RAMAN SPECTROSCOPY OF GRAPHENE, ITS DERIVATIVES
AND GRAPHENE-BASED HETEROSTRUCTURES

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ABSTRACT

In less than a decade of research, graphene has earned a long list of superlatives to its name and is expected to have applications in various fields such as electronics, photonics, optoelectronics, materials, biology and chemistry. Graphene has also attracted a lot of attention because its properties can be engineered either via intrinsic changes or by modification of its environment. Raman spectroscopy has become an ideal characterization method to obtain qualitative and quantitative information on these changes. This thesis investigates the possibility to change, supplement and monitor the electronic and optical properties as well as the chemical reactivity of graphene. It is achieved by i) substrate effect, ii) introduction of defects in the structure of graphene and iii) the combination of graphene with other two-dimensional crystals such as hexagonal boron nitride (h-BN) and transition metal dichalcogenides. In particular, the experimental work presented here describes:

I The influence of the type of substrate on the Raman intensity of graphene. This work leads to the calculation of the Raman scattering efficiency of graphene after CaF$_2$ is found to be a suitable substrate for this kind of study in contrast to Si/SiO$_x$ that strongly modulates the Raman intensities. The G peak scattering efficiency is found to be about $200 \times 10^{-5}$ m$^{-1}$ Sr$^{-1}$ at 2.4 eV while that of the 2D peak is one order of magnitude higher, confirming the resonant nature of the 2D peak Raman scattering process.

II An attractive method to produce large (up to several hundreds of µm across) and high quality graphene by anodic bonding. This cheap, fast and solvent-free method also allows introduction of vacancy like defects in the samples in a relatively controllable way.

III The Raman signatures of several types of defect such as sp$^3$ sites, vacancies and substitutional atoms. For low defect concentration (stage 1) the intensity ratio I(D)/I(D’) is constant and is 13 for sp$^3$ sites, 9 for substitutional atoms and 7 for vacancies. This signature is explained using the local activation model recently proposed to model the amorphization trajectory of graphene with containing vacancy-like defects.
IV Controlled modification of graphene through mild oxygen plasma. The influence of sp$^3$ sites on monolayer and bilayer graphene’s electrical properties are discussed. In the case of bilayer under controlled conditions, it is possible to modify only the top layer. This may lead to decoupling between the two layers, which could explain the good mobility measured for this system. The possibility to use such system as a sensor is discussed.

V The characteristic Raman signature of aligned graphene/h-BN superlattices. The Raman spectrum shows strong changes in perfectly aligned superlattices, which could be attributed to the reconstruction of the Dirac spectrum.

VI A prototype photovoltaic cell made of a graphene and tungsten disulphide (WS$_2$) heterostructure with an external quantum efficiency of about 30%. The beneficial combination of an excellent absorption in WS$_2$ atomically thin films due to the presence of Van Hove singularities and graphene used as a transparent, flexible and conductive electrode is demonstrated.
LIST OF PUBLICATIONS


Candidate Name: Axel Eckmann

Faculty: Engineering and Physical Sciences

Thesis Title: Raman spectroscopy of graphene, its derivatives and graphene-based heterostructures

Declaration to be completed by the candidate:

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Axel Eckmann
Manchester, June 2013
Three-dimensional (3-D) carbon-based materials, such as diamond and graphite have been extensively studied. The former allotrope is an isotropic material made of carbon atoms bonded in a tetrahedral configuration while the latter is anisotropic due to its layered structure. At the end of the 1980s and 1990s, zero- and one-dimensional carbon forms were discovered: fullerenes and nanotubes, respectively. Graphene is the remaining two-dimensional (2-D) carbon form and was discovered in 2004 and can be seen as the fundamental building block of graphite, nanotubes or fullerenes: graphite is a stack of graphene layers loosely bonded by van der Waals forces, nanotubes are rolled sheets of graphene and fullerenes are wrapped pieces of graphene. For this reason, graphene has been theoretically studied as early as 1947 but was thought to be unstable at room temperature because of thermal fluctuations.

