulfilled by all

semiconductors prior to its commercialization. Therefore, in the case of graphene, the same requisite has to be accomplished before its industrial application.

Graphene transfer

The required transfer process for both exfoliated and CVD graphene has evolved drastically over time. The method that was initially developed for this purpose [45, 48] is widely used. It is performed manually, and starts protecting graphene with a polymer deposited by spin-coating, typically polymethyl methacrylate (PMMA). The next step consists of a chemical etch, in which the growth substrate is dissolved, but graphene and the protective polymer are intact, released in the liquid. Finally, after several cleaning steps using deionized water (DIW), the graphene/polymer resulting layer is transferred to the selected target substrate. Once graphene is adhered to the substrate, the protective polymer can be dissolved, leaving graphene exposed on top of the selected substrate.

Defining the previously described process as the basic one, incremental upgrades have been developed. The simplest ones are based on residue minimization [49–52] or its removal through thermal annealing [53]. Some other upgrades of higher complexity are the selection of the transfer region on the target substrate [40, 54–56], the recovery of the growth substrate for its reutilization [57–59] by using the named *bubbling transfer*, or a film handling enhancement that minimizes the mechanical damage on the graphene, either by adding a rigid carrier [5, 60–64] or by using capillarity effects [65] or electrostatic forces [66, 67] that restrict the type of target substrate. Most of these existing methods are simple and cost-effective, but they are time-consuming and require handling skills, which affects the yield and reproducibility of the transfer process.

The variety of approaches available to perform this process points to the importance of this technical issue. Still, further advances are required. One of the most cited upgrades is based on adapting the transfer to a roll-to-roll process [10, 68], where graphene is transferred in a continuous way to a flexible substrate. To grasp the magnitude of investment needed for this last method, only companies from the electronics industry such as Samsung or Sony are capable of developing them.

Although these methods provide a scalable method to obtain graphene film attached to flexible substrates, when applied to rigid substrates such as SiO₂/Si wafers they tend to cause undesired mechanical defects on graphene films, which considerably degrade their electrical properties [62].

From the background of this technique, it is clear that an automatic method that can be used onto rigid substrates, scalable and with high yield is still needed, but not available yet.

Graphene characterization

When referring to standardization and quality assessments in graphene, no matter if it is performed directly on the raw material or in fabricated devices, a figure of merit has to be selected. Among the properties mentioned in the previous sections, graphene uniquely high intrinsic carrier mobility, that has been predicted to be as high as $200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [69, 70] at room temperature, is the best indicator of the material quality. Due to this property, graphene has already proved to be an outstanding material for high-speed electronics applications [71, 72]. One of the most relevant devices that benefits from this high mobility is the graphene field-effect transistor (GFET) [73], in which cut-off frequencies of 300 GHz [42, 74] have already been reported. Therefore, GFETs could be an ideal platform to study the material electrical properties quantitatively, as this structure allows to interact easily with its electronic band structure. Because of this, the characterization methods presented in this thesis are based on these devices.

In order to explain GFET electrical behavior, models that link electrical characterization measurements and graphene properties already exist in the literature. Some of these models can be used as a method to calculate the material intrinsic properties from the experimental electrical output. Therefore, they can be regarded as characterization tools, and not as ideal mathematical models that are disconnected from the experimental data. A simple method [75] is generally applied for this goal [46, 50, 58, 76]. It consists in fitting the GFET output characteristic curves to a single equation model with three fitting parameters: mobility, contact resistance and fixed surface charge density. One drawback of this method, derived from the limited set of equations that are involved, is that it cannot separate between electron and hole carrier mobility values. A revised version of this simple method [77] uses an additional capacitance characterization for calculating the oxide capacitance accurately. However, missing features such as different electron and hole mobilities, or direct link between the output features and the material properties are desirable. An alternative model based on silicon FET theory [78] designed for circuit integration modeling uses empirical equations to simulate the device output characteristics. Computation-wise, this models is fast, but the missing electron and hole mobilities separation and a direct

link between the model output and intrinsic physical parameters make the model less appealing for using it as a characterization tool.

Taking into account this distinction between carrier types, a theoretical model exists [79]. In this first principles model, the same parameters available on the previously mentioned methods appear, but carrier mobility for electrons and holes are provided to the calculations separately. This distinction adds more flexibility for analyzing the effect that residues or dopants generate for each carrier type in GFETs. At this point, the main existing issue is how to transform the chosen physical model into a characterization tool that helps to standardize quality assessments in graphene.

As a different approach for characterizing graphene, the optical properties of graphene instead of its electrical properties can be explored. For this purpose, the most remarkable technique, which provides the highest amount of information, is Raman spectroscopy [80]. In a simplistic way, Raman spectroscopy consist of illuminating the material under test with a coherent source of monochromatic light, typically a laser. Changes due to the light-matter interaction can be read on the outcome collected light. This controlled source of photons will interact with vibrational states of the material, where electrons, due to the high frequency of the light, play an important role. The perturbation is imprinted on the output scattered light, which is classically defined in the units of the inverse of wavelength displacement when compared to the incident wavelength (simply $1/(\lambda_{in} - \lambda_{out})$, in cm^{-1}). These are energy units, and the measured shifts and its intensities are commonly related with vibrational states of the probed material. In this paradigm, the higher the shift, the higher the energy involved in the process.

In the case of graphene, due to the special properties of the electronic band structure, the Raman phenomena is called *resonant* for all the near infrared and visible excitation frequencies. This implies that the scattering phenomena is more probable, and the readout of the process will be especially strong. This is surprising, as graphene consists on a atomically-thin layer that only absorbs 2.3 % of the incoming light [81] in the visible range. Although the resulting spectrum of pristine graphene is not directly related to its phonon density of states, a lot of information regarding the number of layers, strain, doping or material defects can be obtained.

When graphene without any defects is probed with this technique, only two peaks will be clearly appreciated in most experimental systems. The first peak, called G, is typically located in 1590 cm^{-1} , and is a one phonon process related with an optical vibrational mode. The

second peak, called 2D, is typically located in 2700 cm^{-1} , and is a doubly-resonant process of a breathing mode of the material. This means that the emission is produced when two phonons interact with the incident light at once, a situation where the total momentum involved remains zero. The breathing mode is related to a vibrational state in which the atoms that comprise an aromatic ring (each graphene hexagon) move cyclically inward and outwards.

Once graphene has some defect concentration, the breathing mode is active as a one phonon process, resulting in a new peak, called D, that is present approximately at 1350 cm^{-1} . Finally, another mode activated by defects generates the called D' peak, which is also doubly-resonant and found at 1600 cm^{-1} , and therefore can overlap sometimes with the G peak.

To be able to compare the electrical characterization with the information obtained from Raman spectroscopy, the relation between the charge carriers and the Raman spectra has to be extracted. On this topic, several studies exist that illustrate the effect of graphene doping in the Raman spectrum [82, 83], but only the study from Lee et al. [84] is broad enough to satisfactorily decouple the effect of strain and doping in graphene. Therefore, as in the previous characterization method, the underlying problem is how to transform the available theoretical framework into a characterization tool.

1.2 Objectives and methods

Regarding the aforementioned existing issues in the topics of graphene growth, transfer and characterization, the main objectives of this thesis arise, and will be described in the next subsections separately for each topic. Although the amount of different paths available for solving these issues is enormous, the decisions made along this thesis are in concordance with the available equipment and facilities at ISOM-UPM, which will determine the methodology followed in this work.

Graphene growth

First, to fully comprehend the differences between the graphene obtention methods, an exploratory study for several ones is performed. From this analysis, CVD graphene raises manifestly as the best option for electronic applications. As the most remarkable issue regarding the material growth is to find how to obtain large, single crystal graphene in a con-

trolled way, a commercial CVD system available at ISOM-UPM has been used with this objective in mind. This system, build by Aixtron (Fig. 1.2) and engineered for graphene fabrication, allows to reduce the growth temperature by means of plasma activation of the precursors. Also, it is prepared for doping with ammonia during growth, or even perform an in-situ oxidation before the material growth.

Figure 1.2: Aixtron Black Magic pro 4" system.

As our main objective is very demanding and shared with most of the graphene research community, our efforts are focused into a smaller topic, that is reducing the nucleation density while increasing the lateral crystal growth rate. In our case, controlled oxidation of the catalytic substrate [85, 86] will be applied. To check the changes both in graphene nucleation density and domain size, the samples are characterized by scanning electron microscopy (SEM) (Fig. 1.3) and Raman spectroscopy. At the same time than the catalytic substrate modification, a reduction on the precursor partial pressures is made. To fix some conditions and reduce the scope of the study, the catalytic substrate used is electropolished copper, thinner than $25\text{ }\mu\text{m}$, a catalyst in which high quality graphene has already been successfully grown [47, 87].

Figure 1.3: SEM FEI Inspect F50.

Graphene processing

Another issue from the state of the art that needs to be addressed is the improvement of the device fabrication method, which includes graphene transfer, a process with high impact into the final device quality. As there exist a plurality of fabrication details that can be amended, our focus regarding this issue is centered into the graphene transfer process, a necessary step when working with CVD-grown graphene. For the rest of processes involved on device fabrication, conventional routes that can be found in the literature have been applied.

Concerning the graphene transfer, as emphasized before, the vast majority of the existing methods are performed either manually, requiring handling skills from the operator, or automatically on flexible substrates, being unavailable for rigid substrates. To solve these issues, an automatic transfer system for arbitrary substrates, either rigid or flexible, will be developed. In Fig. 1.4, a schematic of the pieces that avoid the manual handling of graphene and the machined pieces used in the final system are shown. To prove the effectiveness of the invention, GFETs were fabricated on samples transferred using this novel method and on sam-

ples transferred with a manual method.

Figure 1.4: Automatic transfer schematic and the machined pieces.

Graphene characterization

In terms of electrical characterization, some important figures of merit have already been identified from the state of the art. To obtain this data from GFET assessments, several methods exist, but none of them is capable to distinguish between hole and electron carriers. To solve this, an existing model [79] that overcomes the issue can be fitted into a method adequate to extract the selected figures of merit. This idea has evolved into an electrical characterization suite, programmed in *python*, where the concepts and equations of the chosen model are included. Using existing optimization packages, the method is capable to output the mobility of both types of carriers (holes and electrons) and the fixed charge density related with doping from experimental output characteristics of GFET devices. Statistical data obtained from a large amount of devices will help to strengthen the accuracy of the figures of merit used to compare alternative processing methods, such as the automatic and manual transfer. It is important to note that the measurement conditions are tightly controlled, as a vacuum environment and a controlled thermal desorption of unintended dopants are required to avoid hysteresis or increased carrier scattering during the measurements.

In terms of optical characterization, the faced problem is simpler, as experimental work capable of extracting the doping level of the material already exists [84]. Therefore, the issue to be solved here is to adapt and make coherent the information obtained optically from Raman

spectroscopy with the information previously extracted from the electrical characterization. In this case, a simpler algebraic conversion of the data has been developed on top of the existing optical model. Again, this calculation is performed using *python* programming. For comparison purposes, the optical characterization was performed on graphene already processed, more precisely on the device channel. Raman spectroscopy mapping has been selected to obtain an average value of the figures of merit.

1.3 Equipment and facilities

To fulfill the objectives of this thesis at ISOM-UPM, inside the 400 m² clean room facilities the following equipment is at our disposal.

- Graphene growth:
 - Chemical vapor deposition reactor: Aixtron BlackMagic Pro PECVD (up to 4" sizes).
 - Tubular quartz oven.
- Processing equipment:
 - Electron beam lithography. Crestec CABL-9000C.
 - UV optical lithography. Karl-Suss MJB4.
 - E-beam metal evaporator.
 - Reactive ion etching/inductively-coupled plasma system Oxford Instruments PlasmaPro 80.
 - Chemical hood.
- Characterization equipment:
 - Semiconductor parameter analyzer Agilent 4156A.
 - Semiconductor parameter analyzer HP 4145B.
 - High/ low temperature probe station Janis-CCR10.
 - Scanning electron microscopy FEI Inspect F50.
 - Veeco NanoScope Multimode AFM.
- Through collaborations, Raman spectroscopy on the following research facilities:

- Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC). Custom-designed Raman-PL system (with Horiba CCD detector).
- Instituto de Cerámica y Vidrio (ICV-CSIC). WITec/ALPHA 300AR confocal Raman microscope system with XYZ automated stage.
- Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT). Horiba LabRam Raman system.

1.4 Thesis outline

Defined the research topics and depicted the existing open issues and their relevance, the results from the selected course of action will be presented on the next chapters.

In Chapter 2, the graphene growth techniques available at ISOM-UPM are explained, with emphasis on graphene growth by the CVD method. In Chapter 3, the in-house developed automatic transfer system is detailed among its working principles and underlying ideas. In Chapter 4, the processing techniques required to fabricate GFETs, the chosen characterization device, are summarize. In Chapter 5, the characterization techniques based on electrical and optical models are described and applied to characterize devices from automatically and manually transferred samples.

Finally, in Chapter 6, some conclusions and the future work are presented.

Material Growth

Graphene can be obtained from a vast amount of different sources. Some of the top-down approaches are based on mechanical exfoliation [1], where artificial graphite, such as highly oriented pyrolytic graphite (HOPG) or kish graphite are mechanically delaminated. This method produces highly crystalline material with excellent properties, but is limited to areas in the micrometer regime, and thus, impractical for industrial applications. Natural graphite, available in large quantities, is also used as graphene source. For this case, either oxidative [88] or shear [89] exfoliation is preferable, leading to graphene with defects or with an uncontrolled number of layers, generally in a liquid suspension.

For the bottom-up approach, typically a carbon precursor and a (metal) catalyst are involved in the growth process. With solid precursors such as polymers [90, 91] or self-assembled monolayers (SAMs) [92], nickel is used as the metal catalyst. Gaseous precursors such as bubbled-ethanol, toluene or methane can be deposited on top of a broader variety of metals, including Cu, Ni and Pt among others. In this thesis, the focus is first on graphene growth on Ni, where carbon is obtained from solid sources, and second and most importantly, on CVD graphene grown on Cu substrates, which is the material of choice for the rest of chapters.

2.1 Mechanical delamination

It is worth mentioning that initial laboratory tests were made using the mechanical exfoliation method. On these experiments, kish graphite, a byproduct from the metallurgy industry, is adhered to Scotch Tape four

or five times consecutively. The resulting flakes are gently pressed to a silicon oxide substrate, with the hope that some individual, isolated graphene flakes ended up deposited on the surface. These experiments resulted in long periods of time searching for single layer graphene using differential interference contrast (DIC) microscopy (as in Fig. 2.1) and a large number of substrate preparations with poor results. Nevertheless, these results encouraged the leap to other graphene sources, specifically those leading to large area samples, and that therefore provide higher processing yields.

Figure 2.1: DIC microscopy images of manually-exfoliated graphene with varied amount of layers. Dotted lines serve as a guide for the thinnest flakes.

2.2 Graphene growth on Ni from solid sources

At the start of this thesis, the CVD system that nowadays is located at ISOM-UPM was not available. Therefore, some effort was directed to circumvent this problem with the resources available at that time. Desirably, the chosen process should be capable to produce large area graphene in a reproducible way.

An option to grow graphene when gaseous carbon precursors are unavailable is the use of solid carbon sources. For this growth technique, an inexpensive solid carbon source is deposited on top of the desired target substrate. Then, the carbon quantity on the surface is controlled and subsequently a Ni catalytic layer is deposited on top of the substrate. After a thermal treatment, the Ni layer is removed, resulting in multilayer graphene directly on top of the desired substrate.

This method has several advantages over other options, such as avoiding the use of flammable gases like CH_4 or H_2 involved in the deposition process, or omitting the implementation of any transfer methods. In addition, this method also keeps the scalability of CVD graphene, with large surface coverage and hence high processing yield.

As the process requires reaching temperatures up to 1200°C during short times, graphene can be deposited only on heat-resistant substrates using this approach. In our case, Si substrates with 300 nm of thermal oxide were chosen. The size of the used substrates is below $1\text{ cm} \times 1\text{ cm}$, but larger substrates could be used, as the limiting factor is the rapid thermal annealing (RTA) oven size. This SiO_2/Si structure has been chosen due to the enhanced optical contrast that provides to graphene layers [93, 94], allowing us to check the sample's homogeneity using DIC microscopy.

Growth method

The first part of the method involves the control of the carbon quantity available for graphene formation. For this purpose, diluted commercial photoresist (Allresist PMMA 950K, 2.5 wt.% in chlorobenzene) was spin coated onto the substrate, resulting in a thickness of $0.25\text{ }\mu\text{m}$. Then, the solvent is removed heating up the sample to 160°C for 10 min. Once the initial baking has been performed, a reactive ion etching (RIE) was carried out on the sample for reducing even more the layer thickness. The conditions used for this process were the following: CF_4 gas at 20 sccm flux with 15 % RF power during 5 min. The processing time was selected using an etch depth monitor as a guide. In this way, the remaining layer thickness is accurately controlled, and the process is more robust and repeatable. After the etching, the layer in contact with the substrate surface behaved chemically different than the original PMMA when rinsed in acetone. Some parts of the layer were torn away after this immersion due to low adhesion, which proved useful for assessing the layer thickness later on. The layer thickness was obtained using atomic force microscopy (AFM) in tapping mode, resulting in a layer of 4.5 nm at this stage. In order

to remove oxygen atoms from the remaining layer, a fast thermal anneal was carried out. Several temperatures in the range of 400 °C to 1200 °C were used during 30 s. A reducing atmosphere of N₂ with 5 % H₂ mixture at 100 mbar was used for this purpose, leaving a thinner layer of amorphous carbon. The final thickness varied from 2 nm to just 0.5 nm, where the smallest value was obtained for the highest temperature. Using a Digital Instruments MultiMode Scanning Probe Microscope, the topography for the thinnest layer can be found in Fig. 2.2.

Figure 2.2: AFM image of the carbon layer after a 1200 °C annealing. The mean measured step height in this case is 0.5 nm.

Apart from thickness assessments, Raman spectroscopy was performed to understand the layer's chemical properties. In Fig. 2.3, Raman spectra for layers obtained using several annealing temperatures can be found. For extracting more information from this spectra, a three-stage model [95] is applied to evaluate the predominant carbon bonds in the material for each temperature. In this model, disordered carbon with mainly sp³ bonding, nanocrystalline graphene with sp² bonding and, finally, large area graphene can be differentiated employing the peak intensity I_D/I_G ratio and G-peak frequency ω_G as indicators. Therefore, we have $I_D/I_G \simeq 0.2$, $\omega_G = 1510 \text{ cm}^{-1}$ for amorphous carbon, $I_D/I_G \simeq 2$, $\omega_G = 1600 \text{ cm}^{-1}$ for nanocrystalline graphite, and $I_D/I_G \simeq 0$, $\omega_G =$

1580 cm^{-1} for graphitic material, which was not present at this processing stage. The variation of these parameters for different maximum temperatures is shown in Fig. 2.3 inset table. It can be appreciated that I_D/I_G increased with the maximum temperature of the annealing process and that ω_G shifted to higher values, meaning that the structure changed partially from amorphous carbon to nanocrystalline graphene, although this last structural stage is not reached yet. Consistently, no 2D peak was found on these samples.

At this point, the Raman spectra indicate a graphene-like structure with presence of C-sp² rings, but with a large amount of disorder and nanocrystallinity. In addition, further graphitization with temperature treatments were insufficient to reach our goal. Therefore, this layer of carbonized polymer served as the controlled carbon source for the next step in the process.

Figure 2.3: Raman spectra for different temperatures. Higher I_D/I_G ratio indicates better material quality at this stage.

Based on several previous publications [45, 90, 96], a Ni catalyst was deposited to improve the crystalline formation. Employing e-beam metal evaporation, different thickness of Ni were deposited on top of the amorphous carbon layer (20, 50 and 80 nm). Again, a RTA oven was used, this time to activate the monolayer catalysis. As there are different stages in the C-Ni system evolution in temperature [97], we decided that a fast cooling down was the best choice for creating a carbon monolayer, moving quickly from temperatures above the segregation limit to temperatures

below the precipitation limit, both dependent of the carbon concentration. As the carbon concentration that accepts the nickel layer is unknown for these conditions, several maximum temperatures were tested in order to find the optimal one. After a test, the temperature for this step was fixed to 1000 °C, as using lower temperatures (800 °C) proved to be insufficient to modify carbon, and higher temperatures (1200 °C) resulted in worse sample uniformity. After the thermal treatment, Ni was etched away using indistinctly HNO_3 : HCl (1 : 3) or FeCl_3 with successful results in both cases. A SEM image of the inhomogeneous carbon layer when the nickel layer was too thin (20 nm) is shown in Fig. 2.4.

Figure 2.4: scanning electron microscopy (SEM) image showing the layer with inhomogeneities (left) and the substrate (right). Ripples and thick carbon deposits are visible on the left part.

This inhomogeneity was due to Ni droplets formation, which left some areas uncovered with metal. On those exposed areas, there was a considerable amount of precipitated carbon. Raman spectra for different thicknesses are shown in Fig. 2.5. From all these measurements we conclude that 50 nm of nickel at 1000 °C for 30 s gave the best results, with the smallest D peak of all the samples. The outcome for 80 nm is not well understood, but uncontrolled temperature in the interface region is suspected to be involved in this result, as a 30 s temperature peak may be insufficient for this metal thickness. For all these cases, a 2D peak

appears, indicating that few layers of graphene are formed in the surface. The D peak is still high for some samples, indicating that we have a large amount of defects or nanocrystalline material. As the growth method implies the use of Ni as catalyst, the I_{2D}/I_G ratio can be used as indicator for the number of layers [45]. In this case, we have a full width at half maximum (FWHM) of approximately 50 cm^{-1} and a $I_{2D}/I_G \simeq 1$, indicating between 2 and 3 layers of graphene for the best case. This fact also showed that our heating system was unable to provide the needed cooling rate to change from precipitation (monolayer) to segregation regime (several layers).

Figure 2.5: Raman spectra variation for different thickness. The presence of the 2D peak indicates multi-layer graphene.

Conclusions of the growth method

As a summary of this method, it is important to emphasize that the underlying idea was to select the thickness of the precursor layer, and hence the amount of carbon available, by means of RIE, with important advantages such as the use of available equipment in the laboratory, or the possibility of dropping the requirement of a transfer process. Unfortunately, several disadvantages as the lack of homogeneity, the need of performing two heating steps, the outcome of an uncontrolled number of layers, or a restricted substrate choice were crucial to discard this method. Also,

some other parameters such as the accuracy in the temperature treatments or the initial carbon concentration on Ni remained uncontrolled. In addition, some electrical test showed poor transconductance, hence this material was discarded for device fabrication.

2.3 Graphene growth by CVD on Cu

Based on the unsatisfactory results obtained from the previous graphene obtention methods, once a CVD system was installed in the laboratory, all our efforts concentrated on CVD growth using the AIXTRON system.

As discussed in the introduction chapter, the knowledge of the critical factors involved in graphene growth has varied over time. Independently of the working pressure, either low pressure or ambient pressure CVD, which is system-dependent, the focus nowadays is on the carbon precursor introduction rate, the ratio of partial pressure between hydrogen gas and the precursor, and, most remarkably, the catalyst surface defect, contaminants, and oxygen contents. Our objective on the graphene growth field is to study the parameter space achievable in our system, and apply it to single layer graphene growth with the highest crystal domain size possible.

Growth system

The system used for this part of the study is the Aixtron Black Magic Pro installed at ISOM-UPM (Fig. 2.6a). Among other technical specifications, the most remarkable one is the cold-wall reactor design, which allows to reach fast heating and cooling rates. The carbon precursor gases available in our system are methane (CH_4) and acetylene (C_2H_2), where only the first one has been used in our growths, providing higher purity and lesser carbon concentration for the same flow when compared with C_2H_2 . Two graphitic heaters that enclose the sample region can reach temperatures up to 1250°C , where a showerhead inlet structure heats up the gas mixture. A pirometer focused on the surface can control the growth temperature. Also, the process automation enables higher accuracy and repeatability of the growth process, where all the parameters can be checked and compared later (flow rates, pressure, heating power, etc.). As an example, for a regular polycrystalline graphene growth, a typical process on this system requires less than two hours and is performed fully unattended once the sample is loaded onto the susceptor. The system is prepared for 4-inch wafers, although flat, square copper

foil from Alfa Aesar (99.8 % purity, 25 μm thick) with 5 cm $\times$ 5 cm sides has been adopted as our standard sample (Fig. 2.6b).

Figure 2.6: a) Aixtron BM Pro. b) Copper foil sample loaded on the system

As the growth pressure is normally on tenths of millibars, a quartz lid, separated from the substrate 4 mm, is placed on top of the growth substrate to avoid depositing copper on the reactor walls and elements [98, 99]. The copper foil on these experiments is not rolled, wrapped or in any enclosed form apart from the quartz lid, hence the programmed gas flows are close to the estimated gas concentrations next to the surface, as opposed to other reported processes [85, 100], where the gas flow is hindered due to the chosen substrate shape.

As the state of the art in graphene growth has varied quickly over time, one of the challenges while growing graphene with this system is to achieve the current $\text{H}_2:\text{CH}_4$ ratios, typically above 100:1, but which in some cases can be up to 2800:1 [47] or 6600:1 [101]. To overcome this limitation in our system, two different solutions have been implemented in our growth processes at the same time.

The first one is based on obtaining the smallest possible precursor flux, in this case, 2 sccm for CH_4 . For achieving this, an initial stabilization at 4 sccm during a few seconds is needed to turn on the mass flow controller. In order to avoid spikes in the flow rate (typically up to 8 sccm), a previous high flux step is needed on this gas line, just before starting to heat up the chamber. As the H_2 flux is also limited to 1000 sccm maximum, our highest achievable rate is $\text{H}_2 : \text{CH}_4 = 500 : 1$. With these flow conditions, the system is able to remain stable at 25 mbar without any problems, although the residence time of the active species is low compared to processes in the literature where less than 0.1 sccm is set. The second method is based on an in-situ oxidation step of the copper surface, where dry air is used as oxidizing agent at a temperature of 400 $^\circ\text{C}$ during 10 min. A similar step is performed by Hao et al. [85], where an ef-

ficient dissociation of hydrocarbons on oxidated surfaces leads to faster growth rates, up to five times faster when compared with oxygen-free samples, and to the suppression most of the nucleation centers.

The relatively low purity of the chosen substrates may be beneficial for graphene growth, as its oxygen content is higher than in purer foils. Right before the growth process, an electropolishing treatment is performed [102]. For this purpose, the foil is cutted in $6\text{ cm} \times 5\text{ cm}$ pieces, where a strip of $4\text{ cm} \times 1\text{ cm}$ is partially liberated from a 5 cm side and twisted upwards to provide electrical contact to the sample. As cathode, a planar copper mesh is placed parallel to the sample. A H_3PO_4 solution diluted in water at 55 wt.% is used as the electrolyte, where no extra additives are needed. As bubble formation in the anode may degrade the surface final roughness, the distance, maximum voltage and maximum current density must be fixed in the process. As electropolishing cell, a customized polytetrafluoroethylene (PTFE) cell of approximately $6\text{ cm} \times 7\text{ cm} \times 3\text{ cm}$ inner dimensions with two slots to fix both anode and cathode to a 3 cm distance was designed. For this geometry, it has been tested that with a maximum current of 450 A cm^{-2} and a maximum voltage of 2 V during 10 min, a polished, smooth surface is obtained. Afterwards, the sample then is immersed in DIW several times, and then dried thoroughly with N_2 flow.

Growth process

The growth process, depicted in Fig. 2.7. Once the copper substrate is loaded, the system waits to reach a pressure of 10^{-2} mbar, close to base pressure. An initial purge is performed, where Ar and the carbon precursor gas (CH_4) are kept flowing for several seconds and the base pressure is reached again afterwards. Then, the oxidation step keeps 150 sccm of dry air between 2 min and 10 min at a pressure of 1 mbar approximately. The temperature for this step ranges from 200 to 450°C in our experimental runs. Again, base pressure is reached after flowing the oxidizing gas. Thereafter, the process pressure is set to 25 mbar and the annealing starts. In order to keep the surface oxygen content while the temperature increases, only Ar flow is kept until the growth step starts, thus avoiding reducing gases.

Once the final temperature of 1030°C is reached in a stable way, the growth step starts. First, a flow of 1000 sccm of H_2 is set. After a short stabilization time, CH_4 flow is introduced into the camera, depending on the desired $\text{H}_2 : \text{CH}_4$ ratio. To study the graphene grain morphology, an unfinished growth is desirable, hence the growth time is limited to 10 min

Figure 2.7: Temperature and flow of process gases vs. time during the graphene growth process, with the different steps indicated.

for this purpose. For stopping the growth and starting the cooldown step, the precursor flow is turned off, and the reducing gas flow is decreased to 100 sccm to avoid undesired graphene etch. Also, higher Ar flux is set to increase the cooling rate. At the end, the sample is unloaded and the top surface is marked for reference.

Structural characterization

At the beginning, a reliable procedure to characterize the material is needed in order to link growth conditions with the resulting material quality. Due to availability in our institute, we chose direct SEM imaging of the copper surface after graphene deposition. This choice avoids transferring graphene to other substrate, or long-waiting times of optical mapping techniques. The main drawback of this technique is that it does not give any information about the material composition, thus a second technique, such as Raman spectroscopy, must confirm that the deposited material is indeed graphene.

Therefore, data from two samples with the same growth conditions but different growth times and hence different coverage (Fig. 2.8) was

checked with both Raman spectroscopy and SEM imaging.

Figure 2.8: SEM images of graphene on Cu foil grown without oxidation step a) during 10 min and b) during 60 min. c) Raman spectra for samples a) (sparse coverage) and b) (full coverage).

When the graphene growth is partial (Fig. 2.8a), SEM images allow to quantify the amount of nucleation centers and the graphene front formation dynamics, as good contrast between the bare copper surface and the graphene-covered one exists. The other contrast changes in regions away from the center graphene grain are due to different Cu grain orientations. In the case of full coverage (Fig. 2.8b), SEM images can still be useful, as a weak fringe pattern and wrinkled graphene are visible at high magnification, thus distinguishable from bare copper surface. To ensure that the deposited material is graphene, unused pieces of these two samples were transferred to SiO_2 substrates, where Raman characterization

was performed (Fig. 2.8c). The measurements were made with a 532 nm wavelength green laser and a 100x objective. High-contrast regions were chosen for these assessments, hence multi-layer graphene Raman spectra were obtained, with narrow G peaks (less than 40 FWHM) and low D-peak, indicating highly ordered material. The information obtained with our optical characterization is from a small region, as an automatic mapping stage was unavailable in the system. Concerning this previous drawback, it is important to point out that the problem is solved by using SEM imaging technique, where large areas of the material can be checked at once.

After checking the suitability of SEM imaging for growth characterization, two samples with different growth conditions were tested to evaluate growth speed and nucleation density in our system (Fig. 2.9).

For these two samples, all the conditions are kept as previously described (1030 °C, 25 mbar, 5 sccm CH₄, 1000 sccm H₂, 500 sccm Ar and 10 min growth time) except the in-situ oxidation step, where the first sample (Fig. 2.9a and Fig. 2.9c) was not oxidized, and the second one (Fig. 2.9b and Fig. 2.9d) was oxidized during 2 min with 100 sccm of dry air at 200 °C. The first acknowledgeable distinction between the two samples may be the size and shape of the individual grains. For lower oxygen concentrations on the surface, grains seem to be hexagonal and approximately 4 μm wide (Fig. 2.9c), whereas on the in-situ oxidized copper surface the growth front seems irregular, with lobular features and a width typically higher than 10 μm (Fig. 2.9d). With these approximate values, the front growth speed of the first sample is 0.4 μm min⁻¹, opposed to 1.4 μm min⁻¹ of the oxidized sample. This difference indicates that an oxidized surface allows graphene growth roughly three times faster in our conditions, a result in agreement with the findings of Hao et al. [85].

For assessing the nucleation density, high resolution images with low magnification have been obtained. With them, just by adjusting the image contrast and manually counting the number of graphene crystals in several 600 μm × 600 μm regions, the order of magnitude of the nucleation density can be estimated. For the less oxidized sample (Fig. 2.9a) values above 1 × 10⁴ cm⁻² are obtained, while for the in-situ oxidized sample the density is approximately reduced in an order of magnitude (Fig. 2.9b). From these results, it is clear that a controllable oxidation step prior to the growth aids to reduce the amount of graphene boundaries while increasing the speed of the individual graphene growth, and hence has been adopted on the succeeding growths.

Thanks to the deeper understanding of the growth process, the possibility to obtain high quality, large area graphene has been acquired. Nev-

Figure 2.9: SEM images of graphene on Cu foil grown during 10 min a), c) without in-situ oxidation step and b), d) with in-situ oxidation. a) and b) : 500x magnification images for nucleation density estimation. c) and d) : 5000x magnification images with differentiated graphene crystals.

ertheless, further optimization of the growth conditions is still needed.

Thermodynamical modeling

Finding the optimal conditions for graphene growth is a complex task, as each growth parameter can affect the conditions in different ways, sometimes even counteractively. For achieving a better understanding of the effects of each thermodynamical parameter modification and the system sensitivity to them, a classical thermodynamical model extracted from the literature [103] has been adapted for our achievable system conditions.

This model involves the assumption of two equilibrium phases (Fig. 2.10): a gas equilibrium phase in most of the CVD chamber volume, and a solid-gas equilibrium phase at the copper-gas interface. Both equilibrium phases are separated by a boundary layer but interconnected by mass transport across this layer. For our purpose, only the gas equilibrium phase will be calculated, as the solid-gas equilibrium phase depends directly from this one. As the chamber volume will enclose the majority of the particles, the first simplification that seems acceptable is to disregard the effect of the solid-gas equilibrium phase over the gas equilibrium phase. More complex effects, such as the role of oxygen on the catalyst surface [85], or the effect of existing carbon impurities on copper [104] are out of the scope of this model.

Figure 2.10: Diagram with two differentiated equilibrium thermodynamical regions. The gas phase is predominant inside the chamber, whereas the solid-gas phase is present only on the catalyst surface. Two mass transport processes are involved in the growth: internal surface migration on the solid-gas phase, and gaseous precursor transport across the boundary layer near the surface. [103]

Therefore, a simplistic Gibbs free energy minimization approach only

for the gaseous phase has been developed. The thermodynamical data for each gas component has been calculated using Shomate equations, whose coefficients have been extracted from the NIST Chemistry Web-Book [105]. In our case only Ar, CH₄, H₂ and their most stable dehydrogenated states, C₂H₂ and monoatomic hydrogen (H[•]) have been added to the calculation. Data obtained with this method has been compared to data from the literature [103] with coincident results on both. An alternative way to obtain this data is to use an existing chemical process simulator. DWSIM [106], a thermodynamics suite with a rich graphical user interface, has been used for this purpose. Although this suit lacks the possibility of using H[•], the results obtained for the rest of gases are in good agreement with the previous methods.

In our case, C₂H₂ and H[•] formation are used as indicators of carbon and hydrogen reactivity, which are estimated as the ratio between dehydrogenated states and its corresponding precursors ($100 \cdot \text{C}_2\text{H}_2/\text{CH}_4$ and $100 \cdot \text{H}^\bullet/\text{H}_2$, respectively). For carbon, methane income is considered as the only precursor, while for hydrogen, the hydrogen gas generation in methane decomposition is also accounted as a precursor. Nevertheless, our typical precursor ratio H₂/CH₄ above 100 ensures that the partial pressure of the incoming hydrogen in the system is the controlling parameter of the H[•] formation. In Fig. 2.11, the sensitivity of these two parameters to temperature and pressure variations is shown.

For this initial study, Ar flow is kept at 500 sccm, although flows up to 8000 sccm could reduce the reactive gases partial pressures while keeping the chamber total pressure in higher values. Also, the main conclusion that can be extracted from this sensitivity study is that both high temperature (Fig. 2.11a) and low pressure (Fig. 2.11b) enhance gases decomposition. Regarding the possibilities of thermodynamical modeling, a comparative study between results in our system and the best conditions from the literature could help to normalize the methane and hydrogen decomposition required to achieve the best graphene properties, independently of the system used. Therefore, this tool will be of great help for further growth optimization.

Figure 2.11: a) Temperature and b) pressure dependency of CH_4 and H_2 gases decomposition into their dehydrogenated states. The inlet flow conditions for argon, methane and hydrogen are kept constant (500 sccm of Ar, 5 sccm of CH_4 and 1000 sccm of H_2). Pressure in a) is 25 mbar and temperature in b) is 1030 °C.

2.4 Summary

In this chapter, the graphene production techniques available in our laboratory have been detailed, where the CVD technique stands out as the preferred one. Special emphasis has been given to the connection between characterization and growth. With the exploration of the parameter space of our system, greater control over the quality of the deposited graphene films is attainable.

Graphene Transfer

As detailed in the previous chapter, graphene growth on copper foil is the desirable method for implementing novel device concepts from the lab into the electronics industry, thanks to its improved quality and larger area when compared with other production methods. Nevertheless, its final application at the industrial scale is problematic, as a polymer-mediated transfer step to a suitable final substrate is still required. This kind of process is performed manually in most cases, although some previous efforts towards automation have been reported [10, 68].

In this chapter, we will focus on the details of the graphene transfer process step, first explaining the required initial target substrate and graphene source preparation, common to all kinds of transference. After this, we will elaborate on the manual transfer method, and finally we will depict an automatic transfer method developed in our institution [107], where the initial material quality is better preserved than during the manual process.

3.1 Substrate and sample preparation

Graphene transfer is a complex task, where tiny details can affect the quality of the resulting samples. As most of these steps are difficult to automatize without any industrial thrust, only on the most critical ones a serious effort towards automation has been exerted. In this section, the previous steps needed on both the graphene-covered copper substrate and the target substrate that are common for both the automatic and manual method will be described.

Substrate preparation

As our purpose is to use graphene for electronics, a crystalline silicon substrate with nominal 290 nm of thermally-grown silicon oxide on top has been selected as our testing platform due to its simplicity, where silicon oxide performs as a dielectric substrate and as a rigid graphene support for the next processing steps. The preferable substrate size in our case is $2\text{ cm} \times 2\text{ cm}$, as the resulting number of devices after processing is high enough (typically about one hundred) and our facilities are well-fitted for these dimensions.

An effective substrate treatment should achieve two goals: The first goal is to remove all types of residues that may be attached to the substrate, which would end trapped between graphene and the dielectric. The second goal is to prepare the surface with the required behavior (hydrophilic in this case). For the first one, an initial cleaning with organic solvents is adequate. It consists of immersing the substrate 5 min in hot, boiling acetone; a 5 min sonication, an isopropyl alcohol (IPA) rinsing and a final drying step with N_2 flow.

For the second goal, either piranha treatment (a mixture of H_2O_2 : H_2SO_4 in 1 : 3 volume proportion) during 1 min to 5 min or mild O_2 plasma may be enough to reach the desired hydrophilicity. Still, if more adhesion of the graphene to the substrate is required, another possible option is to incorporate self-assembled monolayers to the surface [108, 109]. In our case, we tested 3-aminopropyltriethoxysilane (APTES) for some of the samples. This treatment guarantees graphene adhesion to the surface, although may affect to the material doping [110].