More than 60 years and a Nobel Prize later, graphene is undoubtedly one of the most intensively researched materials in the world and has been selected as one of only two flagship research projects that will lead Europe’s research in the next ten years. All around the globe, dedicated graphene research centres open while companies such as IBM, Nokia, Samsung, BASF and many more also study the possible use of graphene’s outstanding properties and explore ways to engineer them.

This thesis is a modest contribution to this exciting and quickly growing field with a focus on optical characterization of graphene, its derivatives and graphene-based heterostructures. It details methods to engineer the properties of graphene and proposes at each step a way to derive quantitative and qualitative information on the systems studied. The work is organized as follows: Part I constitutes the introduction to the experimental results, which are then discussed in details in Part II.

Chapter 1 summarizes the main properties of graphene and its derivatives as well as the other (2-D) materials used in this thesis. Chapter 2 gives a background to Raman spectroscopy and the fundamental results that are prerequisite to Part II. Chapter 3 describes the Raman spectrometers, the scanning photocurrent apparatus and the plasma chamber used in the experiments as well as an etching recipe to drill micrometer sized holes in silicon wafers. Chapter 4 studies the influence of the substrate on the Raman intensities of graphene and gives a value for the Raman cross section of the G and the 2D peaks.

Chapter 5, 6 and 7 discuss methods to introduce defects of different types and control-
lable concentrations. Chapter 5 delves into the production of graphene by anodic bonding. It is a fast, cheap, solvent- and tape-free method that allows the deposition of large high quality flakes, but also of flakes with vacancy like defects. In Chapter 6, a careful and systematic study of graphene with different types of defects leads to the discovery of the Raman fingerprint of specific types of defects which is supported by theory and explained in the framework of the so-called local activation model. Chapter 7 focuses on defects arising from the change in hybridization of graphene from sp² to sp³ and compares the reactivity of monolayer and bilayer graphene. First it shows that graphene bilayers are less reactive than monolayers for one sided plasma exposure as the bottom layer of a bilayer graphene is only marginally affected. This is especially interesting for the purpose of sensors since the modified bilayer shows a relatively good mobility. Second, it highlights the relevance of substrate engineering which is proven as an efficient method to control the chemical reactivity of bilayer graphene. A substrate with a hole allows the creation of suspended membranes that can be modified on both sides.

Finally Chapter 8 and 9 explore graphene based heterostructures as a new way to modify or supplement graphene’s properties. Chapter 8 evidences the effect of a graphene/graphene and a graphene/BN moiré pattern obtained for small rotation angles on the Raman spectrum of graphene. For graphene/BN structures, the modified Raman features lead to the estimation of the moiré wavelength or equivalently to the estimation of the position of the lowest energy minibands for small twist angles. Chapter 9 demonstrates the possibility to use graphene in photovoltaic applications by combining it with atomically thin WS₂ to compensate for the low absorption properties of graphene.
Part I

Introduction
1.1 Graphene production methods

Graphene was first isolated by the so-called micromechanical exfoliation of graphite, or "scotch tape method". The method has been discussed at length in the literature and in other theses from Manchester University. Briefly, a natural graphite flake available commercially is peeled several times between two pieces of scotch tape and the resulting mixture of thick and thin flakes is deposited on a substrate, typically an oxidized Si wafer. This method is still widely used in the research community as it allows the production of flakes from a single crystal grain and with a very low defect concentration. However, its poor yield and the relatively small sizes of the flakes (max. 1 mm) have forced the emergence of other methods able to create graphene on a larger, industrial scale.

Chemical exfoliation of graphite is an alternative to mechanical exfoliation that has received much attention. Graphite or graphite oxide crystals are placed in a solvent (for instance dimethylformamide) and left in an ultrasonic bath for several hours to several days. These solutions can contain a majority of dissolved graphene or graphene oxide monolayers as large as a few microns. It is then possible to produce thin films, laminates or graphene paper after filtration of the solution. Water-based exfoliation methods also exist but require the use of surfactants to overcome the high surface energy of water.