Graphene on Cu sample

In order to detach graphene from the metallic catalyst, a protective layer (normally a spin-coated polymer) must be deposited on top of graphene, as a wet etching step is needed to remove the Cu foil. With this copper removal method, only one of the graphene-covered surfaces can remain unharmed. As copper substrates where graphene is grown can be extremely thin (sometimes thinner than $25\text{ }\mu\text{m}$ after electropolishing), a rigid carrier substrate is attached to it, typically a plastic as a polyethylene terephthalate (PET) sheet. Regular scotch tape applied over the edges of the Cu foil can both attach the metal to the plastic and avoid the resist overflow reaching the bottom surface of the copper, whose cleanliness is required for achieving total copper removal.

Once the back of the Cu is protected, the sample can be spin-coated

with PMMA (950K 2.5 % mass chlorobenzene). When the rotational speed is set from 4000 r.p.m. to 5000 r.p.m., a layer of selectable thickness of 0.25 μm or less is obtained. This thickness would make the PMMA/graphene system flexible enough for achieving conformal coverage on the target substrate after the transference [61, 111], and thus will improve the final graphene adhesion. This improved adhesion is required to perform PMMA removal by solvent dissolution rather than thermal decomposition [84].

As the protective plastic sheet on the Cu bottom part is no longer needed at this point, it can be detached to expose the graphene grown on the back side. Sometimes, the unwanted graphene layer deposited on this surface is composed of several graphene layers. Initially, a chemical Cu etchant was used for several minutes to remove this layer, and the sample was rinsed in DIW afterwards, ready for the transference using a fresh etchant solution. Over time, the used catalytic substrates have become thinner, and this method was no longer valid, as holes were created during this first etch step. Therefore, a mild plasma with the PMMA layer facing down was selected to remove unwanted graphene. Either the inductively-coupled plasma (ICP) system or a plasma cleaner have been successfully for this purpose.

After all this preparation, the sample can be transferred to the target substrate, either by the manual method or automatically.

3.2 Graphene transfer using a manual method

Once both the target substrate and the PMMA/graphene/Cu sample are prepared as previously explained, a manual transfer can be performed. For this purpose, Marble's reagent, an aqueous mixture of copper sulfate (CuSO_4) and hydrochloric acid (HCl), was chosen as Cu etchant. Other possibilities mentioned in the literature are iron (III) chloride (FeCl_3) or ammonium peroxydisulfate (APS). From these options, the FeCl_3 preparation was found to leave more residues and was discarded, while APS requires longer times than Marble's reagent for dissolving Cu completely.

In a typical process, the sample is placed floating in 50 mL of etchant solution on a 100 mL beaker. Typically, a 45° angle approach to the liquid surface will allow the sample to float without being immersed. For this, a secondary rigid substrate can be used as temporary carrier. Then, the etch step is performed at 60 °C during 30 min, leaving a fragile

PMMA/graphene membrane floating on top of the etchant liquid.

Based on the initial approach for graphene transfer [45, 48], the floating membrane is picked with an intermediate substrate from the liquid. A flat, chemical resistant, and conductive substrate is preferable for this procedure. A silicon wafer piece can fulfill these requirements. Interactions between the membrane and the intermediate substrate at this stage may create wrinkles and defects on the membrane, and these generate a low process yield and sample degradation. This procedure is commonly called *fishing*, and our goal in this thesis is to avoid it by means of an automatic process.

Once the membrane is caught from the etchant using the intermediate substrate, it is quickly floated onto DIW for at least 5 min. A second and third fishing steps are needed, where DIW is renewed. The reason behind this is to remove all possible etchant residues, always using a clean intermediate substrate as carrier. Finally, the target substrate, in this case, an insulating surface, is used for the final catch. As in the previous rinsing steps, the graphene membrane may end up damaged and oddly-centered.

Although the manual method is simple, its variability is delaying the progress of the material into the industry. In the next section, a method to overcome the issues involving this processing step is presented.

3.3 Graphene transfer using an automatic system

The focus in this section is to overcome the main issues that arise during the transfer process, which mainly are two: the outcome variability and the limited scalability of the operator-dependent steps. For solving these, a new system that automatically transfers the graphene layer grown on Cu foil to an arbitrary target substrate is demonstrated, avoiding the need of an operator and the waiting times (for the operator) of a typical manual transfer process. Furthermore, on Chapter 5, the quality and yield of the automatically transferred graphene are tested, and the improvement compared to that manually transferred is demonstrated by means of optical and electrical characterization of graphene field-effect transistors (GFETs) fabricated with both kind of processes. The system reported has been developed for lab-scale transfer, but it is fully scalable and, thus, suitable for industrial applications [112].

The underlying idea on the automatic transfer system is simple: if the

membrane movement is restricted and controlled, and at the same time the liquid level, temperature, and composition can be selected, the steps where the membrane must be fished will be avoided, reducing significantly the procedure risks.

As several parameters have to be controlled separately, various subsystems are required. The automatic transfer system and its subsystems are described schematically in Fig. 3.1 [107].

Figure 3.1: (a) Schematic of the automatic transfer system components. A microcontroller connects sensors and actuators. Liquid flows only from the DIW tank to the etch beaker and from the latter to the residues tank. Temperature is controlled with a heating plate and a temperature sensor. (b) PTFE holding structure for the automatic transfer system. The retainer tubes, mounted on the alignment base, keep the membrane centered. The target substrate is placed in the substrate tray underneath. The inset shows a detail of the stack of SAMs coating the inner wall of the retainer tube (c) Schematic of the centering mechanism of the membrane inside the retainer tube, where both electrostatic interaction and capillary forces take place [107].

Graphene position control

As starting point, the polymer-protected graphene layer on a metal foil is introduced into a polytetrafluoroethylene holding structure contained in a regular borosilicate glass beaker. This plastic structure will serve as the base element to fulfill the first part of the underlying idea: to restrict the membrane movement. The PTFE holding structure has been specifically designed to assist the automatic process (Fig. 3.1b). The chosen material avoids degradation and contamination issues, a topic of remarkable importance to achieve the maximum intrinsic material properties on the final devices. Other options were considered, such as polylactate acid (PLA) from a 3D printer, or polycarbonate. The first option would allow a compact system design, whereas the second one has similar chemical resistance than PTFE while being cheaper. Nevertheless, either due to leakage or to chemical reactivity issues respectively, these options were discarded.

The structure consists of three parts: the substrate tray, where the target substrates are loaded, the retainer tubes, that ensure the centered position of the graphene film, and the alignment base, that fixes the position between the substrate tray and the retainer tubes. A two-substrate loading system was designed to demonstrate the parallel processing capability of the system and to optimize the space inside the beaker. However, the system can be scaled-up, both in the size of the substrates and in the number of simultaneous substrates. As the interaction between the PTFE pieces and the fragile, floating graphene membrane is not the required one, additional treatments must be performed.

A special treatment carried out to the inner surface of the retainer tubes is able to modify the PTFE properties to assist the automatic transfer process (inset in Fig. 3.1c). A stack of self-assembled monolayers (SAMs) [113] is placed onto these inner surfaces. This kind of molecular coverage enables a change both in the hydrophobicity and the charge of the desired surface. For adding this coverage to the tubes, several steps must be performed. First, the retainer tubes are immersed in piranha solution during 5 min and rinsed afterwards thoroughly in DIW. This step ensures the cleanliness of the pieces and is intended to prepare the chemically inert PTFE surface to retain some oxygen groups on it, which on the next step would provide anchorage to the charged molecules. For the same reason as in the sample preparation, an oxygen plasma may help to enhance the effect generated by the piranha step. N_2 drying is performed after each DIW rinsing step. Next, the retainer tubes are immersed in an aqueous solution of polystyrene sodium

sulfonate (PSS) (2 wt.%) for 30 s, rinsed in DIW, and dried with N₂ afterwards. After this, another 30 s immersion in an aqueous solution of polydiallyldimethylammonium chloride (PDDA) (2 wt.%), DIW rinse and N₂ drying are performed. A last PSS treatment identical to the previous one is performed. Therefore, the final coating is composed of a layered PSS/PDDA/PSS structure.

This coating makes the PTFE surface hydrophilic, opposite to the hydrophobic character of the untreated material, and charges it negatively. The hydrophilicity avoids the liquid surface tension to damage the graphene during the transfer process, maintaining the graphene away from the walls of the retainer tube. Also, once the metal catalyst is etched away, the graphene layer inside the retainer tube is forced to stay centered due to a combined effect of the meniscus formed on the wall and the electrostatic repulsion. It has been found that the electrostatic repulsion between the retainer tube inner surface and the protective polymer layer is critical. In our case, both elements are negatively charged (Fig. 3.1c). Therefore, adding a SAMs treatment to the inner wall surface with the wrong charge culminates with the graphene membrane adhered to the wall, while the liquid meniscus is the same as the obtained with the correct ending charge. As the target substrate is centered with respect to the retainer tube by the alignment base, this mechanism grants the final centered position of the transferred graphene onto the final substrate.

Liquid control: system modules

The automatic system has been designed to carry out the second part of the underlying idea: to control the liquid that is in contact first with the bare copper back surface, and later with the PMMA/graphene membrane. Therefore, a programmable control system and the subsystems that allow to select the temperature, the liquid flow, and the drying conditions during the process are presented in this section.

The first of these subsystems is the electronics control. It consists of an Arduino UNO microcontroller that is used for connecting, timing and reading the other system modules. A serial connection to a PC is used for programming and logging the process. This kind of embedded system is widely used for prototyping, but a cheaper and tailored designed could carry out the same tasks, where the PC would not be necessary.

Regarding the fluidics, two peristaltic pumps are used for introducing and removing liquid from the etch beaker. Chemical-resistant tubing connects the three containers of the liquid system: the etch beaker, and the DIW and the residues tanks. For the liquid flow, three states are avail-

able: idle, liquid introduction and liquid removal. By means of two check valves, the liquid can only flow from the DIW tank to the etch beaker and from the etch beaker to the residues tank, corresponding with the liquid introduction and liquid removal states in the peristaltic pumps system, respectively. The on/off pump conditions are controlled by means of relay switches, as the required power to actuate them is higher than the one provided by the microcontroller ports.

A contactless, ultrasound-based distance sensor reads directly the liquid level inside the etch beaker, providing the feedback signal for controlling the fluidics and determining the filling state. This sensor does not disturb the liquid surface, and is reliable even when the liquid composition is changing, as opposed to infrared sensors tested in previous system versions. The distance sensor is mounted on a micropositioner that allows fine tuning the initial distance before running the automatic process. Minimum and maximum liquid levels are defined in order to keep the graphene constantly floating in the liquid without touching the target substrate underneath until the very last step of the transfer process. This is a key characteristic of the automatic transfer system, as compared to the manual transfer methods, where the sample is changed abruptly to different liquid solutions using an intermediate holding substrate. Thus, the all-fluidic automatic manipulation prevents the graphene from any strain, damage, or contamination induced by the intermediate holding substrate, ditching the need of a membrane catching step (or *fishing* step). In Fig. 3.2, the conductivity change during the liquid modification is shown. On it, the initial etchant solution is diluted with DIW, and an exponential decrease in the conductivity is appreciated, which indicates that the method ensures the etchant removal.

The heating plate, along with the temperature sensor, constitute the temperature control unit. A proportional-integral-derivative (PID) controller is used for setting the temperature, being optimized for the working temperature range of the system (20 °C to 60 °C). As the room conditions may be uncontrollable, this subsystem ensures, even for room temperature (RT) conditions, that the system time constraints will be respected consistently. In order to compare with the manual transfer, the temperature is set at 60 °C during 30 min, although etch conditions that involve lower temperatures and longer etch times are being explored.

Finally, a fan positioned on top of the retainer tubes is activated during the last step of the transfer process to help drying the samples. This step is not always necessary, but it may ensure that at least one side of the sample is attached to the target substrate, thus keeping its centered state before collecting the transferred sample from the tray.

Figure 3.2: Ionic conductivity measurements of the liquid inside the automatic transfer system during the dilution steps. Conductivity values close to Type I ultrapure water can be reached in 26 dilution steps. [107].

Automatic transfer operation

Once all the subsystems have been described, how the system works step by step can be explained. As prior preparation, if the target substrate is chemical resistant, it can be loaded onto the substrate tray before starting the automatic system operation. After this, the whole PTFE structure is introduced inside the etch beaker, with the alignment base and retainer tubes in place as shown in Fig. 3.1b. The beaker is manually filled with the etchant solution, and the graphene sample (with the graphene surface coated with a protective polymer layer) is carefully introduced inside the retainer tube, leaving it floating with the unprotected metal surface in contact with the etchant liquid. As in the manual method, Marble's reagent has been used as etchant and PMMA, spin-coated at 5000 r.p.m., has been used as protective polymer. At this initial stage, the sample may touch the inner walls of the treated retainer tube surface since the metal screens the electrostatic repulsion. Finally, the distance sensor on top of the beaker is checked through its electronic readout and readjusted if needed, and the tubing end is introduced at the bottom of the beaker. After this point, the system operation is fully automated with no need of operator intervention.

In Fig. 3.3 the series of steps in the automatic transfer process are detailed. First the temperature is raised to 60 °C and a 30 min timer starts. As the metal is being etched, the screening is canceled out, allowing the self-centering mechanism of the membrane to act. Once the metal is fully etched, the etchant liquid is left cooling down for 20 min. At this point, the PMMA/graphene film is floating freely inside the retainer tube. Then, the peristaltic pumps are set to the liquid removal state until the minimum liquid level is reached. Afterwards, a set of diluting steps starts. First, DIW is introduced in the etch beaker using the liquid introduction pump state until the maximum liquid level is reached. Second, the diluted solution in the etch beaker is removed with the peristaltic pumps set to the liquid removal state until the minimum liquid level is reached. These two steps are repeated consecutively several times in order to minimize the etchant concentration in the final liquid. Repeating the process six times was found to be a good compromise between a reduced process time and a good overall process cleanliness, as the liquid molarity is decreased more than five orders of magnitude in a 2.5 h period. Further cleaning steps can be performed without meaning a hassle for the operator, as the process is automated.

After the dilution loop, the target substrate can be manually loaded onto the system. At this point, the critical part of the transfer process starts, filling the etch beaker with DIW up to the maximum liquid level, and then draining it completely. In this step, the PMMA/graphene film is softly transferred to the target substrate, in a centered position due to the combined action of the electrostatic repulsion forces and the liquid meniscus. Once the liquid is depleted, the sample lies on top of the target substrate, though a thin water layer separates the graphene from the substrate surface. In order to remove this water interlayer and have a strong adhesion to the surface, the sample may be heated up to 40 °C for 20 min while a perpendicular air flow generated with a fan helps to efficiently dry it out. This last step is not necessary as long as the sample is quickly moved from the system to the next processing step.

Once the automatic process ends, the target substrate is unloaded from the system and the PMMA is removed from the graphene using acetone or other solvent. Extra cleaning steps can be performed once reached this point. In Fig. 3.3i, the final substrate with the transferred PMMA/graphene film is shown. With the conditions described above, the whole automatic transfer process lasts 3.5 h, with no action needed from the operator during that time.

In addition to the technological advantages inherent to an automated process (no handling skills required, good reproducibility, large through-

put, etc.), an automatic transfer process is expected to provide better quality graphene in terms of cleanliness (i.e. lower amount of residues) and structural integrity, since the manipulation of the graphene is done in a smoother way with no intermediate holding substrate involved. A detailed analysis of the automatic system output is presented in Chapter 5, where the comparison with a manual transfer procedure and the discussion can be found.

Figure 3.3: Process flow diagram of the automatic transfer. (a) The sample is introduced in the system containing the etching solution. (b) The temperature is set to 60°C during 30 min for the Cu etching state. (c) Once the sample is completely free of Cu, the etchant solution is drained. Subsequent DIW dilutions (d) and liquid removal steps (e) are performed to remove any trace of the etchant solution. (f) After 6 iterations of steps (c) and (d), the sample is floating in pure DIW. (g) DIW is fully drained and the PMMA/graphene membrane is transferred to the target substrate. (h) The temperature is set to 40°C during 20 min to remove the interstitial water between the graphene and the substrate. (i) Transferred PMMA/graphene membrane to the target substrate after the process. The photographs show the centered position of the membrane inside the retainer tube along the whole process (the dashed red line is a guide for the eye) [107].

3.4 Transferred sample preparation

Either by the manual or automatic method, at this point of the sample processing the same structure was obtained through both processing paths. It consisted of the target substrate with a graphene/PMMA membrane on top (Fig. 3.3i). Ideally, a thin water layer on the substrate/graphene interface may be desirable, as slowly removing the interstitial liquid relaxes the PMMA layer and improves the adhesion between graphene and the substrate. For this liquid removal, a membrane vacuum pump has been used, where any wrinkle or water pockets on the membrane got removed easily, without damaging the material. Other options, such as perpendicularly directed N_2 flow, are also valid for this purpose, but haven't proved to be as effective as mild vacuum conditions.

The samples were stored overnight under vacuum (typically 8 h). Once the adhesion to the substrate was guaranteed, the polymeric layer had to be dissolved. Note that heating steps after this point were avoided, as increasing the interaction between the substrate and graphene is known to contribute to increased doping levels [84]. As the adhesion between graphene and the polymer is strong, a low dissolution pace is desirable. Either RT acetone for 2 h or acetic acid [114] during 24 h were used for this purpose, but no changes were appreciated between these two methods, hence acetone was kept as the preferable one. Other experiments were made according to a different approach [115], where high temperatures during polymer dissolution were intended to change the polymer-solvent dynamics to a more favorable one. Hot n-methyl-2-pyrrolidone (NMP) at 90 °C or more was selected as the solvent with this idea in mind. Although the remaining parts of graphene attached to the surface were almost pristine, the solving action was too strong when compared to the graphene/substrate adhesion, which is limited, and ended up detaching most of the graphene layer.

Once the polymer removal step has been performed, the sample was rinsed in IPA to remove the solvents, and dried with N_2 flow. On this state, the sample is kept under clean room conditions, ready for the next processing steps.

3.5 Summary

In this chapter, two options for transferring graphene from the growth template to a desired final substrate have been presented: one manual, other automatic. Among them, the automatic transfer performed

with our system via the all-fluidic manipulation of the graphene should avoid mechanical damage, strain and contamination when compared to the manual transfer. A simple idea has been carried out, where an induced electrostatic repulsion between the graphene and its container to center the film respect to the target substrate is at the core of the system functionality. This structure avoids random, risky catching of floating membranes that hinder the manual transfer. In addition to the intrinsic advantages of any automated process, this system, initially developed as a lab-scale tool, is fully scalable for industrial applications [107], allowing the large-scale transfer of graphene films with superior quality to arbitrary substrates.

This technology has conducted to a granted patent in collaboration with MIT, and it is being used in several graphene-related projects in optoelectronics, energy harvesting and biosensing performed in our group at ISOM-UPM.

Nevertheless, as the state of the art stage in graphene research evolves quickly, multiple changes are still being made in order to adapt our results to cutting-edge research level imposed by the scientific community. As an example, numerous test with low temperature [116] are being conducted, where the amount of residues is lowered even further by using polyvinyl alcohol (PVA) as intermediate level. Other changes in the etching and cleaning steps and its timing can also contribute to improve the material quality.

Graphene Processing

Independently of the graphene transfer technique used, and also independently if the goal is to characterize optical and electrically graphene or to seek for any material applications, graphene must be manipulated employing technological processes. As graphene is an intrinsic 2D-material, traditional planar process technology from the semiconductor industry can be easily adapted for device fabrication, thus the material can benefit from decades of development and industrial investment. This fact is a big advantage compared with other promising nanomaterials for electronics such as CNT, where the adoption of planar technology is painful, and the best packing density achieved is still orders of magnitude lower than in the state of the art digital circuits [117]. For graphene, it does not exist such a limitation.

When the goal is to fabricate GFETs, the basic processing steps that need to be performed involve defining regions in the material, both for insulating and defining the device geometry, etching certain regions, and depositing other material, such as metals, dielectrics or other protective layers. As graphene surface cleanliness strongly affects its electrical properties, sample cleaning processes will also be emphasized. All the graphene samples used in this section are CVD graphene grown on Cu foil. A scheme of the process is available in Fig. 4.1.

Figure 4.1: Process overview. A backgate contact is created first. Lithographic, dry etching, and deposition methods are alternated in order to define the device geometry.

4.1 Target substrate and backgate contact

As noted in the previous chapter, CVD graphene is typically transferred from the catalytic metallic substrate to a different one that is suitable for the desired application. When aiming to fabricate GFETs, crystalline silicon substrates (n^{++} doped) with 290 nm of thermally-grown silicon oxide on top have been used. In this layered structure, doped silicon acts as an extended metallic plate that enables device gating (called typically *backgate* in the literature), whereas silicon oxide performs as gate insulator and rigid support. The thickness of the oxide has been selected to enhance optical contrast between bare substrate regions and graphene-covered ones [93]. Dielectric strength for thick, thermally grown silicon dioxide is approximately 7 MV cm^{-1} [118], allowing to bias the gate with up to 200 V without reaching dielectric breakdown conditions. Nevertheless, it has been found for some of our devices that above 100 V gate bias, non-reversible gate leakage appeared. Therefore, gate bias voltage has been limited to 100 V and the gate leakage current has been limited to 10 nA for devices as small as $2.1 \times 10^{-8} \text{ m}^2$ including the metal contact area. This approach avoids damaging the dielectric and affecting the device performance.

For adding a front contact region to the doped-silicon backgate, the silicon oxide is removed mechanically using a diamond scribe in zones far from the active sample zone. This way, the doped silicon is exposed and the backgate can be contacted from the front part of the sample. This process is done just after the graphene transfer process, while the polymer layer is still protecting the graphene film. An alternative method involving buffered oxide etch (BOE) prior to the transfer may be used [119] to avoid scratching the oxide. Before metal deposition steps, these exposed Si zones are cleaned from polymer in order to deposit metal on them.

4.2 Patterning

Device patterning can be performed using several different lithographic techniques. A common, simple way to pattern devices is by means of a shadow mask [120–123]. This technique is cleaner compared to resist-based ones, as the patterning is done under vacuum conditions without covering the sample with any type of photoresist. It can be useful for specific device designs, and it is mostly used for defining the device contact area in a strip-shaped manner. However, when insulation between

devices is needed, a more adaptable method has to be used.

One of these methods is electron beam lithography (EBL). It has been extensively used for proof-of-concept devices that rely either on exfoliated graphene [1, 38, 124], 2D materials heterostructures [40, 125] or on oddly-shaped, CVD graphene single crystals [126]. Although it permits to design devices with features on the nanometer scale with a customized layout, EBL is not as fast and cost-efficient as other competing techniques. Nevertheless, groundbreaking frequency-cutoff values for GFETs [87, 127] are only possible using this lithography method. In this thesis, electron beam lithography has been used for some electrical measurement tests. A transmission line model (TLM) structure as the one shown in Fig. 4.2 can be used to evaluate both the resistivity and the contact resistance of the material.

Figure 4.2: a) Optical microscope 100x image showing an EBL customized layout with TLM and Hall structures for an initial electrical characterization and b) 200x detail showing graphene with better contrast.

Alternatively to the previous methods, deep-UV optical lithography is also a good choice for device patterning. Apart from being a resist-based method, hence affecting the surface cleanliness, one drawback of this technique is that an optical mask must be designed for each application, limiting the device geometry flexibility. To cite some advantages, fair resolution (in the μm scale), large sample area, increased device density and yield [50], or edge definition are key factors for choosing this technique over the rest.

For improving the optical mask alignment during consecutive patterning steps, in some target substrates Ti marks were deposited prior to the graphene transfer. This step is not necessary, but reduces the alignment

time, as bare graphene is difficult to observe using the mask aligner optical system, even when using contrast-friendly substrates.

For implementing this technique, the Karl-Suss MJB4 mask aligner (HgXe lamp, 250 nm) has been used. As a standard procedure, PMMA 950K (5 wt.% in chlorobenzene) is spin coated on the sample at 4000 r.p.m. during 1 min, and then soft baked at 160 °C during 10 min, resulting in a 0.5 μm coating layer. The system is used in the contact lithography mode with long exposition time, nevertheless resulting in well-defined edges, necessary for a good lift-off.

4.3 Dry etching

As device performance relies on its geometry, etching graphene from selected areas is a necessary step in device fabrication. Despite graphene is a single atomic layer, the C–C covalent bonding results in low chemical reactivity. Therefore, mild wet etching techniques only work on edges or lattice defects. In contrast, very strong oxidative mixtures such as Piranha are able to remove graphene effectively, but they also may attack metal structures or polymer masks and are not suitable for fabrication purposes. Layer by layer graphene removal using defect generation and HCl treatment [128] may be an option for certain cases, but the preferred graphene removal method in the literature is the reactive ion etching (RIE), where oxygen plasma anisotropically burns the exposed graphene regions. For optimizing this technique, an optical etch-point detection system permitted us to select the chamber conditions. As a result, a 30 s mild plasma (20 W at 80 mTorr) ensures the graphene removal whereas avoids affecting graphene protected regions.

4.4 Metal contacts

Even though graphene is accessible from the device top surface, reliable metallic contacts are needed to improve the interaction with the electrical measurement probes, contributing also to the device geometry definition. As conduction between the graphene basal plane and a metal is inefficient [129], metal-dependent [130], or even leads easily to a Schottky barrier formation when transferred onto semiconductors [131], several strategies to overcome this issue have been reported in the literature. Some of them rely on contacting graphene edges with the metal, either using one-dimensional contacts [132, 133] or by means of patterned re-

gions [134, 135]. Another simple, well spread strategy is based on metal-graphene hybridization [136] in conjunction with large metal-graphene interaction areas.

For the latter contact mechanism, the metallic stack is typically composed of two layers: a first layer for improving adhesion with the graphene, typically formed with Ti, Ni or Pd, and a second layer of thicker metal, that avoids oxidation and adds robustness to the metal pad. Reliable contacts were obtained for the regular electrical characterization when Ti/Au, 15/80 nm thick contacts were deposited. For some special cases, such as Hall effect measurements, the Au thickness was increased to 200 nm to avoid scratches and other issues while using rough probe positioners.

4.5 Lift-off

During the lift-off procedure, the sample has to be handled with care, as adhesion between the metal contact and graphene is poor at this processing stage. In our initial experiments, some samples with residues attached to graphene led to low production yield, hence prior to the metal deposition the surface cleanliness must be ensured. Both hot acetone with strong convective flow and sonication can affect the layer integrity and therefore are avoided in the process. Only mildly warm acetone and gentle shaking are necessary for a successful lift-off. It is worth mentioning that hardened resist, deposited one or several days before metal deposition, leads in general to worse results.

4.6 Device cleaning by annealing

After all the processing steps, a final in-situ device cleaning prior to the electrical device characterization is necessary for removing adsorbates from the surface, primarily water molecules [137] that may generate p-type doping through $\text{H}_2\text{O}-\text{O}_2$ redox reactions [138]. This process is performed under vacuum conditions and heat-assisted, either by the current-cleaning method [139] (Fig. 4.3), or by mild sample heating [120] (Fig. 4.4).

In the current-cleaning method, resistive heating is localized in the device active region, therefore it has proven to be device-dependent and difficult to control. As a result, sometimes burst regions arise that modify the device electrical properties. As the local temperature reaches values

Figure 4.3: I-V characteristics from a back-gated transistor ($W = 100 \mu\text{m}$; $L_g = 20 \mu\text{m}$) before and after current cleaning at 500 A m^{-1} during 30 min.

Figure 4.4: I-V characteristics from a back-gated Hall structure ($W = 120 \mu\text{m}$; $L_g = 720 \mu\text{m}$). Each heating step is performed during 20 min under vacuum conditions. A slight shift in the Dirac voltage is observed.

above a certain temperature (typically close to 300°C), graphene interaction with the substrate is increased, leading to substrate-induced doping [84, 140, 141]. For the case depicted in Fig. 4.4, where an APTES-treated surface ($\phi = 3.9 \text{ eV}$ [142]) is used [109], a clear shift from p-doped ($V_{Dirac} > 0 \text{ V}$) to n-doped ($V_{Dirac} < 0 \text{ V}$) graphene is achieved when graphene interacts with the amino-terminated molecules anchored

to the surface.

For the thermal cleaning method, an external heater is employed for adsorbate removal under vacuum conditions. In our case, a Janis CCR-10 probe station (Fig. 4.5), which allows heating temperatures up to 675 K, is used to perform this procedure. In Fig. 4.4, the doping changes for each temperature step is shown, clearly visible in the Dirac voltage shift to the left (lower p-type doping). As previously noted, annealing steps at high temperature lead to unwanted substrate induced doping, therefore our typical cleaning is performed at 500 K in 1 h steps.

Figure 4.5: Janis CCR-10 vacuum probe station used for device cleaning and electrical characterization. An external light excitation source and RF probes increase the versatility of the system.

4.7 Summary

In this chapter, necessary processing steps to convert transferred graphene samples into devices were detailed among other topics, such as in-situ cleaning prior to the characterization. Nevertheless, these processes are in constant evolution as graphene literature gets broader. Therefore, the challenges that are faced vary quickly over time. As an example, the way metal interacts with graphene encourages to change to a two-step metal deposition process, where increased adhesion of the metal pads is accomplished using the bare, uncovered substrate area surrounding graphene regions.

On the next chapter, it will be emphasize how these processing steps may affect the final device quality, as well as how to decouple processing-induced issues from the intrinsic material properties.

Graphene Characterization

Once graphene is processed into field-effect transistors, as described in Chapter 4, the outcome device quality has to be assessed. In order to extract as much information as possible from both the devices and the performed processing steps, several analysis methods based on the electronic and optical properties of graphene will be implemented. With this objective in mind, the chosen course of action has been divided into several steps: The first step is to select a model among the literature, adapt it for our needs, and ensure that the implementation works. The second one, to apply the developed method to the electrical and optical experimental data obtained from the fabricated devices. Finally, the last step is to compare the extracted data of devices that have had differences during their fabrication. In this case, the differences between manually and automatically transferred samples will be discussed.

In terms of electrical properties, a first principles physical model has been selected [79] as the starting point. This choice is backed up when considering the amount of variables included in it, such as geometric parameters, dielectric properties, fixed charge sheet density, and, more importantly, electron and hole mobility in graphene. These last properties are good indicators of the device quality, which is of the highest importance, as is directly linked to the graphene crystalline domain size remarked in Chapter 2. An uncommon property of the selected method is the possibility to decouple intrinsic from extrinsic device performance, allowing us to differentiate between material quality and processing-related issues.

To ensure that our model adaptation works properly, several device characteristics both from the literature and the ones fabricated at ISOM-

UPM have been tested. This way, a wide range of material qualities and device geometries have been checked within the model, and a physical framework has been shaped into a tool for electrical device characterization.

As an alternative characterization method, Raman spectroscopy, and more precisely, Raman mapping of the device active area, is a desirable method for characterizing graphene by optical means, as explained thoroughly in Chapter 1. The Raman spectrum peaks, their frequencies, and their intensity relations are deeply connected with the material crystalline structure and, therefore, its electrical properties. In this case, the selected initial model [84] is far easier to implement than the electrical model. Therefore, there is no need to validate the method in a deeper level than the authors do; only the generalization and implementation of the equations are needed.

With all these tools at reach, they can be applied to the samples to check differences between samples transferred manually and automatically, thus providing the ability to compare the transfer methods themselves. It is worth mentioning that both characterization methods end up into a cohesive conclusion.

The chapter is structured with the electrical characterization method discussion first, then the optical characterization method discussion, and finally the simultaneous application of both to compare the manual and automatic transfer.

5.1 Electrical characterization

Graphene is nowadays one of the best candidates for future high-speed electronics [71], as its intrinsic carrier mobility has been theorized to be as high as $200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [69, 70] at RT, a figure of merit only possible to obtain due to the ballistic carrier transport regime. As explained in Chapter 4, a simple yet ubiquitous device that can exploit this property is the FET, called GFET [73] when fabricated in graphene. Cut-off frequencies for these devices up to 300 GHz [42, 74] can be found in the literature, just to help to grasp the idea of how fast is this progress. In these three-terminal devices, the typical name convention is gate (G) for the contact that modulates the perpendicular electric field of the device, and drain (D) and source (S) for the contacts that modulate the electric field across the device and define the active region. The gate is separated from the active region by a dielectric, whereas source and drain are

directly in contact with the material. This configuration is depicted in Fig. 5.1.

Figure 5.1: A simple scheme with the field-effect transistors elements names.

In order to understand GFET properties and electrical behavior, several models that correlate electrical characterization measurements and graphene properties have been developed. Some of these models can be used as a method to extract electrical parameters from the experimental drain-source current (I_{DS}) versus gate-source voltage (V_{GS}) curves. An ubiquitous compact method [75] is widely used for this purpose [46, 50, 58, 76]. It consists in fitting the I_{DS} vs. V_{GS} curves to a equation model with three fitting parameters: FET carrier mobility (μ_{FET}), contact resistance (R_C), and fixed charge sheet density (n_0). The first parameter, μ_{FET} , indicates the quality of the transport across the material. R_C is an indicative of how efficient is the electrical connection on the metal-graphene interface, and the last parameter, n_0 , indicates the concentration of dopants, either intended or unintended, that are close to the graphene.

However, due to its simplicity, this model cannot separate between electron and hole carrier values. An optimized version of the compact method reported by Zhang et al. [77] relies on the capacitance characterization for obtaining a more accurate oxide capacitance. Nevertheless, it still lacks features such as different electron and hole mobilities, or direct correlation between the extracted features and the material properties. Methods based on silicon FET theory [78], especially designed for circuit integration modeling, use empirical equations and are focused on short-channel devices. They require short computation time, but again lack of differentiation between carrier properties and of a clear connection between the device output characteristics and the physical parameters of the material.

Therefore, an extracting method that distinguishes between electron and hole mobilities and that relies on fundamental physical parameters is needed. In this section, a method that addresses these two issues while keeping all the information of the previous methods is presented.

As anticipated, a theoretical model based on first principles [79] has been chosen as the underlying physical framework. This model allows to correlate the GFET transfer characteristics with the electron and hole carrier mobilities, the fixed charge at the surface and the contact resistance. In contrast with all the other models, where the carrier concentration is approximated with a simple formula, this model makes use of the Fermi-Dirac distribution and the density of states in graphene to accurately model the electron and hole carrier densities. This enables to understand the device operation from a physical perspective, linking the Fermi energy level, the two carrier local densities along the channel, and the total current with a closed set of equations. It also lets us to differentiate between electron and hole properties, which is a highly appreciated feature for asymmetric devices, as may occur when doping through substrate proximity [143] or organic molecules [144]. Another advantage of this model is the possibility of checking device performance in a compact way, allowing us to find issues during device processing, such as the quality [130] or type [145] of metal contact, or the unintended doping concentration [120, 137].

5.1.1 Electrical model framework

To be capable of including a theoretical framework into a characterization tool, which enables both accessing to raw experimental data and fitting it to a theoretical model, all the electrical characterization method that is presented in this thesis has been coded using *python* programming language, whose existing libraries are extremely powerful for research activities.

Here, a brief description of the available equations and the involved parameters are presented. In the chosen model [79], most of the equations are directly derived from the energy-momentum dispersion relation of graphene, allowing us to correlate the device behavior with intrinsic material properties. Using the local Fermi energy across the device channel, it is possible to calculate numerically the electron (n) and hole (p) local densities. These quantities are typically measured in cm^{-2} , which implies a pure two-dimensional material. The link between all those quantities is explicitly depicted in equations 5.1 to 5.4:

$$n = N_G \mathcal{F}_1(\eta_F), p = N_G \mathcal{F}_1(-\eta_F), \quad (5.1)$$

$$\eta_F = \frac{\varepsilon_F - \varepsilon_D}{k_B T}, \quad (5.2)$$

$$N_G = \frac{g_s g_v}{2\pi} \left(\frac{k_B T}{\hbar v_F} \right)^2, \text{ and} \quad (5.3)$$

$$\mathcal{F}_i(\pm\eta_F) = \frac{1}{\Gamma(i+1)} \int_0^\infty \frac{u^i}{1 + e^{\mp\eta_F} e^u} du, \quad (5.4)$$

where g_s and g_v are the spin and valley degeneracies respectively, which indicate the amount of electrons that can coexist at the same energy level. As two different electron spins are possible and two Dirac cones exist (at K and K') in the Brillouin zone, four electrons are allowed for each energy level. ε_F and ε_D are the Fermi energy and the Dirac energy respectively. While the first one may vary depending on the material environment, such as the perpendicular electric field, as happens in FETs, the Dirac energy is a formalism to indicate the energy level where both the conduction and valence-like bands contact. Under no-field, no-doping conditions, ε_F and ε_D are expected to have the same value. This condition can be forced through a perpendicular electric field value selected with V_{GS} . In that particular case, the applied voltage is called Dirac voltage (V_{Dirac}), which will be used later. v_F is the Fermi velocity of carriers in graphene, directly related with the previously mentioned ballistic transport regime. η_F is an auxiliary term, which indicates the relative measure of the Fermi energy with respect to the Dirac energy. N_G is the effective density of states and $\mathcal{F}_i(\pm\eta_F)$ is the complete Fermi-Dirac integral.

In order to find the ε_F along the channel, a voltage loop (Eq. 5.5) is used to link it, explicitly in η_F and implicitly in Q_{net} , with the device parameters, especially influenced by the gate voltage and the gate oxide electrical properties:

$$\begin{aligned} V_{GS} - V_{ch} + \frac{1}{C_{ox}} Q_{net} - \frac{k_B T}{q} \eta_F \\ + \frac{1}{C_{ox}} Q_f - \frac{1}{q} (\phi_{mo} - \phi_{so}) = 0 \end{aligned} \quad (5.5)$$

Here V_{GS} is the gate-source voltage, V_{ch} is the channel voltage (a voltage value included between the source voltage and the drain voltage, locally dependent), $C_{ox} = \varepsilon_{ox}/t_{ox}$ is the gate oxide capacitance (dependent of the oxide thickness t_{ox} and its dielectric constant ε_{ox}), $Q_{net} = q(p - n)$ is the net charge of carriers in the channel, and Q_f is the fixed charge sheet density on the graphene surface, typically related with

graphene doping, as mentioned earlier. ϕ_{mo} is the gate metal-oxide offset, and ϕ_{so} is the semiconductor-oxide offset (in this case, the graphene-oxide offset). These two last offsets are indicative that graphene may not be suspended and isolated from its surroundings, but affected from them.

For devices with a very thin gate dielectric, substituting the oxide capacitance calculation with its experimental value is a good practice for enhancing the method output.

The intrinsic current density (J) that flows through the device is related to the ε_F and to the electron (μ_e) and hole (μ_p) mobilities, as shown in Eq. 5.6:

$$J = \mu_p p \nabla \varepsilon_F + \mu_n n \nabla \varepsilon_F, \quad (5.6)$$

Where n and p are the electron and hole densities. The effect of the source and drain contact resistance (R_s and R_d) on the modeled device can be added, modifying the device effective drain and source voltages, as explained by Champlain [79]. In our method, we simplify the calculation assuming $R_s = R_d$, as the studied devices have symmetric source and drain contacts, in order to reduce the computation time required by the self-consistent method to obtain the device final extrinsic current.