Graphene growth by chemical vapor deposition (CVD) is another alternative method. Here graphene is grown on a metal substrate such as copper foil in a high temperature furnace (≈1000°C) with a flow of methane and hydrogen. Under carefully chosen conditions, the methane molecules dissociate at the surface of the metal substrate and self assemble in a single layer sheet of graphene. This method allowed the production and the transfer of a 30 inch sheet of graphene to arbitrary flexible substrates.

Finally, graphene can be grown by epitaxy on either face of a silicon carbide (SiC) crystal. But the size and the quality of the graphene sheet heavily depend on that of the starting SiC material and are typically highly doped and expensive.

Chapter 5 presents yet another production method based on the anodic bonding of
CHAPTER 1. GRAPHENE AND OTHER TWO-DIMENSIONAL CRYSTALS

graphite flakes on glass substrates.

1.2 Electronic structure

![Graphene lattice diagram](image)

Figure 1.1: a) Graphene’s real space lattice and b) reciprocal space lattice with the high symmetry points $\Gamma$, $K$ and $K'$. (Adapted from Ref. 19)

The crystal lattice of graphene contains two sub-lattices composed of the atoms A and B, as shown in Figure 1.1.a. Thus, there are two atoms contained in the unit cell of graphene. The C-C bond length is 1.42 Å and the lattice constant $a$ is 2.46 Å. Figure 1.1.b depicts the lattice of graphene in the reciprocal space. Its primitive cell is known as the first Brillouin zone and is also hexagonal. The reciprocal space of a crystal is the dual representation of the wave vector momentum $k$ and is obtained by Fourier transformation of the Cartesian crystal structure. The Brillouin zone’s centre $\Gamma$ is the origin of the reciprocal space with $k = 0$ while its corners are named $K$ and $K'$ points. These are inequivalent points, because they are related to the two atoms A and B. The other corners can be obtained by a rotation of $120^\circ$, which also corresponds to the symmetry of the crystal lattice.

The electronic structure, which is a representation of the allowed energies of the electronic states as a function of $k$, can be calculated by a simple tight binding model as described in the early work of Wallace\(^4\). The nearest neighbour approximation gives:

$$E(k) = \pm t \sqrt{3 + f(k)}$$  \hspace{1cm} (1.2.1)

where $t$ is the nearest neighbour hopping energy and $f(k)$ is

$$f(k) = 2\cos(\sqrt{3}k_y a) + 4\cos\left(\frac{\sqrt{3}}{2} k_y a\right)\cos\left(\frac{3}{2} k_x a\right)$$  \hspace{1cm} (1.2.2)

Therefore, the full band structure, according to the Bloch band description, is composed of two energy bands, the valence band and the conduction band, which are separated by a gap in the entire Brillouin zone, with the exception of six points, as shown in
1.3. ELECTRONIC PROPERTIES

Figure 1.2. The valence and conduction bands touch exactly at those six points, called Dirac points (corresponding to the $K$ and $K'$ points), giving a conical spectrum at low energy, inset of Figure 1.2. In (undoped) graphene the Fermi energy lies exactly at the Dirac points, the Fermi surface consequently consists of six points.

Figure 1.2: Graphene electronic band structure. The inset shows a zoom on the so called Dirac cones at the $K$ and $K'$ corners of the Brillouin zone. (Adapted from Ref 20)

One of the key features of the band structure of graphene is the linear dependence between the low energy levels $E(k)$ and the electron wavevectors ($k$) near the Dirac cones where:

$$E = \pm \nu_F \sqrt{k_x^2 + k_y^2}$$  \hspace{1cm} (1.2.3)

where $\nu_F \simeq 10^6$ m/s is the Fermi velocity and $k_x$ and $k_y$ are the components of the momentum in the x and y directions of the plane. This electronic structure states that graphene is a gapless semiconductor or semimetal. However, in contrast to standard semimetals, the linear dispersion between energy and momentum imposes the speed of the electrons to remain constant. It implies that charge carriers in graphene should be described as massless relativistic fermions, where the speed of light is replaced by $\nu_F$. Thus, electrons in graphene are described by the Dirac equation, in place of the usual Schrödinger equation, which usually describes the electrons and holes in standard parabolic semiconductors.