Up to this point, the most remarkable features of this model are that the temperature is an explicit parameter on Eq. 5.2 and Eq. 5.3, that most of the shift in the Dirac point can be explained with Q_f , and that the different carriers have separated mobilities.

In the next section, the required steps to apply a theoretical model into a electrical characterization method are explained.

Experimental fitting procedure

The aim of the developed method is to find the values of $\mu_{p,n}$, R_s and Q_f that, once introduced into the model, minimize the difference between the results provided by the model equations and the experimental device output characteristics. In order to achieve this, an algorithm to modify the values of $\mu_{p,n}$, R_s , and Q_f monitoring the features of the simulated and experimental curves has been designed, as shown in Fig. 5.2. As all the important features are found on the transconductance curve (g_m), it has to be calculated directly as the derivative from the I_{DS} vs. V_{GS} curve for all the covered cases. In terms of noise, this calculation may be problematic, as it will be propagated through the calculations. To solve this, the experimental measurements must exhibit a low noise level, easily attainable by increasing the I_{DS} value. Also, any signal smoothing

treatment should be performed on the as-measured data (i.e, the I_{DS} vs. V_{GS} curves), prior to the derivative calculation.

Figure 5.2: Features obtained from the (a) I_{DS} vs. V_{GS} curve and (b) the plot of its derivative g_m vs. V_{GS} [146].

The method is explained schematically in Fig. 5.3. It starts introducing the experimental data under study and the corresponding fixed parameters. Again, the experimental data consist of the I_{DS} vs. V_{GS} curves of a device. The fixed parameters are given by the geometry (W_{ch} , L_G , t_{ox}) of the device and the gate metal and oxide properties (ϵ_{ox} , ϕ_{so} , ϕ_{mo}). The device temperature and the drain-source applied voltage (T and V_{DS}) are also introduced as fixed parameters. Finally, in order to increase the calculation speed, the Fermi functions are generated only once during the method execution, storing the calculated values as a spline for further interpolation.

With all the inputs to the method previously described, the experimental transconductance is calculated and the experimental features are extracted. With these features, a calculation is performed in order to get the initial values for the output parameters ($\mu_{p,n}$, R_s and Q_f) that ensure the convergence of the method. For this calculation, the transconductance

Figure 5.3: Flow diagram where the electrical characterization fitting method is detailed. Experimental data is input and physical parameters are obtained as the output method, among other information [146].

slope close to the Dirac point is used to calculate an initial overestimation of the mobility value.

Merging all this information, the model is fitted on a first iteration, after which the transconductance features, experimental and simulated, are compared in the algorithm steps shown in Fig. 5.3.

The features from the g_m shape, detailed in Fig. 5.2, depend on the parameters that are obtained as the method outputs. The maximum and minimum transconductance values ($g_{m\max}$ and $g_{m\min}$) are linked to μ_n and μ_p respectively. The slope of g_m before the minimum and after the maximum ($\Delta g_m / \Delta V_{GS} (V_{GS} < V_{GS}(g_{m\min}))$ and $\Delta g_m / \Delta V_{GS} (V_{GS} > V_{GS}(g_{m\max}))$) are both related to R_s . It is important to emphasize that these features are interdependent, so varying the mobility values in the model will also change g_m before the minimum and after the maximum. Finally, the Q_f from the model depends directly on the experimental Dirac point obtained, $V_{Dirac} = V_{GS}(g_m = 0)$.

The difference between the experimental and modeled transconductance features are checked hierarchically against a tolerance value. The method is performed in the order shown in Fig. 5.3 to avoid convergence issues. The previously mentioned interdependence is the reason why such a complex algorithm is needed to ensure convergence. Every time a certain feature is not within tolerance, its dependent intrinsic value is modified proportionally to the distance between the experimental and the simulated features.

Once all the g_m features are within tolerance, the target parameters $\mu_{p,n}$, R_s , and Q_f are given as the method output. Also, a simulated I_{DS} vs. V_{GS} curve is output for comparison with the experimental data. Additional information, such as n and p for different V_{GS} values can be extracted, just by introducing the method outputs again into the model.

For special asymmetric cases, two different R_s values can be used for the hole and electron regions. Using this approximation, it is granted that in the case where the graphene-metal charge transfer depends on the ε_F , the calculated mobility values are not distorted by this fact.

5.1.2 Electrical characterization techniques

For evaluating the developed electrical characterization method, GFET devices were prepared on commercially-available CVD monolayer graphene, but of lower quality than the one used in subsequent studies. A 290 nm $\text{SiO}_2/\text{Si } n^{++}$ wafer diced into smaller pieces was used as the target substrate. After the transfer, graphene is patterned using mild oxygen plasma inside a RIE system, which is less controllable than the

ICP system available now. Then, Ti/Au (15/80 nm) contacts are deposited using e-beam evaporation.

For its electrical characterization, once the processing steps are over, the sample is introduced inside the Janis-CCR10 probe station. This probe station allows to anneal the sample under vacuum conditions (10^{-5} mbar), monitoring the electrical behavior while controlling the sample ambience. Our samples are heavily p-type doped due to molecules adsorbed to the graphene surface during the processing. Thus, samples are annealed at 500 K for periods of 30 min until no displacement in the V_{Dirac} is observed, a dopant desorption method that has been upgraded slightly over time. Once the electrical characteristics are stable, the GFETs are characterized. V_{GS} is typically varied from -90 to 90 V due to the thick gate dielectric used. Again, slight differences in the characterization method exist between these devices characterization and the one performed on the final samples. An example of the I_{DS} vs. V_{GS} curves obtained for different geometries is shown in Fig. 5.4. The asymmetry is related with processing residues, and is addressed in the next section.

Figure 5.4: Experimental curves of GFETs with different gate lengths. Inset: Scheme of the back-gated FET on CVD graphene, where the voltage names involved in the characterization are defined [146].

Method verification

In addition to applying the proposed electrical characterization method to the back-gated GFETs fabricated on CVD graphene with the processing described in the previous section (slightly different than the processing mentioned in Chapter 4), the method has also been tested with GFETs based on different graphene types and device geometries reported in the literature. This includes suspended devices with exfoliated graphene [147], top-gated devices on CVD graphene [78] and epitaxial graphene on SiC [148]. The latter device output characteristics also allow to compare the results from our fitting method with Champlain's calculations [79] on the same device type. The simulation output results for all these different devices are summarized in Table 5.1.

The fitting of the characteristics of the GFET on exfoliated suspended graphene is shown in Fig. 5.5a and Fig. 5.5b for $T = 90$ K and $T = 230$ K respectively. In this case, as the V_{DS} value is not mentioned by the authors, we have used an arbitrary value of $V_{DS} = 2$ V to convert the ρ vs. n curve into a I_{DS} vs. V_{GS} curve. This arbitrary conversion does not affect the method outcome, and the method perfectly matches the experimental device characteristics measured at 90 K. However the method provides a much wider g_m curve than the experimental data for 230 K. The output values match the reported ones, resulting in a mobility value close to the reported one ($135\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ in our simulation and $120\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ reported by the authors). The parameters used in the method, such as the C_{ox} or the L_g , have been estimated from the text and from the figures, adding an extra error source. For this type of ultraclean, exfoliated samples (charge impurities in the order of 10^{10} cm^{-2}),

Table 5.1: Experimental Hall mobilities and method outputs for the GFETs on different types of graphene studied. The different hole and electron contact resistances are shown with (h) and (e) indicators after the output value for the assymmetric cases.

Type of graphene	Gate	T (K)	μ_{Exp} ($\text{cm}^2\text{ V}^{-1}\text{ s}^{-1}$)	μ_{Sim} ($\text{cm}^2\text{ V}^{-1}\text{ s}^{-1}$)	Q_f/q (cm^{-2})	R_s ($\Omega\text{ m}$)
Exfoliated [147]	Back gate	230	120 000	135 000	-2.7×10^{10}	3.1×10^{-5}
Epitaxial [148]	Top gate	300	3200 - 6000	4800 - 6000	-2.4×10^{11}	1.3×10^{-3} (h) 2.6×10^{-4} (e)
CVD [78]	Top gate	300	1400 - 1700	1600	-2.6×10^{12}	3.5×10^{-3}
CVD	Back gate	300	980 - 1200	960	-2.9×10^{12}	8.5×10^{-3} (h) 9.2×10^{-3} (e)

a mobility distribution as empirically shown by Zhang et al. [38] instead of two fixed values may be more appropriate, helping to improve the fit quality near V_{Dirac} , where the carrier concentration is the lowest. For showing the similarity between the experimental and simulated curves in Fig. 5.5b, the $V_{BG\ Exp}$ (bottom axis) and $V_{BG\ Sim}$ (top axis) must be scaled in this case.

For the GFET on epitaxial graphene on SiC (Fig. 5.5c), a μ_n value ranging from $4700\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ to $6000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ is obtained from the simulation, depending on the V_{DS} value, that is comparable with the author's values (in the $3200\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ to $6000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ range). In this simulation, the same approximation as Zhang et al. [77] has been used, using the experimental C_{ox} instead of that calculated from the device geometry. Some experimental features as the kink close to the Dirac point can not be reproduced within the method, as it may be due to a complex electrical transport process. The hole branch of the simulation affects the quality of the fitting, as the strong scattering process present in SiC samples [149] has not been introduced into the model equations.

Figure 5.5: Comparison of I_{DS} vs. V_{GS} and g_m vs. V_{GS} curves from experimental data and from the method for (a), (b) suspended exfoliated graphene [147], (c), (d) top-gated epitaxial graphene [148], (e) top-gated CVD graphene [78] and (f) back-gated CVD graphene. The insets show an schematic of each FET structure geometry [146].

In Fig. 5.5d, a comparison of the method output and the calculated curve by Champlain [79] is shown. Although in the electron-regime part of the curves ($V_{TG} \gtrsim 1$ V) both simulations are close to the experimental values, in the hole-regime part of the curves a large divergence of Champlain's calculation from the experimental data is observed that does not occur using the developed method. This divergence is related with the extraordinarily high value for the hole mobility chosen by Champlain ($9000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and remarks the advantage of using the method algorithm for the analysis of the GFET.

The fitting of the characteristics of the top-gated FET on CVD graphene [78] (Fig. 5.5e) presents an offset in the I_{DS} curve, but the shape is correct. This might be due to the top-gate extra process steps, that includes a 3-nm thick Al e-beam-deposited layer oxidized in air on top of the graphene as a nucleation layer prior to the atomic layer deposition of Al_2O_3 , that can lead to an extra parallel, electrical current contribution. As the g_m curve is not affected by the offset in the I_{DS} vs. V_{GS} curve, the intrinsic material values provided by the method are reliable. The value of μ_n obtained of $1600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is in good agreement with the range of $1400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $1700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from the Hall measurements reported by the authors.

Finally, the experimental device characteristics and the model fitting of one of our back-gated FET on commercial CVD graphene are shown in Fig. 5.5f. The values from Table 5.1 corresponding to this device are the mean values from a batch of devices. The experimental Hall mobility has been obtained from several Van Der Pauw structures located along the same sample.

The proposed method has also been tested as a reliability and quality control tool at this stage, although this topic will be detailed more thoroughly to compare the automatic and manual transfers later on. With this purpose in mind, a batch of different devices processed with our initial techniques has been measured and evaluated using the method. From the V_{Dirac} distribution in Fig. 5.6a the fixed charge (Q_f) attached to graphene is calculated. As holes are the charge carriers at 0 V, the shift in the V_{Dirac} is probably due to water adsorbed molecules [137] on the graphene surface.

In Fig. 5.6b and Fig. 5.6c, the difference in the mobility values for electrons and holes respectively indicates that the GFET processing is affecting the electron transport more than the hole transport, varying the mobility from $960 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes to $390 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons. Organic residues from PMMA [53] are suspected produce this asymme-

Figure 5.6: (a) Dirac point (V_{Dirac}) and fixed charge (Q_f), (b) electron (μ_n) and (c) hole (μ_p) mobility distributions extracted from back-gated CVD GFETs fabricated with the initial processing recipe using the developed method [146].

try between the two carrier types. Therefore, an improvement on the used technological process, such as the automatic transfer technique or different protective resist formulations should address this issue.

5.2 Optical characterization

The goal in this section is to extract the maximum attainable information from the graphene devices fabricated as described in Chapter 3 and Chapter 4. In this case, as opposed to the results accounted in the previous section, both automatically and manually-transferred devices will be studied.

As described in Chapter 1, the optical properties of graphene strongly depend on the electrical carrier properties. More precisely, Raman spectroscopy features, such as peak widths, frequencies and relative intensities are closely linked to graphene's electronic band structure. Therefore, an optical model that correlates the experimental Raman spectroscopy mapping with graphene electrical properties from the previously described electrical model will be presented. In order to extract quantitative results from the model, a mechanical strain decoupling method has been selected [84].

5.2.1 Optical model framework

We have chosen the optical model by Lee et al. [84]. For applying this procedure, first, Raman spectra corresponding only to monolayer regions have to be selected, as the frequency shifts generated in multilayer regions do not depend only on the strain and the doping level. For our measurement conditions, these regions can be easily found and discarded just by selecting spectra where I_{2D}/I_G is, at least, higher than one. This way, a binary mask can be calculated, capable of selecting only monolayer regions and their corresponding spectra in a fast, compact calculation.

Then, for each monolayer spectrum obtained, the strain and doping induced shifts on the G and 2D Raman mode frequencies (ω_G and ω_{2D} respectively, in cm^{-1}) have to be analyzed separately. The meaning of these peaks is treated thoroughly in Chapter 1 and labeled in Fig. 5.7 (in the next section). For this decomposition, an algebraic change of basis has to be performed, converting from the experimental $\{\omega_G, \omega_{2D}\}$ basis to the strain and doping base. To be able to do this transformation, each point of the first basis must be linked exclusively to a single point of the

second basis. This relation will be defined by a base conversion matrix. With this objective in mind, the matrix components have been calculated using values from the literature.

This method implies a linear assumption for the doping, which is found to be valid for the range of values included in this thesis, but might be inaccurate for doping values of ultra-clean, undoped graphene, which is not our case. This validity will be checked later by means of electrical measurements and the electrical model fitting output, where consistency between the two methods will be discussed.

Due to the existence of a slight shift in the 2D mode is related to the laser wavelength ($\lambda = 532$ nm in our case, as will be detailed later), the coordinates origin reported by Lee et al. [84] for the frequency base has been corrected using a ω_{2D} shift of 88 cm eV^{-1} [150]. Considering that the laser wavelength they use in their study is $\lambda = 514.5$ nm, the correction is shown in Eq. 5.7:

$$O = (1581.6, 2676.9 + 88 \cdot \Delta E(\text{eV})) = (1581.6, 2669.9) \text{ cm}^{-1} \quad (5.7)$$

Once the origin is set, two different unitary basis (B_1 and B_2) sharing the same origin point (O from Eq. 5.7) are defined for the frequency space $\{\omega_G, \omega_{2D}\}$ (both in cm^{-1} units):

$$B_1 = \{\vec{e}_{\Delta\omega_G}, \vec{e}_{\Delta\omega_{2D}}\} = \{(1, 0), (0, 1)\}, \quad (5.8)$$

$$B_2 = \{\vec{e}_{\Delta\omega_{Q_f}}, \vec{e}_{\Delta\omega_\varepsilon}\} = \{(0.81, 0.57), (-0.41, -0.91)\}, \quad (5.9)$$

where B_2 unitary vectors have been calculated using the slope values of the model [84]:

$$\left(\frac{\Delta\omega_{2D}}{\Delta\omega_G}\right)_\varepsilon = 2.2; \quad \left(\frac{\Delta\omega_{2D}}{\Delta\omega_G}\right)_{Q_f} = 0.70 \quad (5.10)$$

B_1 defines any point $\overrightarrow{OP}$ in terms of the ω_G and ω_{2D} shift from the origin, whereas B_2 defines any point in terms of the ‘strain-free’ ($\vec{e}_{\Delta\omega_{Q_f}}$) and ‘charge-neutral’ ($\vec{e}_{\Delta\omega_\varepsilon}$) unit vectors. Although lacking orthogonality, this second basis is the desirable one for describing the frequency shifts, as the effect of strain and doping is directly decoupled:

$$\overrightarrow{OP} = \Delta\omega_G \cdot \vec{e}_{\Delta\omega_G} + \Delta\omega_{2D} \cdot \vec{e}_{\Delta\omega_{2D}} = \Delta\omega_{Q_f} \cdot \vec{e}_{\Delta\omega_{Q_f}} + \Delta\omega_\varepsilon \cdot \vec{e}_{\Delta\omega_\varepsilon} \quad (5.11)$$

Therefore, a simple matrix M and its inverse (M^{-1}) can be used for changing from B_1 to B_2 and vice versa:

$$\begin{pmatrix} \Delta\omega_G \\ \Delta\omega_{2D} \end{pmatrix} = M \cdot \begin{pmatrix} \Delta\omega_{Q_f} \\ \Delta\omega_\varepsilon \end{pmatrix} = \begin{pmatrix} 0.81 & -0.41 \\ 0.57 & -0.91 \end{pmatrix} \cdot \begin{pmatrix} \Delta\omega_{Q_f} \\ \Delta\omega_\varepsilon \end{pmatrix} \quad (5.12)$$

$$\begin{pmatrix} \Delta\omega_{Q_f} \\ \Delta\omega_\varepsilon \end{pmatrix} = M^{-1} \cdot \begin{pmatrix} \Delta\omega_G \\ \Delta\omega_{2D} \end{pmatrix} \quad (5.13)$$

Then, for any point expressed in the B_1 basis $(\Delta\omega_G, \Delta\omega_{2D})$, the frequency shift can be expressed in terms of the B_2 basis $(\Delta\omega_{Q_f}, \Delta\omega_\varepsilon)$, thus the frequency displacement separated for doping $(\Delta\omega_G(Q_f), \Delta\omega_{2D}(Q_f))$ and strain $(\Delta\omega_G(\varepsilon), \Delta\omega_{2D}(\varepsilon))$ can be obtained by changing back to B_1 each vector component when expressed in the B_2 basis alone:

$$\begin{pmatrix} \Delta\omega_G(Q_f) \\ \Delta\omega_{2D}(Q_f) \end{pmatrix} = M \cdot \begin{pmatrix} \Delta\omega_{Q_f} \\ 0 \end{pmatrix} \quad (5.14)$$

$$\begin{pmatrix} \Delta\omega_G(\varepsilon) \\ \Delta\omega_{2D}(\varepsilon) \end{pmatrix} = M \cdot \begin{pmatrix} 0 \\ \Delta\omega_\varepsilon \end{pmatrix} \quad (5.15)$$

With these frequency shift values and using the sensitivity values $d\omega_{2D}(Q_f)/dQ_f = -1.04 \text{ (cm}^{-1}/10^{12} \text{ cm}^{-2})$, $d\omega_G(\varepsilon)/d\varepsilon = -23.5 \text{ (cm}^{-1}/\% \varepsilon)$ extracted from the literature [82, 84], the doping and strain distributions can be extracted for all Raman spectra:

$$Q_f = \frac{\Delta\omega_{2D}(Q_f)}{d\omega_{2D}(Q_f)/dQ_f} \quad (10^{12} \text{ cm}^{-2}) \quad (5.16)$$

$$\varepsilon = \frac{\Delta\omega_G(\varepsilon)}{d\omega_G(\varepsilon)/d\varepsilon} \quad (\%). \quad (5.17)$$

This two material properties comprise the output of this method. One of them, Q_f , has the same physical meaning as one of the outputs obtained from the electrical method, hence both are named equally.

5.2.2 Optical characterization techniques

Along this thesis, different experimental Raman setups have been used for optical characterization. Among them, the only one capable of mapping the device active region was a WITec Alpha 300AR Raman confocal

microscope, available as an external service at Instituto de Cerámica y Vidrio (ICV-CSIC). Hence, this is the system that has been used for the Raman spectroscopy mapping of the channel area of the GFETs. The Raman spectra were obtained in backscattering geometry using a 50x objective lens (numerical aperture $NA = 0.8$) in ambient conditions. A 532 nm wavelength laser set to a power of 3 mW was used as the excitation source. Typical mapped areas were $110 \mu\text{m} \times 8 \mu\text{m}$ in size, scanned with steps of $0.33 \mu\text{m}$. Therefore, thousands of spectra are recorded from each region.

Just to make a quick material assessment and as a reference for the peak names, in Fig. 5.7, a typical Raman spectrum from a monolayer region ($I_{2D}/I_G > 2$) of the commercially-available graphene used is shown, where almost no defects or grain boundaries are appreciated (no D-peak is visible).

Figure 5.7: Raman spectrum of the commercially-available graphene used. The different peaks monitored during the optical fitting model are labeled. No defect D peak is visible on this spectrum [107].

At this point, both electrical and optical characterization conditions and their corresponding underlying fitting models have been described. Now, it is only necessary to apply them to the manually and automatically transferred samples fabricated during the thesis.

5.3 Combined electrical and optical characterization

Once tools for electrical and optical characterization have been developed on the previous sections of this chapter, they can be applied to demonstrate that cleaner and less damaged samples are obtained using the automatic transfer process. For this, the performance of GFETs fabricated on manually and automatically transferred samples is compared. Thus, two groups of samples from the same graphene material were processed with the same conditions (See chapters 3 and 4 for details), except for the graphene transfer method: the first group was transferred manually following the method derived from Sun et al. [96], whereas the second group was transferred using our automated transfer system. The graphene material used in both cases was commercially available CVD single layer/bilayer graphene on 25 μm -thick Cu foil. The chosen target substrates were 20 mm $\times$ 20 mm pieces diced from a 290 nm-thick $\text{SiO}_2/\text{Si } n^{++}$ wafer, where Si is used as the back-gate (inset to Fig. 5.8). The size of the target substrate is important, as one drawback of the automatic transfer process is the need of machining custom PTFE pieces for each desired target substrate. For simplicity, this size has been fixed for both types of transfer process (automatic and manual).

The two types of samples were processed as described in Chapter 4. For the characterization, the samples were introduced inside the same Janis-CCR10 probe station used for measuring the devices fabricated to test the electrical model. Again, this probe station was used for cleaning the last residues in graphene at 500 K for 3 h under vacuum conditions (10^{-5} mbar). After letting the probe station cool down and without breaking vacuum, the current-voltage characteristics of a large number of devices in each sample were measured at room temperature. Back-gate voltage values between -40 and 65 V and a drain-source voltage of 0.2 V were used.

In this section, first, the electrical characterization will be discussed. Then, the optical characterization for these devices will be explained. As the last step, the result of both methods will be compared.

For analyzing the quality of the transferred graphene *via* electrical characterization, the previously described physical model has been used for extracting relevant electric parameters from the GFET characteristics. The two key parameters extracted are the mobility (μ) (Fig. 5.8a) and the unintended doping concentration or fixed charge attached to the graphene (Q_f) (Fig. 5.8b). As previously described, this last model out-

put parameter indicates the amount of residues on top of the graphene, which, in turn, increase the scattering and degrade the mobility.

Figure 5.8: Histograms of the (a) mobility μ and (b) doping, Q_f extracted from the GFET devices fabricated using automatically and manually transferred graphene. The inset in (a) shows the schematic of the GFET. The values of the magnitudes indicated correspond to the fit of the histograms to a normal distribution (lines). Yield of the GFETs with (c) mobility and (d) doping values above a given threshold. Higher average mobility and lower average doping values, as well as much better yields, are observed for the devices fabricated on automatically transferred graphene [107].

In the case of the mobility, a clear improvement is observed for the automatically transferred samples, with a 70 % increase in the mobility mean value when compared to the manually transferred samples. This

increase in the mobility is consistent with the decrease of 30 % in the unintended doping for the automatically transferred samples, indicating less adsorbed impurities than in the manual method and, thus, less scattering centers reducing the mobility of the current carriers in the graphene film. With these results, it is confirmed that the automatic method developed degrades less the electrical properties of the material.

To explain this result, it is proposed that the gradual dilution procedure used in the automatic transfer process is likely to remove more efficiently the etchant from the graphene surface in contact with the liquid, thus reducing the unintentional doping concentration that could be induced by etchant residues. Additionally, the all-fluidic manipulation of the graphene membrane in the automatic transfer process avoids inducing mechanical stress during the successive DIW rinse steps and the final transfer step to the target substrate when compared to the manual method. It is worth reminding that in this last transfer method, an intermediate holding substrate is used to fish the graphene membrane out of the liquid, adding uncertainty and operator dependence to the process. Nevertheless, for both types of samples, the standard deviation in the mobility is similar, indicating that the dispersion may be related with the intrinsic properties of the commercial CVD-graphene used in all cases.

It is also important to point out that the automatic transfer method provides a much larger yield. The yields of the manual and automatic transfer processes, expressed as the fraction of devices with higher mobility or lower doping values than certain thresholds, are shown in Fig. 5.8c and Fig. 5.8d, respectively. The threshold values are ordered from less to more demanding, as the decreasing tendency indicates. In the case of the mobility, the increase in the yield for the automatically transferred devices compared with the manually transferred ones goes from more than two-fold for the less demanding threshold value ($1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) to eight-fold for the most demanding threshold value ($2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). A similar behavior is found for the unintentional doping level, with a seven-fold increase in the yield for the automatically transferred devices compared with the manually transferred ones for doping concentrations as low as 10^{12} cm^{-2} .

Once the results from the electrical characterization have been discussed, our focus is directed to the optical characterization and the underlying optical model used for extracting sample information.

As described previously in this chapter, Raman spectroscopy mapping has been performed in the channel area of several GFETs fabricated on both automatically and manually transferred graphene samples in order to evaluate the amount of strain and doping present in each kind of

samples and correlate them with the results obtained from the electrical characterization of the devices. Just to summarize the optical method, the analysis is based on the correlation of the frequencies of the Raman modes G (ω_G) and 2D (ω_{2D}) and their decomposition on a basis of strain- and charge-sensitivity [82–84]. In Fig. 5.9, the data extracted from two of the devices is presented using histograms. From this data representation, it is legitimate to infer that datasets obtained using the optical model follow a normal distribution, characterized by a mean value and its dispersion.

Figure 5.9: Histograms with automatically and manually transferred device-channel data for (a) strain and (b) doping extracted from Raman spectroscopy measurements [107].

Fig. 5.10 shows the correlation between the frequencies ω_G and ω_{2D} corresponding to the channel area of four GFETs, two devices on automatically transferred graphene and another two on manually transferred graphene. The diagonal evolution of the data distribution is well described when ω_G and ω_{2D} are decomposed in a doping- and stress-related basis, as shown by the internal set of axes. The automatically transferred samples present (ω_G, ω_{2D}) distributions with smaller values than the manually transferred ones, that correspond with a lower amount of both strain and doping. The reduction in strain for the automatically transferred samples may be related to the way the graphene film contacts the target substrate. Hence, in the manual transfer, an abrupt fishing method is performed that forces the PMMA/graphene membrane to adapt quickly to the target substrate, whereas in the automatic transfer

Figure 5.10: Distribution of the frequency shifts of the Raman G and 2D modes measured in the channel of various GFETs fabricated on automatically (A1 and A2) and manually (M1 and M2) transferred graphene. The center of mass and standard deviations of the distributions are shown by the symbol and the error bars, respectively. The embedded internal axes decouple the doping and tensile strain effects, showing less doping and strain for the devices fabricated on automatically transferred graphene [107].

method the contact is made slowly, allowing the PMMA/graphene membrane to accommodate smoothly to the surface of the target substrate and releasing most of the strain. The reduction in doping for the automatically transferred samples is likely related to the more efficient removal of contaminants as discussed previously. The doping ratio between the manually and automatically transferred samples obtained from the optical analysis (Fig. 5.10) is 1.47, very similar to the value of 1.42 obtained

from the electrical analysis (Fig. 5.8). The small mismatch between the electrically and optically obtained doping levels might be related to the fact that the doping conversion used in the optical decoupling method is based on data from induced charge with liquid gating [82], whereas doping in the samples of this work is related to adsorbed dopants.

5.4 Summary

In this chapter, a method that applies a physical model to extract electrical parameters from the experimental GFET characteristics has been presented. More precisely, it has been shown that the I_{DS} vs. V_{GS} output characteristics can be used to obtain $\mu_{p,n}$, R_s and Q_f as figures of merit. In addition, it has been checked that the method can be useful for different device geometries or material qualities.

To establish an alternative characterization, a second method based on graphene optical properties has been introduced. In this method, comprising Raman spectroscopy mapping of the active region of GFET devices, the frequencies of the Raman modes G (ω_G) and 2D (ω_{2D}) in monolayer graphene are monitored, and its strain and Q_f components are algebraically separated by applying an existing optical model.

Finally, these two characterization methods are applied to samples with differences during the material transfer. As our focus is on the transfer system developed on this thesis, the first set of samples were transferred automatically, whereas the second set were transferred manually for comparison purposes. Higher $\mu_{p,n}$ and yield, less Q_f , and less strain is found on the automatically-transferred samples, indicating that the developed system leads to overall better device quality.

Conclusions

The conclusions derived from the work developed during this thesis will be presented. In addition, the future work, based on the designed processes and methods, will be introduced. Some of this future work has already been started during the writing of this manuscript, although, due to the early stage of development, it is not ready for its publication yet.

6.1 Conclusions

On the graphene growth topic, the first conclusion that can be extracted is that CVD is well-positioned to become the graphene growth method capable to boost the material from the laboratories into the electronics industry. From our experiments, the importance of the surface pretreatment is stressed, as a quick in-situ oxidation is capable of reducing the nucleation density several orders of magnitude while increasing the front growth speed, both desirable effects. These results are in agreement with previous studies, where the reduction of the precursor partial pressure is capable of increasing even more this beneficial double effect. In terms of the underlying thermodynamical mechanism, information of the precursor decomposition has been obtained for the range of conditions attainable by our system.

Regarding graphene transfer, a system that automatically transfers graphene to an arbitrary target substrate has been developed. Thanks to the all-fluidic manipulation of the graphene, the system can avoid the mechanical damage, strain and contamination that otherwise is created during the manual transfer. This outcome is possible owing to the induced electrostatic repulsion between the graphene and its container,

which centers the film respect to the target substrate. In addition to the intrinsic advantages of any automated process (i.e. no handling skills required, good reproducibility, time saving, etc.), the automatic system also provides higher quality graphene. To test this, GFETs with back gate geometry were fabricated.

With this purpose, a whole fabrication process involving device patterning, dry etching, and metal deposition, among other technological processes, has been optimized for the equipment available at ISOM-UPM. To compare, GFETs were fabricated both on automatically and manually transferred samples.

For automatically transferred devices, higher mobility values, lower unintentional doping and strain, and better yields were obtained as compared to those fabricated on manually transferred material. The system, initially developed as a lab-scale tool, is fully scalable for industrial applications, allowing the large-scale transfer of graphene films with superior quality to arbitrary substrates. The industrial property regarding this invention has been protected in collaboration with MIT, and it is applicable to the other components of the two-dimensional materials family, such as MoS_2 or WS_2 .

Concerning our contribution to graphene electrical characterization, a method that applies a physical model to extract information from experimental data has been designed. More precisely, it has been shown that the I_{DS} vs. V_{GS} GFET output characteristics can be used to obtain $\mu_{p,n}$, R_s and Q_f as figures of merit. In addition, it has been demonstrated that this method can be useful for a quick characterization of a batch of devices, allowing us to find issues during the device processing. Even more, when the characterization method is applied to graphene devices from samples transferred using different methods, statistically relevant changes on the yield and the figures of merit are appreciated. As the underlying model is versatile and relies on fundamental material properties, the method can be the foundation for further device and material optimization and can be tailored for different applications such as, for example, GFET-based sensors with liquid gating.

Associated with the optical characterization, the main outcome of this thesis is a method capable of distinguishing between strain and doping effects on Raman spectra. Based on previous studies, an algebraic method that converts the experimental 2D and G peak frequencies into Q_f and tensile strain in the material has been formulated. When this technique is adapted to assess measurements on GFET device channels, the obtained information can be compared with the one extracted with the electrical characterization method. As expected, similar figures of

merit have been obtained from both methods, where the additional strain information available from the optical characterization method helps to understand in more detail several processing-related issues.

For the programming of both characterization methods, *python* was the language of choice, as its versatility permits to perform minimization calculations or algebraic manipulations in a simple way.

6.2 Future work

As pending topics on graphene growth, the main issue that needs to be solved is to decrease the amount of carbon in the system. In this case, either the carbon initially present on the Cu catalytic substrate or the high flow rate of the gaseous carbon precursor are known to affect negatively to the graphene nucleation density. An Ar/CH₄ mixture, where the carbon precursor has been diluted, will be used as the new carbon source. This modification will adapt our system to the state of the art conditions. In terms of additional Cu pretreatment, alternative oxidative methods are being tested.

In the development of the automatic transfer system, new designs for achieving improved cleanliness are being designed and tested. Nevertheless, the underlying ideas of the system remain unaltered in these upgrades. A 3D printer is being used to test novel designs, as the mechanization of new pieces in PTFE has become the time-limiting step. Finally, the sample cleanliness will be assessed using the already developed electrical and optical characterization methods.

For a project recently granted (see Appendix A.3), whose goal is to avoid the formation of fibrotic tissue using graphene/macrophage patches or devices, the electrical characterization method presented in this thesis will be applied. Prior to this, it will need to be adapted to account for liquid gating, as the graphene-cell interaction in the liquid media has to be quantified. With this improvement in the method, polarization changes in cells are expected to be measured. Initial experiments, where the interaction between human macrophages and graphene is tested, have already started.

Publications

In this appendix, the articles and patents produced, and the participation in projects during this thesis are listed.

A.1 Articles

- M. J. Tadjer, A. Constant, P. Godignon, S. Martin-Horcajo, A. Boscá, F. Calle, M. Berthou, and J. Millán, “Gate oxide stability of 4H-SiC MOSFETs under on/off-state bias-temperature stress,” *Mater. Sci. Forum*, vol. 740–742, pp. 553–556, 2013.
- M. J. Tadjer, M. A. Mastro, J. M. Rojo, A. Boscá, F. Calle, F. J. Kub, and C. R. Eddy, “MnO₂-Based electrochemical supercapacitors on flexible carbon substrates,” *J. Electron. Mater.*, vol. 43, no. 4, pp. 1188–1193, 2014.
- S. Martin-Horcajo, A. Wang, A. Boscá, M. F. Romero, M. J. Tadjer, A. D. Koehler, T. J. Anderson, and F. Calle, “Trapping phenomena in AlGa_N and InAl_N barrier HEMTs with different geometries,” *Semicond. Sci. Technol.*, vol. 30, no. 3, p. 35015, 2015.
- S. Ruiz-Gómez, A. Boscá, L. Pérez, J. Pedrós, J. Martínez, A. Páez, and F. Calle, “Graphene foam functionalized with electrodeposited nickel hydroxide for energy applications,” *Diam. Relat. Mater.*, vol. 57, pp. 63–67, 2015.
- A. Boscá, J. Pedrós, J. Martínez, and F. Calle, “Method for extracting relevant electrical parameters from graphene field-effect tran-

- sisters using a physical model,” *J. Appl. Phys.*, vol. 117, p. 44504, 2015.
- D. J. Choi, A. Boscá, J. Pedrós, J. Martínez, V. Barranco, J. M. Rojo, J. J. Yoo, Y.-H. Kim, and F. Calle, “Improvement of the adhesion between polyaniline and commercial carbon paper by acid treatment and its application in supercapacitor electrodes,” *Compos. Interfaces*, vol. 6440, no. November 2015, pp. 1–11, 2015.
 - A. Boscá, J. Pedrós, J. Martínez, T. Palacios, and F. Calle, “Automatic graphene transfer system for improved material quality and efficiency,” *Sci. Rep.*, vol. 6, no. October 2015, p. 21676, 2016.
 - J. Pedrós, A. Boscá, J. Martínez, S. Ruiz-Gómez, L. Pérez, V. Barranco, and F. Calle, “Polyaniline nanofiber sponge filled graphene foam as high gravimetric and volumetric capacitance electrode,” *J. Power Sources*, vol. 317, pp. 35–42, 2016.
 - P. Romero, P. A. Postigo, E. Baquedano, J. Martínez, A. Boscá, and R. Guzmán de Villoria, “Controlled synthesis of nanocrystalline glass-like carbon thin films with tuneable electrical and optical properties,” *Chem. Eng. J.*, 2016.
 - A. Ladrón de Guevara, A. Boscá, J. Pedrós, E. Climent-Pascual, A. de Andrés, F. Calle, and J. Martínez, “Graphene-based electrochemical capacitors fabricated by laser,” (submitted to *Nanotechnology*).
 - M. F. Romero, A. Boscá, J. Martínez, J. Pedrós, T. Palacios, and F. Calle, “Impact of 2D-Graphene on SiN passivated AlGaIn/GaN MIS-HEMTs under mist exposure,” (submitted to *Nano Lett.*)
 - A. Ladrón de Guevara, A. Boscá, J. Pedrós, R. Fandan, J. Martínez and F. Calle, “Nickel-activated seeding for CVD-graphene growth.” (in preparation)
 - A. Boscá, A. Povo-Retana, J. Pedrós, A. Ladrón de Guevara, M. Mojena, F. Calle, L. Boscá, “Graphene-dependent phagocytosis in phenotypically targeted human macrophages. Relevance for the use in graphene-macrophages devices.” (in preparation)

A.2 Patents

- Procedimiento de transferencia de nanocapas y aparato de realización del mismo
 - Inventors: A. Boscá Mojena, J. Pedrós Ayala, J. Martínez Rodrigo, F. Calle Gómez, T. Palacios Gutiérrez
 - Patent no.: P 6400/2013, ES2014/070859
 - Priority regions: Spain
 - Priority date: 21/11/13
 - Ownership: UPM, MIT
- Hierarchical composite structures based on graphene foam or graphene-like foam
 - Inventors: J. Pedrós Ayala, A. Boscá Mojena, J. Martínez Rodrigo, F. Calle Gómez, M.S. Ruiz-Gómez, L. Pérez, M.V. Barranco, A. Páez Dueñas, J. García San Luis
 - Patent no.: EP14382428.2
 - Priority regions: Europe
 - Priority date: 31/10/14
 - Ownership: Repsol S.A
- Direct process for fabrication of functionalised 3D graphene foams
 - Inventors: A. Páez Dueñas, J. García San Luis, F. Alía Moreno-Ortiz, M.V. Barranco, E. Climent, A. de Andrés, J. M. Rojo, J. Pedrós Ayala, J. Martínez Rodrigo, A. Boscá Mojena, F. Calle Gómez.
 - Patent no.: EP16382227.3
 - Priority regions: Europe
 - Priority date: 24/05/16
 - Ownership: Repsol S.A

A.3 Projects

- Ministerio de Ciencia e Innovación: *Advanced Wide Band Gap Semiconductor Devices for Rational Use of Energy*, (RUE) Consolider CSD2009-00046 (2009 - 2014).