1.3 Electronic properties

In order to experimentally study the electronic properties of graphene, the flake is integrated in an electronic device. Usually, flakes are exfoliated on Si wafers covered by a SiO$_x$ layer (Si/SiO$_x$). The preferred oxide thickness is either 90 nm or 300 nm for reasons that are explained in Section 1.4. Graphene is later patterned into a Hall bar of standard geometry (usually about 1 µm in width) with at least four terminals. A double layer of
5 nm Cr and 50 nm Au contacts are later deposited by e-beam lithography. Figure 1.3.a shows a sketch of a six terminal device deposited on a Si/SiO\textsubscript{x} substrate. Macroscopic contacts from the terminals to a chip carrier are later made by hand using silver paint and gold wires.

The bulk Si substrate is heavily p-doped and is therefore conductive while the oxidized layer is insulating. This geometry allows one to apply a so-called gate voltage $V_g$ between the graphene flake and the underlying silicon and allowed the observation of the electric field effect in graphene, as measured in the very first experimental work ever reported on graphene\textsuperscript{21}.

![Graphene device with 6 contacts deposited on a Si/SiO\textsubscript{x} substrate b) Resistivity of a graphene sheet against gate voltage. (Adapted from Ref. 3)](image)

Ref 21 indeed showed that the Fermi energy of graphene could be moved away from its undoped position at the Dirac point, i.e. to increase the charge concentration in the graphene plane, a gate voltage is applied between the gate and the sample (see device geometry in Figure 1.3.a). This is known as the ambipolar electric field effect because the majority charge carriers can be tuned continuously from holes to electrons, as shown in Figure 1.3.b. The neutrality point corresponds to the point where the Fermi energy exactly matches the Dirac point energy and where the density of state (DOS) in graphene vanishes. As a result, the resistivity, measured from $V_{xx}$ (Figure 1.3.a) of the graphene sheet sharply increases. Taking into account a simple two plate capacitor where the two electrodes are graphene and the p-doped Si substrate, and SiO\textsubscript{x} the dielectric spacer, the concentration of charge carriers ($n$) is related to the gate voltage ($V_g$) applied:

$$n = \frac{\epsilon_0 \epsilon V_g}{ed}$$  \hspace{1cm} (1.3.1)

where $\epsilon_0 \epsilon$ is the dielectric constant of the spacer material (here SiO\textsubscript{x}), $d$ the thickness of the spacer and $e$ the charge of the electron.

The implications of the presence of Dirac fermions on the properties of graphene have been thoroughly described in Ref 22 with a systematic formalism to most aspects of graphene research such as electronic transport, mechanical, optical and magnetic properties.
In particular, the existence of massless Dirac fermions in graphene produces unique features when graphene is placed in a magnetic field. In this case, a discrete distribution of energy levels appears: the Landau levels. For Dirac fermions, the Landau levels are not equidistant and the zero Landau level lies at zero energy in contrast to massive particles\textsuperscript{23}. It results that the zero Landau level of undoped graphene is equally populated by holes and electrons which explains the observation of the anomalous integer quantum Hall effect (measured from $V_{xy}$), and this is even visible at room temperature\textsuperscript{23–25}. Conversely, the longitudinal resistivity of graphene in a magnetic field shows oscillations called Shubnikov-de Haas oscillations that are a direct consequence of the Landau levels\textsuperscript{23}.

Another consequence of the existence of massless Dirac fermions, owing this time to their chiral nature, is the Klein paradox\textsuperscript{26}, i.e. the insensitivity of the charge carriers of graphene to smooth potential barriers. Quantum mechanics for massive particles indeed predicts that, in the presence of such a barrier, the electron would have a certain probability to tunnel through depending on the height and the width of the barrier. In the case of massless relativistic chiral particles, the electron will be transmitted with 100% probability, independent of the barrier height. The occurrence of the Klein paradox can explain why graphene shows a high charge mobility (exceeding 200,000 cm$^2$ V$^{-1}$ s$^{-1}$ obtained on suspended graphene\textsuperscript{27}). The highest mobility in supported devices has been achieved for graphene deposited on hexagonal boron nitride\textsuperscript{28} because it has an atomically smooth surface relatively free of charge traps and dangling bonds with a structure and lattice constant very similar to graphene\textsuperscript{29}. This makes graphene a very promising material for electronic devices.

### 1.4 Optical properties

Graphene is only one atom thick and is therefore almost transparent, with an opacity of about 2.3% for suspended flakes\textsuperscript{30}. Ref. 30 showed that, up to five layers, the opacity of the graphene thin film is proportional to the number of layers. Furthermore, the opacity of graphene is constant over the entire visible spectrum. Thus the observation of graphene under an optical microscope is a difficult task and no improvement in the contrast of graphene should be expected by using a band-pass filter. However, it is possible to enhance the contrast of graphene on a substrate by using interference effects observed when a substrate is covered by a thin film\textsuperscript{31}. A careful choice of the thickness and refractive index of the substrate and film can induce a coherent change in the light path, which enhances the contrast of graphene on the substrate. This multiple interface problem sketched in Figure 1.4.a can be modeled using the transfer matrix method (TMM) described in Ref. 32.

Figure 1.4.b shows the theoretical contrast obtained by TMM for graphene deposited on a Si/SiO$_2$ substrate versus the thickness of the SiO$_2$ layer for visible excitation wavelengths. The maximum contrast in the green region of the visible spectrum (region at
which the human eye is most sensitive) between graphene and Si/SiOx can be obtained by using a silicon oxide thickness of about 90 nm ($\approx 18\%$) or 300 nm ($\approx 10\%$). It explains why graphene is optically visible on Si/SiO$_x$, while it is almost invisible on others, such as glass and quartz. This interference effect will be discussed again in Chapter 4.

There has been a lot of effort to try to combine the electronic and optical properties of graphene. One such attempt led to the demonstration of graphene photodetectors. The combination of graphene devices with plasmonic structures also allows the fabrication of new devices with extremely high speed, low driving voltage, low power consumption and compact sizes.

Typically, photodetectors rely on the conversion of light into an electric current. The so-called photovoltaic effect relies on two mechanisms that should occur as sketched in Figure 1.5.a:

- the absorption of a photon by creation of an electron/hole pair depicted by the vertical arrow in Figure 1.5.a.

- the collection of the photoexcited charges. To achieve this, the charges must reach the gold electrodes before a recombination occurs.

Absorption in semiconductors is the result of the promotion of an electron from the valence band to the conduction band provided that the excitation energy can overcome the gap. In graphene, because of the peculiar electronic band structure, photons over a wide region of the spectrum can be absorbed with a similar efficiency. Then, to systematically collect the photoexcited electrons, there should be a preferred direction for the electrons to flow, i.e. an electric field must be present within the material. Collection must take place in a time shorter than the typical lifetime of the electron/hole pair. For
1.4. OPTICAL PROPERTIES

Figure 1.5: a) Contact effect at a gold/graphene interface. An electron/hole pair is created after absorption of a photon and is later separated by the electric field generated at the gold/graphene junction. The Dirac cone labeled (1) represents the band structure of graphene under the gold electrode or in the direct vicinity. The Dirac cone labeled (2) is the band structure of pristine graphene further from the contact. Because of a difference in work function between graphene and gold, the Dirac cones (1) and (2) are shifted with respect to each other and create a field able to separate the photo excited charges. b) Optical image of a photovoltaic device with graphene, MoS$_2$ and gold contacts. c) Example of photocurrent map obtained on such structures. Doping can also be introduced by other materials such as MoS$_2$. The mechanism has a similar origin and a photocurrent can also be generated at the MoS$_2$/graphene junction.

Graphene photodetectors, a bias can for example be applied between the two electrodes, thus creating a potential gradient across the device. Unfortunately, this solution consumes energy and cannot always be used. Interestingly, a potential gradient naturally occurs at the graphene/gold electrode where a junction is created within the graphene channel with different levels of doping near or far from the contact, as shown on Figure 1.5.a. Because of the difference in the work function of graphene and gold, graphene is p-doped near the contacts, therefore creating a local built-in field able to separate photoexcited electron/hole pairs, similar to a p-n junction.