- Ministerio de Ciencia e Innovación: *High Frequency Resonators on AlN/Diamond Structures*, (READI). TEC2010-19511 (2010 - 2013).
- Programa Inspire Repsol-UPM: *Sistemas de Almacenamiento de Energía con Grafenos para Vehículos Eléctricos*, (SAVE) (2012 - 2015).
- Plan Nacional, categoría Retos de la Sociedad: *Grafeno para Dispositivos de Generación y Almacenamiento de Energía*, (GRAFA-GEN) ENE2013-47904-C3-1-R (2014 - 2017).
- KIC-EIT Raw Materials, *Graphene Nanocomposites Reactors at Preindustrial Technology Readiness*, (NANOGREAT) (2016 - 2018).
- MISTI Global Seed Funds, *Automatic Transfer of 2D Materials to Flexible Substrates and Benchmarking as Chemical Sensors* (2016 - 2017).
- Fundación Ramón Areces, Ayudas a la Investigación en Ciencias de la Vida y de la Materia: *Biomateriales basados en grafeno:macrófagos: caracterización funcional para su aplicación en patología cardiovascular*, (2017 - 2019).

Bibliography

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films," *Science*, vol. 22, no. October, pp. 2–6, 2004.
- [2] P. Wallace, "The Band Theory of Graphite," *Physical Review*, vol. 329, no. 9, pp. 622–634, 1947.
- [3] A. Geim, "Nobel Lecture: Random walk to graphene," *Reviews of Modern Physics*, vol. 83, no. 3, pp. 851–862, 2011.
- [4] M. F. El-Kady, V. Strong, S. Dubin, and R. B. Kaner, "Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors," *Science*, vol. 335, no. 6074, pp. 1326–1330, 2012.
- [5] H. H. Kim, Y. Chung, E. Lee, S. K. Lee, and K. Cho, "Water-Free Transfer Method for CVD-Grown Graphene and Its Application to Flexible Air-Stable Graphene Transistors," *Advanced Materials*, vol. 26, no. 20, pp. 3213–3217, 2014.
- [6] M. F. El-Kady and R. B. Kaner, "Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage." *Nature Communications*, vol. 4, p. 1475, 2013.
- [7] S. M. Kim, E. B. Song, S. Lee, J. Zhu, D. H. Seo, M. Mecklenburg, S. Seo, and K. L. Wang, "Transparent and flexible graphene charge-trap memory." *ACS Nano*, vol. 6, no. 9, pp. 7879–84, 2012.
- [8] S. J. Park, O. S. Kwon, S. H. Lee, H. S. Song, T. H. Park, and J. Jang, "Ultrasensitive flexible graphene based field-effect transistor (FET)-type bioelectronic nose." *Nano Letters*, vol. 12, no. 10, pp. 5082–90, 2012.

- [9] N. Liu, H. Tian, G. Schwartz, J. B.-H. Tok, T.-L. Ren, and Z. Bao, "Large-Area, Transparent, and Flexible Infrared Photodetector Fabricated Using P-N Junctions Formed by N-Doping Chemical Vapor Deposition Grown Graphene." *Nano Letters*, 2014.
- [10] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei *et al.*, "Roll-to-roll production of 30-inch graphene films for transparent electrodes," *Nature Nanotechnology*, vol. 5, no. 8, pp. 574–578, 2010.
- [11] S. Hu, R. Rajamani, and X. Yu, "Flexible solid-state paper based carbon nanotube supercapacitor," *Applied Physics Letters*, vol. 100, no. 10, p. 104103, 2012.
- [12] J. Chen, M. Badioli, P. Alonso-González, S. Thongrattanasiri, F. Huth, J. Osmond, M. Spasenović, A. Centeno *et al.*, "Optical nano-imaging of gate-tunable graphene plasmons." *Nature*, vol. 487, no. 7405, pp. 77–81, 2012.
- [13] S. Thongrattanasiri, F. Koppens, and F. García de Abajo, "Complete Optical Absorption in Periodically Patterned Graphene," *Physical Review Letters*, vol. 108, no. 4, pp. 1–5, 2012.
- [14] M. Liu, X. Yin, E. Ulin-Avila, B. Geng, T. Zentgraf, L. Ju, F. Wang, and X. Zhang, "A graphene-based broadband optical modulator." *Nature*, vol. 474, no. 7349, pp. 64–7, 2011.
- [15] A. Pospischil, M. Humer, M. M. Furchi, D. Bachmann, R. Guider, T. Fromherz, and T. Mueller, "CMOS-compatible graphene photodetector covering all optical communication bands," *Nature Photonics*, vol. 7, no. 11, pp. 892–896, 2013.
- [16] F. Xia, T. Mueller, Y.-M. Lin, A. Valdes-Garcia, and P. Avouris, "Ultrafast graphene photodetector." *Nature Nanotechnology*, vol. 4, no. 12, pp. 839–43, 2009.
- [17] X.-C. Dong, H. Xu, X.-W. Wang, Y.-X. Huang, M. B. Chan-Park, H. Zhang, L.-H. Wang, W. Huang *et al.*, "3D graphene-cobalt oxide electrode for high-performance supercapacitor and enzymeless glucose detection." *ACS Nano*, vol. 6, no. 4, pp. 3206–13, 2012.
- [18] X. Dong, X. Wang, L. Wang, H. Song, H. Zhang, W. Huang, and P. Chen, "3D graphene foam as a monolithic and macroporous carbon electrode for electrochemical sensing." *ACS Applied Materials & Interfaces*, vol. 4, no. 6, pp. 3129–33, 2012.

- [19] X. Dong, Y. Ma, G. Zhu, Y. Huang, J. Wang, M. B. Chan-Park, L. Wang, W. Huang *et al.*, "Synthesis of graphene–carbon nanotube hybrid foam and its use as a novel three-dimensional electrode for electrochemical sensing," *Journal of Materials Chemistry*, vol. 22, no. 33, p. 17044, 2012.
- [20] D. A. C. Brownson, L. C. S. Figueiredo-Filho, X. Ji, M. Gómez-Mingot, J. Iniesta, O. Fatibello-Filho, D. K. Kampouris, and C. E. Banks, "Free-standing three-dimensional graphene foam gives rise to beneficial electrochemical signatures within non-aqueous media," *Journal of Materials Chemistry A*, vol. 1, no. 19, p. 5962, 2013.
- [21] W. Fu, M. El Abbassi, T. Hasler, M. Jung, M. Steinacher, M. Calame, C. Schönenberger, G. Puebla-Hellmann *et al.*, "Electrolyte gate dependent high-frequency measurement of graphene field-effect transistor for sensing applications," *Applied Physics Letters*, vol. 104, no. 1, p. 013102, 2014.
- [22] W. Wang, S. Guo, I. Lee, K. Ahmed, J. Zhong, Z. Favors, F. Zaera, M. Ozkan *et al.*, "Hydrous ruthenium oxide nanoparticles anchored to graphene and carbon nanotube hybrid foam for supercapacitors." *Scientific Reports*, vol. 4, no. ii, p. 4452, 2014.
- [23] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, and G. P. Nanofiber, "Supercapacitors based on flexible graphene/polyaniline nanofiber composite films." *ACS Nano*, vol. 4, no. 4, pp. 1963–70, 2010.
- [24] Z.-S. Wu, K. Parvez, X. Feng, and K. Müllen, "Graphene-based in-plane micro-supercapacitors with high power and energy densities." *Nature Communications*, vol. 4, p. 2487, 2013.
- [25] H. Huang, Y. Tang, L. Xu, S. Tang, and Y. Du, "Direct Formation of Reduced Graphene Oxide and 3D Lightweight Nickel Network Composite Foam by Hydrohalic Acids and Its Application for High-Performance Supercapacitors." *ACS Applied Materials & Interfaces*, 2014.
- [26] L. Zhang and G. Shi, "Preparation of Highly Conductive Graphene Hydrogels for Fabricating Supercapacitors with High Rate Capability," *The Journal of Physical Chemistry C*, vol. 115, no. 34, pp. 17 206–17 212, 2011.
- [27] J. Yan, Q. Wang, T. Wei, L. Jiang, M. Zhang, X. Jing, and Z. Fan, "Template-assisted low temperature synthesis of functionalized graphene for ultrahigh volumetric performance supercapacitors." *ACS Nano*, vol. 8, no. 5, pp. 4720–9, 2014.
- [28] J. J. Yoo, K. Balakrishnan, J. Huang, V. Meunier, B. G. Sumpter, A. Srivastava, M. Conway, A. L. M. Reddy *et al.*, "Ultrathin planar graphene supercapacitors." *Nano Letters*, vol. 11, no. 4, pp. 1423–7, 2011.

- [29] C. Liu, Z. Yu, D. Neff, A. Zhamu, and B. Z. Jang, "Graphene-Based Supercapacitor with an Ultrahigh Energy Density." *Nano Letters*, pp. 4863–4868, 2010.
- [30] X. Cao, Y. Shi, W. Shi, G. Lu, X. Huang, Q. Yan, Q. Zhang, and H. Zhang, "Preparation of novel 3D graphene networks for supercapacitor applications." *Small*, vol. 7, no. 22, pp. 3163–8, 2011.
- [31] H. Xiang, K. Zhang, G. Ji, J. Y. Lee, C. Zou, X. Chen, and J. Wu, "Graphene/nanosized silicon composites for lithium battery anodes with improved cycling stability," *Carbon*, vol. 49, no. 5, pp. 1787–1796, 2011.
- [32] Z.-l. Wang, D. Xu, H.-G. Wang, Z. Wu, and X.-b. Zhang, "In situ fabrication of porous graphene electrodes for high-performance energy storage." *ACS Nano*, vol. 7, no. 3, pp. 2422–30, 2013.
- [33] R. Mukherjee, A. V. Thomas, A. Krishnamurthy, and N. Koratkar, "Photothermally reduced graphene as high-power anodes for lithium-ion batteries." *ACS Nano*, vol. 6, no. 9, pp. 7867–78, 2012.
- [34] B. Wang, X. Li, X. Zhang, B. Luo, M. Jin, M. Liang, S. A. Dayeh, S. T. Picraux *et al.*, "Adaptable silicon-carbon nanocables sandwiched between reduced graphene oxide sheets as lithium ion battery anodes." *ACS Nano*, vol. 7, no. 2, pp. 1437–45, 2013.
- [35] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, "Graphene-based ultracapacitors." *Nano Letters*, vol. 8, no. 10, pp. 3498–502, 2008.
- [36] C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene." *Science*, vol. 321, no. 5887, pp. 385–8, 2008.
- [37] A. H. Castro Neto, N. M. R. Peres, K. S. Novoselov, A. K. Geim, and F. Guinea, "The electronic properties of graphene," *Reviews of Modern Physics*, vol. 81, no. 1, pp. 109–162, 2009.
- [38] Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, "Experimental observation of the quantum Hall effect and Berry's phase in graphene." *Nature*, vol. 438, no. 7065, pp. 201–4, 2005.
- [39] B. E. Feldman, B. Krauss, J. H. Smet, and A. Yacoby, "Unconventional sequence of fractional quantum Hall states in suspended graphene." *Science*, vol. 337, no. 6099, pp. 1196–1199, 2012.
- [40] T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y.-J. Kim, A. Gholinia *et al.*, "Vertical field-effect transistor based on graphene-WS₂ heterostructures for flexible and transparent electronics." *Nature Nanotechnology*, vol. 8, no. 2, pp. 100–3, 2013.

- [41] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov *et al.*, "Ultrathin Epitaxial Graphite: 2D Electron Gas Properties and a Route toward Graphene-based Nanoelectronics," *The Journal of Physical Chemistry B*, vol. 108, no. 52, pp. 19 912–19 916, 2004.
- [42] Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and P. Avouris, "100-GHz transistors from wafer-scale epitaxial graphene." *Science*, vol. 327, no. 5966, p. 662, 2010.
- [43] W. S. Hummers and R. E. Offeman, "Preparation of Graphitic Oxide," *Journal of the American Chemical Society*, vol. 80, no. 6, pp. 1339–1339, 1958.
- [44] J. Shelton, H. Patil, and J. Blakely, "Equilibrium segregation of carbon to a nickel (111) surface: A surface phase transition," *Surface Science*, vol. 43, no. 2, pp. 493–520, 1974.
- [45] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, "Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition," *Nano Letters*, vol. 9, no. 1, pp. 30–35, 2009.
- [46] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni *et al.*, "Large-area synthesis of high-quality and uniform graphene films on copper foils." *Science*, vol. 324, no. 5932, pp. 1312–4, 2009.
- [47] L. Gan and Z. Luo, "Turning off Hydrogen To Realize Seeded Growth of Subcentimeter Single-Crystal Graphene Grains on Copper," *ACS Nano*, vol. 7, no. 10, pp. 9480–9488, 2013.
- [48] A. Reina, H. Son, L. Jiao, B. Fan, M. S. Dresselhaus, Z. Liu, and J. Kong, "Transferring and Identification of Single- and Few-Layer Graphene on Arbitrary Substrates," *The Journal of Physical Chemistry C*, vol. 112, no. 46, pp. 17 741–17 744, 2008.
- [49] X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R. D. Piner, L. Colombo *et al.*, "Transfer of large-area graphene films for high-performance transparent conductive electrodes." *Nano Letters*, vol. 9, no. 12, pp. 4359–63, 2009.
- [50] X. Liang, B. A. Sperling, I. Calizo, G. Cheng, C. A. Hacker, Q. Zhang, Y. Obeng, K. Yan *et al.*, "Toward clean and crackless transfer of graphene." *ACS Nano*, vol. 5, no. 11, pp. 9144–53, 2011.
- [51] T. Hallam, C. Wirtz, and G. S. Duesberg, "Polymer-assisted transfer printing of graphene composite films," *Physica Status Solidi (b)*, vol. 250, no. 12, pp. 2668–2671, 2013.

- [52] T. Hallam, N. C. Berner, C. Yim, and G. S. Duesberg, "Strain, Bubbles, Dirt, and Folds: A Study of Graphene Polymer-Assisted Transfer," *Advanced Materials Interfaces*, vol. 1, no. 6, p. 1400115, 2014.
- [53] Y.-C. Lin, C.-C. Lu, C.-H. Yeh, C. Jin, K. Suenaga, and P.-W. Chiu, "Graphene annealing: how clean can it be?" *Nano Letters*, vol. 12, no. 1, pp. 414–9, 2012.
- [54] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi *et al.*, "Boron nitride substrates for high-quality graphene electronics." *Nature Nanotechnology*, vol. 5, no. 10, pp. 722–6, 2010.
- [55] L. A. Ponomarenko, A. K. Geim, A. A. Zhukov, R. Jalil, S. V. Morozov, K. S. Novoselov, I. V. Grigorieva, E. H. Hill *et al.*, "Tunable metal–insulator transition in double-layer graphene heterostructures," *Nature Physics*, vol. 7, no. 12, pp. 958–961, 2011.
- [56] C. Dean, A. Young, L. Wang, I. Meric, G.-H. Lee, K. Watanabe, T. Taniguchi, K. Shepard *et al.*, "Graphene based heterostructures," *Solid State Communications*, vol. 152, no. 15, pp. 1275–1282, 2012.
- [57] Y. Wang, Y. Zheng, X. Xu, E. Dubuisson, Q. Bao, J. Lu, and K. P. Loh, "Electrochemical delamination of CVD-grown graphene film: toward the recyclable use of copper catalyst." *ACS Nano*, vol. 5, no. 12, pp. 9927–33, 2011.
- [58] L. Gao, W. Ren, H. Xu, L. Jin, Z. Wang, T. Ma, L.-P. Ma, Z. Zhang *et al.*, "Repeated growth and bubbling transfer of graphene with millimetre-size single-crystal grains using platinum," *Nature Communications*, vol. 3, p. 699, 2012.
- [59] C. J. L. de la Rosa, J. Sun, N. Lindvall, M. T. Cole, Y. Nam, M. Loffler, E. Olsson, K. B. K. Teo *et al.*, "Frame assisted H₂O electrolysis induced H₂ bubbling transfer of large area graphene grown by chemical vapor deposition on Cu," *Applied Physics Letters*, vol. 102, no. 2, p. 022101, 2013.
- [60] Y. Lee, S. Bae, H. Jang, S. Jang, S.-E. Zhu, S. H. Sim, Y. I. Song, B. H. Hong *et al.*, "Wafer-scale synthesis and transfer of graphene films." *Nano Letters*, vol. 10, no. 2, pp. 490–3, 2010.
- [61] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg *et al.*, "Transfer of CVD-grown monolayer graphene onto arbitrary substrates." *ACS Nano*, vol. 5, no. 9, pp. 6916–24, 2011.

- [62] J. Kang, S. Hwang, J. H. Kim, M. H. Kim, J. Ryu, S. J. Seo, B. H. Hong, M. K. Kim *et al.*, "Efficient transfer of large-area graphene films onto rigid substrates by hot pressing," *ACS Nano*, vol. 6, no. 6, pp. 5360–5365, 2012.
- [63] X.-D. Chen, Z.-B. Liu, C.-Y. Zheng, F. Xing, X.-Q. Yan, Y. Chen, and J.-G. Tian, "High-quality and efficient transfer of large-area graphene films onto different substrates," *Carbon*, vol. 56, pp. 271–278, 2013.
- [64] S. Y. Yang, J. G. Oh, D. Y. Jung, H. Choi, C. H. Yu, J. Shin, C.-G. Choi, B. J. Cho *et al.*, "Metal-Etching-Free Direct Delamination and Transfer of Single-Layer Graphene with a High Degree of Freedom," *Small*, vol. 11, no. 2, pp. 175–181, 2015.
- [65] L. Gao, G.-X. Ni, Y. Liu, B. Liu, A. H. Castro Neto, and K. P. Loh, "Face-to-face transfer of wafer-scale graphene films," *Nature*, vol. 505, no. 7482, pp. 190–194, 2013.
- [66] D.-Y. Wang, I.-S. Huang, P.-H. Ho, S.-S. Li, Y.-C. Yeh, D.-W. Wang, W.-L. Chen, Y.-Y. Lee *et al.*, "Clean-lifting transfer of large-area residual-free graphene films." *Advanced Materials*, vol. 25, no. 32, pp. 4521–6, 2013.
- [67] W. Jung, D. Kim, M. Lee, S. Kim, J.-h. Kim, and C.-S. Han, "Ultraconformal Contact Transfer of Monolayer Graphene on Metal to Various Substrates," *Advanced Materials*, vol. 26, no. 37, pp. 6394–6400, 2014.
- [68] T. Kobayashi, M. Bando, N. Kimura, K. Shimizu, K. Kadono, N. Umezu, K. Miyahara, S. Hayazaki *et al.*, "Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process," *Applied Physics Letters*, vol. 102, no. 2, p. 023112, 2013.
- [69] S. Morozov, K. Novoselov, M. Katsnelson, F. Schedin, D. Elias, J. Jaszczak, and A. Geim, "Giant Intrinsic Carrier Mobilities in Graphene and Its Bilayer," *Physical Review Letters*, vol. 100, no. 1, p. 016602, 2008.
- [70] J.-H. Chen, C. Jang, S. Xiao, M. Ishigami, and M. S. Fuhrer, "Intrinsic and extrinsic performance limits of graphene devices on SiO₂," *Nature Nanotechnology*, vol. 3, no. 4, pp. 206–9, 2008.
- [71] P. Avouris, "Graphene: Electronic and Photonic Properties and Devices." *Nano Letters*, vol. 10, pp. 4285–4294, 2010.
- [72] T. Palacios, A. Hsu, and H. Wang, "Applications of graphene devices in RF communications," *IEEE Communications Magazine*, vol. 48, no. 6, pp. 122–128, 2010.