Figure 1.5.b is an optical image of a device where a graphene flake is contacted at its extremities with a MoS$_2$ monolayer flake sitting across it. The maps of the current generated upon laser illumination reveal the areas that act as photodetectors. Two regions around the contacts show currents of similar magnitude but different polarities. This is attributed to the opposite directions of the p-n junctions at each electrode as sketched on
1.5 Mechanical properties

The mechanical properties of graphene are also remarkable as it is the strongest material known due to the robustness of the covalent carbon-carbon bonds\(^{39}\). The Young’s modulus of graphene could be measured by indentation with an AFM tip on a suspended sheet. In such an experiment, the membrane is stretched until rupture and the breaking strength and Young’s modulus can be measured. The latter was measured at about 1 TPa\(^{39}\) and the breaking strength was estimated at 42 N.m\(^{-1}\) but is dependent on the tip radius\(^{40}\). Other complementary methods have been used to calculate the Young’s modulus of graphene such as resonators\(^{41}\) or even Raman spectroscopy\(^{42}\) and yielded similar values.

Thus, graphene is harder than diamond, which has a Young’s modulus of about 900 GPa. Moreover, graphene can be stretched elastically up to 20%\(^{39}\) and it can easily be bent or folded\(^{43}\). It is indeed common to observe folds of single layer flakes produced by micro mechanical exfoliation (see Chapter 8). Such systems have for instance been used to study stacking faults in bilayer graphene\(^{44}\). The unusual combination of brittleness and pliability, together with the outstanding electronic properties, makes graphene a perfect material to be used for flexible electronics and touch screen devices\(^{16}\).

Finally, graphene membranes are impermeable to all gases\(^{45}\), including helium. Graphene can even be used as a gas detector\(^{46}\). One such detector was achieved with a device similar to the one described in Figure 1.3.a. When gas molecules adsorb on the free graphene surface, a change in resistivity is measured\(^{46}\). Since graphene is strictly 2-D, the whole material is in direct contact with adsorbants, making it sensitive to very low gas concentrations. On the other hand, the ability to open pores in graphene of desired size opened up the possibility to use graphene membranes as a gas separation membrane\(^{47–49}\) or even as a DNA sequencing tool\(^{50–52}\).

1.6 Graphene derivatives and other 2-D materials

1.6.1 Graphene oxide

As mentioned earlier, graphene is a plane of sp\(^2\) bonded carbons with only surface atoms. This feature is analogous to that of single-walled carbon nanotube for which covalent functionalization has played a decisive role, in particular for the separation and manipulation of the tubes\(^{53}\). There are a plethora of examples of graphene covalent functionalization as described in Ref 54 and references therein. The first chemical derivative of graphene ever studied is graphene oxide due to the simplicity of its isolation by sonica-
1.6. GRAPHENE DERIVATIVES AND OTHER 2-D MATERIALS

The formation of graphite oxide\(^\text{10}\) is its structure contains various chemical groups such as hydroxyl, epoxy, carbonyl, and carboxyl functional groups, as depicted in Figure 1.6, which are responsible for the good solubility of graphene oxide in water\(^\text{55}\). Furthermore, these groups can be used as anchors for further covalent functionalization and more complex chemistry of graphene\(^\text{54}\). For instance, oligothiophene chromophores can bind to the carboxyl groups with potential application in optoelectronics\(^\text{56}\) and photovoltaics\(^\text{57}\).

Figure 1.6: a) Structure of a graphene oxide flake\(^\text{58}\) and b) artist view of hydrogenated graphene\(^\text{59}\)

However the electronic performance of graphene oxide platelets are far inferior to that of pristine graphene and strategies were developed to restore its mobility, such as chemical reduction\(^\text{60,61}\). Although the functional groups cannot be entirely removed, reduced graphene oxide films exhibit lower sheet resistance than the graphene oxide ones\(^\text{12,62}\).