- [73] F. Schwierz, "Graphene transistors." *Nature Nanotechnology*, vol. 5, no. 7, pp. 487–96, 2010.
- [74] Y. Wu, K. A. Jenkins, A. Valdes-Garcia, D. B. Farmer, Y. Zhu, A. A. Bol, C. Dimitrakopoulos, W. Zhu *et al.*, "State-of-the-art graphene high-frequency electronics." *Nano Letters*, vol. 12, no. 6, pp. 3062–7, 2012.
- [75] S. Kim, J. Nah, I. Jo, D. Shahrjerdi, L. Colombo, Z. Yao, E. Tutuc, and S. K. Banerjee, "Realization of a high mobility dual-gated graphene field-effect transistor with Al₂O₃ dielectric," *Applied Physics Letters*, vol. 94, no. 6, p. 062107, 2009.
- [76] Y. M. Lin, H. Y. Chiu, K. A. Jenkins, D. B. Farmer, P. Avouris, and A. Valdes-Garcia, "Dual-gate graphene FETs with fT of 50 GHz," *IEEE Electron Device Letters*, vol. 31, no. 1, pp. 68–70, 2010.
- [77] Z. Zhang, H. Xu, H. Zhong, and L.-M. Peng, "Direct extraction of carrier mobility in graphene field-effect transistor using current-voltage and capacitance-voltage measurements," *Applied Physics Letters*, vol. 101, no. 21, p. 213103, 2012.
- [78] H. Wang, A. Hsu, J. Kong, D. A. Antoniadis, and T. Palacios, "Compact virtual-source current–voltage model for top-and back-gated graphene field-effect transistors," *IEEE Transactions on Electron Devices*, vol. 58, p. 1523, 2011.
- [79] J. G. Champlain, "A first principles theoretical examination of graphene-based field effect transistors," *Journal of Applied Physics*, vol. 109, no. 8, p. 084515, 2011.
- [80] A. C. Ferrari and D. M. Basko, "Raman spectroscopy as a versatile tool for studying the properties of graphene," *Nature Nanotechnology*, vol. 8, no. 4, pp. 235–246, 2013.
- [81] F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," *Nature Photonics*, vol. 4, no. 9, pp. 611–622, 2010.
- [82] A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R. Krishnamurthy *et al.*, "Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor," *Nature Nanotechnology*, vol. 3, no. 4, pp. 210–215, 2008.
- [83] A. Das, B. Chakraborty, S. Piscanec, S. Pisana, A. Sood, and A. Ferrari, "Phonon renormalization in doped bilayer graphene," *Physical Review B*, vol. 79, no. 15, p. 155417, 2009.

- [84] J. E. Lee, G. Ahn, J. Shim, Y. S. Lee, and S. Ryu, "Optical separation of mechanical strain from charge doping in graphene," *Nature Communications*, vol. 3, no. May, p. 1024, 2012.
- [85] Y. Hao, M. S. Bharathi, L. Wang, Y. Liu, H. Chen, S. Nie, X. Wang, H. Chou *et al.*, "The role of surface oxygen in the growth of large single-crystal graphene on copper." *Science*, vol. 342, no. 6159, pp. 720–3, 2013.
- [86] Y. Hao, L. Wang, Y. Liu, H. Chen, X. Wang, C. Tan, S. Nie, J. W. Suk *et al.*, "Oxygen-activated growth and bandgap tunability of large single-crystal bilayer graphene," *Nature Nanotechnology*, vol. 11, no. 5, pp. 426–431, 2016.
- [87] Y. Wu, Y.-m. Lin, A. A. Bol, K. A. Jenkins, F. Xia, D. B. Farmer, Y. Zhu, and P. Avouris, "High-frequency, scaled graphene transistors on diamond-like carbon," *Nature*, vol. 472, no. 7341, pp. 74–78, 2011.
- [88] S. Gilje, S. Han, M. Wang, K. L. Wang, and R. B. Kaner, "A Chemical Route to Graphene for Device Applications," *Nano Letters*, vol. 7, no. 11, pp. 3394–3398, 2007.
- [89] K. R. Paton, E. Varrla, C. Backes, R. J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya *et al.*, "Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids." *Nature Materials*, vol. 13, no. 6, pp. 624–30, 2014.
- [90] S.-J. Byun, H. Lim, G.-Y. Shin, T.-H. Han, S. H. Oh, J.-H. Ahn, H. C. Choi, and T.-W. Lee, "Graphenes Converted from Polymers," *The Journal of Physical Chemistry Letters*, vol. 2, no. 5, pp. 493–497, 2011.
- [91] Z. Peng, Z. Yan, Z. Sun, and J. M. Tour, "Direct Growth of Bilayer Graphene on SiO₂ Substrates by Carbon Diffusion through Nickel," *ACS Nano*, vol. 5, no. 10, pp. 8241–8247, 2011.
- [92] Z. Yan, Z. Peng, Z. Sun, J. Yao, Y. Zhu, Z. Liu, P. M. Ajayan, and J. M. Tour, "Growth of bilayer graphene on insulating substrates." *ACS Nano*, vol. 5, no. 10, pp. 8187–92, 2011.
- [93] P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, and A. K. Geim, "Making graphene visible," *Applied Physics Letters*, vol. 91, no. 6, p. 063124, 2007.
- [94] X. Wang, M. Zhao, and D. D. Nolte, "Optical contrast and clarity of graphene on an arbitrary substrate," *Applied Physics Letters*, vol. 95, no. 8, p. 081102, 2009.

- [95] A. C. Ferrari and J. Robertson, "Interpretation of Raman spectra of disordered and amorphous carbon," *Physical Review B*, vol. 61, no. 20, pp. 95–107, 2000.
- [96] Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu, and J. M. Tour, "Growth of graphene from solid carbon sources," *Nature*, vol. 2, no. 2, pp. 549–552, 2010.
- [97] M. Eizenberg and J. Blakely, "Carbon monolayer phase condensation on Ni(111)," *Surface Science*, vol. 82, no. 1, pp. 228–236, 1979.
- [98] A. L. Lee, L. Tao, and D. Akinwande, "Suppression of Copper Thin Film Loss during Graphene Synthesis," *ACS Applied Materials & Interfaces*, vol. 7, pp. 1527–1532, 2015.
- [99] V. Miseikis, D. Convertino, N. Mishra, M. Gemmi, T. Mashoff, S. Heun, N. Haghighian, F. Bisio *et al.*, "Rapid CVD growth of millimetre-sized single crystal graphene using a cold-wall reactor," *2D Materials*, vol. 2, no. 1, p. 014006, 2015.
- [100] S. Chen, H. Ji, H. Chou, Q. Li, H. Li, J. W. Suk, R. Piner, L. Liao *et al.*, "Millimeter-Size Single-Crystal Graphene by Suppressing Evaporative Loss of Cu During Low Pressure Chemical Vapor Deposition," *Advanced Materials*, vol. 25, no. 14, pp. 2062–2065, 2013.
- [101] H. Zhou, W. J. Yu, L. Liu, R. Cheng, Y. Chen, X. Huang, Y. Liu, Y. Wang *et al.*, "Chemical vapour deposition growth of large single crystals of monolayer and bilayer graphene," *Nature Communications*, vol. 4, p. 2096, 2013.
- [102] A. Awad, N. A. Ghany, and T. Dahy, "Removal of tarnishing and roughness of copper surface by electropolishing treatment," *Applied Surface Science*, vol. 256, no. 13, pp. 4370–4375, 2010.
- [103] A. M. Lewis, B. Derby, and I. A. Kinloch, "Influence of gas phase equilibria on the chemical vapor deposition of graphene." *ACS Nano*, vol. 7, no. 4, pp. 3104–17, 2013.
- [104] P. Braeuninger-Weimer, B. Brennan, A. J. Pollard, and S. Hofmann, "Understanding and Controlling Cu-Catalyzed Graphene Nucleation: The Role of Impurities, Roughness, and Oxygen Scavenging," *Chemistry of Materials*, vol. 28, no. 24, pp. 8905–8915, 2016.
- [105] "http://webbook.nist.gov/chemistry/," *NIST Chemistry WebBook*.
- [106] "Dwsim," <http://dwsim.inforside.com.br/>.

- [107] A. Boscá, J. Pedrós, J. Martínez, T. Palacios, and F. Calle, "Automatic graphene transfer system for improved material quality and efficiency," *Scientific Reports*, vol. 6, no. October 2015, p. 21676, 2016.
- [108] H. Xu, Z. Zhang, R. Shi, H. Liu, Z. Wang, S. Wang, and L.-M. Peng, "Batch-fabricated high-performance graphene Hall elements." *Scientific Reports*, vol. 3, p. 1207, 2013.
- [109] R. Shi, H. Xu, B. Chen, Z. Zhang, and L.-M. Peng, "Scalable fabrication of graphene devices through photolithography," *Applied Physics Letters*, vol. 102, no. 11, p. 113102, 2013.
- [110] J. Baltazar, H. Sojoudi, S. A. Paniagua, J. Kowalik, S. R. Marder, L. M. Tolbert, S. Graham, and C. L. Henderson, "Facile formation of graphene P-N junctions using self-assembled monolayers," *Journal of Physical Chemistry C*, vol. 116, no. 36, pp. 19 095–19 103, 2012.
- [111] A. Pirkle, J. Chan, A. Venugopal, D. Hinojos, C. W. Magnuson, S. McDonnell, L. Colombo, E. M. Vogel *et al.*, "The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO₂," *Applied Physics Letters*, vol. 99, no. 12, p. 122108, 2011.
- [112] A. Boscá, J. Pedrós, J. Martínez, F. Calle, and T. Palacios, "Procedimiento de transferencia de nanocapas y aparato de realización del mismo," 2013.
- [113] G. Decher, J. Hong, and J. Schmitt, "Buildup of ultrathin multilayer films by a self-assembly process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces," *Thin Solid Films*, vol. 210-211, pp. 831–835, 1992.
- [114] M. Her, R. Beams, and L. Novotny, "Graphene transfer with reduced residue," *Physics Letters A*, vol. 377, no. 21-22, pp. 1455–1458, 2013.
- [115] B. A. Miller-Chou and J. L. Koenig, "A review of polymer dissolution," *Progress in Polymer Science*, vol. 28, no. 8, pp. 1223–1270, 2003.
- [116] H. Van Ngoc, Y. Qian, S. K. Han, and D. J. Kang, "PMMA-Etching-Free Transfer of Wafer-scale Chemical Vapor Deposition Two-dimensional Atomic Crystal by a Water Soluble Polyvinyl Alcohol Polymer Method," *Scientific Reports*, vol. 6, no. August, p. 33096, 2016.
- [117] H. Park, A. Afzali, S.-J. Han, G. S. Tulevski, A. D. Franklin, J. Tersoff, J. B. Hannon, and W. Haensch, "High-density integration of carbon nanotubes via chemical self-assembly," *Nature Nanotechnology*, vol. 7, no. 12, pp. 787–791, 2012.

- [118] D. J. DiMaria, E. Cartier, and D. Arnold, "Impact ionization, trap creation, degradation, and breakdown in silicon dioxide films on silicon," *Journal of Applied Physics*, vol. 73, no. 7, pp. 3367–3384, 1993.
- [119] C.-C. Chen, M. Aykol, C.-C. Chang, A. F. J. Levi, and S. B. Cronin, "Graphene-silicon Schottky diodes." *Nano Letters*, vol. 11, no. 5, pp. 1863–7, 2011.
- [120] H. E. Romero, N. Shen, P. Joshi, H. R. Gutierrez, S. A. Tadigadapa, J. O. Sofo, and P. C. Eklund, "n-Type behavior of graphene supported on Si/SiO(2) substrates." *ACS Nano*, vol. 2, no. 10, pp. 2037–44, 2008.
- [121] R. Piner, H. Li, X. Kong, L. Tao, I. N. Kholmanov, H. Ji, W. H. Lee, J. W. Suk *et al.*, "Graphene Synthesis via Magnetic Inductive Heating of Copper Substrates," *ACS Nano*, vol. 7, no. 9, pp. 7495–7499, 2013.
- [122] M. B. Lerner, F. Matsunaga, G. H. Han, S. J. Hong, J. Xi, A. Crook, J. M. Perez-Aguilar, Y. W. Park *et al.*, "Scalable production of highly sensitive nanosensors based on graphene functionalized with a designed G protein-coupled receptor," *Nano Letters*, vol. 14, no. 5, pp. 2709–2714, 2014.
- [123] W. S. Leong, C. T. Nai, and J. T. L. Thong, "What does annealing do to metal-graphene contacts?" *Nano Letters*, vol. 14, no. 7, pp. 3840–3847, 2014.
- [124] S. Kim, I. Jo, J. Nah, Z. Yao, S. K. Banerjee, and E. Tutuc, "Coulomb drag of massless fermions in graphene," *Physical Review B - Condensed Matter and Materials Physics*, vol. 83, no. 16, pp. 1–4, 2011.
- [125] L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, A. Mishchenko, T. Georgiou, M. I. Katsnelson *et al.*, "Field-Effect Tunneling Transistor Based on Vertical Graphene Heterostructures." *Science*, vol. 947, no. 6071, pp. 947–50, 2012.
- [126] P. Yasaei, B. Kumar, R. Hantehzadeh, M. Kayyalha, A. Baskin, N. Reprin, C. Wang, R. F. Klie *et al.*, "Chemical sensing with switchable transport channels in graphene grain boundaries," *Nature Communications*, vol. 5, p. 4911, 2014.
- [127] L. Liao, Y.-C. Lin, M. Bao, R. Cheng, J. Bai, Y. Liu, Y. Qu, K. L. Wang *et al.*, "High-speed graphene transistors with a self-aligned nanowire gate." *Nature*, vol. 467, no. 7313, pp. 305–8, 2010.
- [128] A. Dimiev, D. V. Kosynkin, A. Sinitskii, A. Slesarev, Z. Sun, and J. M. Tour, "Layer-by-layer removal of graphene for device patterning." *Science*, vol. 331, no. 6021, pp. 1168–72, 2011.

- [129] F. Xia, V. Perebeinos, Y.-m. Lin, Y. Wu, and P. Avouris, "The origins and limits of metal-graphene junction resistance." *Nature Nanotechnology*, vol. 6, no. 3, pp. 179–84, 2011.
- [130] J. A. Robinson, M. LaBella, M. Zhu, M. Hollander, R. Kasarda, Z. Hughes, K. Trumbull, R. Cavaleiro *et al.*, "Contacting graphene," *Applied Physics Letters*, vol. 98, no. 5, p. 053103, 2011.
- [131] H. Yang, J. Heo, S. Park, H. J. Song, D. H. Seo, K.-E. Byun, P. Kim, I. Yoo *et al.*, "Graphene barristor, a triode device with a gate-controlled Schottky barrier." *Science*, vol. 336, no. 6085, pp. 1140–3, 2012.
- [132] L. Wang, I. Meric, P. Y. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe *et al.*, "One-dimensional electrical contact to a two-dimensional material." *Science*, vol. 342, no. 6158, pp. 614–7, 2013.
- [133] T. Chu and Z. Chen, "Understanding the Electrical Impact of Edge Contacts in Few-Layer Graphene." *ACS Nano*, no. 4, pp. 3584–3589, 2014.
- [134] J. T. Smith, A. D. Franklin, D. B. Farmer, and C. D. Dimitrakopoulos, "Reducing contact resistance in graphene devices through contact area patterning." *ACS Nano*, vol. 7, no. 4, pp. 3661–7, 2013.
- [135] W. S. Leong, H. Gong, and J. T. L. Thong, "Low-contact-resistance graphene devices with nickel-etched-graphene contacts." *ACS Nano*, vol. 8, no. 1, pp. 994–1001, 2014.
- [136] A. L. Hsu, R. J. Koch, M. T. Ong, W. Fang, M. Hofmann, K. K. Kim, T. Seyller, M. S. Dresselhaus *et al.*, "Surface-Induced Hybridization between Graphene and Titanium." *ACS Nano*, vol. 8, no. 8, pp. 7704–13, 2014.
- [137] P. Joshi, H. E. Romero, A. T. Neal, V. K. Toutam, and S. A. Tadigadapa, "Intrinsic doping and gate hysteresis in graphene field effect devices fabricated on SiO₂ substrates." *Journal of Physics: Condensed Matter*, vol. 22, no. 33, p. 334214, 2010.
- [138] P. L. Levesque, S. S. Sabri, C. M. Aguirre, J. Guillemette, M. Siaj, P. Desjardins, T. Szkopek, and R. Martel, "Probing charge transfer at surfaces using graphene transistors." *Nano Letters*, vol. 11, no. 1, pp. 132–7, 2011.
- [139] J. Moser, A. Barreiro, and A. Bachtold, "Current-induced cleaning of graphene," *Applied Physics Letters*, vol. 91, no. 16, p. 163513, 2007.
- [140] S. Ryu, L. Liu, S. Berciaud, Y.-J. Yu, H. Liu, P. Kim, G. W. Flynn, and L. E. Brus, "Atmospheric Oxygen Binding and Hole Doping in Deformed Graphene on a SiO₂ Substrate," *Nano Letters*, vol. 10, no. 12, pp. 4944–4951, 2010.

- [141] A. Nourbakhsh, M. Cantoro, A. Klekachev, F. Clemente, B. Soree, M. H. van der Veen, T. Vosch, A. Stesmans *et al.*, "Tuning the Fermi Level of SiO₂-Supported Single-Layer Graphene by Thermal Annealing," *The Journal of Physical Chemistry C*, vol. 114, no. 15, pp. 6894–6900, 2010.
- [142] J. Park, W. H. Lee, S. Huh, S. H. Sim, S. B. Kim, K. Cho, B. H. Hong, and K. S. Kim, "Work-Function Engineering of Graphene Electrodes by Self-Assembled Monolayers for High-Performance Organic Field-Effect Transistors," *The Journal of Physical Chemistry Letters*, vol. 2, no. 8, pp. 841–845, 2011.
- [143] Y. Shi, X. Dong, P. Chen, J. Wang, and L. J. Li, "Effective doping of single-layer graphene from underlying SiO₂ substrates," *Physical Review B - Condensed Matter and Materials Physics*, vol. 79, no. 11, pp. 1–4, 2009.
- [144] Z. Yan, J. Yao, Z. Sun, Y. Zhu, and J. M. Tour, "Controlled ambipolar-to-unipolar conversion in graphene field-effect transistors through surface coating with poly(ethylene imine)/poly(ethylene glycol) films." *Small*, vol. 8, no. 1, pp. 59–62, 2012.
- [145] C. Gong, S. McDonnell, X. Qin, A. Azcatl, H. Dong, Y. J. Chabal, K. Cho, and R. M. Wallace, "Realistic metal-graphene contact structures." *ACS Nano*, vol. 8, no. 1, pp. 642–9, 2014.
- [146] A. Boscá, J. Pedrós, J. Martínez, and F. Calle, "Method for extracting relevant electrical parameters from graphene field-effect transistors using a physical model," *Journal of Applied Physics*, vol. 117, p. 044504, 2015.
- [147] K. I. Bolotin, K. J. Sikes, J. Hone, H. L. Stormer, and P. Kim, "Temperature-Dependent Transport in Suspended Graphene," *Physical Review Letters*, vol. 101, no. 9, p. 096802, 2008.
- [148] J. Moon, D. Curtis, S. Bui, M. Hu, D. Gaskill, J. Tedesco, P. Asbeck, G. Jernigan *et al.*, "Top-Gated Epitaxial Graphene FETs on Si-Face SiC Wafers With a Peak Transconductance of 600 mS/mm," *IEEE Electron Device Letters*, vol. 31, no. 4, pp. 260–262, 2010.
- [149] C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, "Quasi-Free-Standing Epitaxial Graphene on SiC Obtained by Hydrogen Intercalation," *Physical Review Letters*, vol. 103, no. 24, p. 246804, 2009.
- [150] D. L. Mafra, G. Samsonidze, L. M. Malard, D. C. Elias, J. C. Brant, F. Plentz, E. S. Alves, and M. A. Pimenta, "Determination of LA and TO phonon dispersion relations of graphene near the Dirac point by double resonance Raman scattering," *Physical Review B*, vol. 76, no. 23, p. 233407, 2007.