1.6.2 Stoichiometric graphene derivatives

Graphene can also be modified by covalent bonding of chosen adatoms, as predicted by Sofo et al.\(^\text{59}\) in their first principles calculations. Since then, several methods such as hydrogenation\(^\text{63}\), fluorination\(^\text{64}\), oxidation\(^\text{65,66}\), chlorination\(^\text{67}\) have led to the creation of stoichiometric chemical derivatives of graphene. The \(\pi\) bonds are replaced by \(\sigma\) carbon-adatom bonds, where the adatom in these instances are hydrogen, fluorine, oxygen or chlorine. The carbon atom hybridization change from sp\(^2\) to sp\(^3\) results in structural changes such as the shrinkage of the lattice constant, different C-C angles and the displacement of carbon atoms out of the sheet plane in order to minimize the steric interactions of the newly formed bonds, as shown in Figure 1.6 b. A direct consequence of this is that a stoichiometric covalent modification of graphene can only occur when both faces of graphene are exposed which is not the case when graphene in supported by a substrate. In the case of hydrogenated graphene, the C-H bonds are weak enough to be broken upon annealing\(^\text{63}\), typically at 300\(^\circ\)C for a few hours in a mixture of Ar and H\(_2\) gases.

The most widely used method to create graphene chemical derivatives is by exposure to a plasma (see Section 3.3), i.e. to a medium with ionized atoms. It relies on the principle that the activation energy for an adatom to bond to graphene is lowered for
ionized atoms in contrast to neutral species. Plasma exposure is particularly well suited for experiments that require a high control on the concentration and type of adatoms bonded to the graphene scaffold because the strength of the plasma, the type of gas and the exposure time can be carefully controlled.

These modifications dramatically change the properties of graphene. The disappearance of the $\pi$ electrons opens a band gap. For hydrogenated and fluorinated graphene, the experimental and theoretical data differ a lot but the resulting band gaps are in any case larger than 3 eV$^{59,68-71}$. Partial hydrogenation on localized areas of the graphene sheet is seen as a potential way to achieve a controllable band gap opening$^{72}$ and presents the advantage of being reversible$^{63}$. Methods to perform functionalization of graphene and the possibility to tune it will be further discussed in Chapter 7.

1.6.3 Boron nitride

Hexagonal boron nitride (h-BN) is a material that is structurally very close to graphene with a hexagonal lattice made of alternating boron and nitrogen atoms. The lattice constant differs from that of graphene by only 1.8% and crystalline h-BN is also a layered material like graphite. Thus the isolation of individual layers can be achieved in similar fashion as for graphene, by micromechanical exfoliation$^{73}$ or by liquid exfoliation$^{74}$. Despite structural similarities, BN and graphene have very different properties in the sense that BN is a wide band gap insulator (5-6 eV)$^{75}$ with a dielectric constant close to SiO$_x$.$^{76}$ BN has attracted a lot attention because of its atomic flatness and low charge inhomogeneity$^{29,77}$ compared to Si/SiO$_x$ substrates. Therefore BN is broadly used both as a substrate and a material for encapsulation of graphene devices$^{29,28}$. It results in a dramatic enhancement of the electronic transport properties of graphene with mean free path of charge carriers of the order of one micron at room temperature$^{28}$. But thin films of BN also have applications as tunneling barriers$^{78}$ and allowed fabrication of field-effect tunneling transistors$^{79}$.

1.6.4 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDC) are layered materials made of two different atoms: a transition metal M such as Mo, W, Ta and two chalcogen atoms X such as S, Se or Te. The TMDC formula is MX$_2$ and has the structure depicted in Figure 1.7 where the M atoms are sandwiched between two layers of X atoms and strong covalent bonds exist between each M layer and its X layers. MX$_2$ layers are only interacting by Van der Waals forces. Because of their layered structure, 2-D flakes have been obtained by micromechanical exfoliation$^6$. Despite their structural similarities, they show a wide range of electronic properties$^{80}$ and chemical stability. For instance NbX$_2$ and TaX$_2$ are metals while MoX$_2$ and WX$_2$ are semiconductors. NbS$_2$, NbSe$_2$, TaS$_2$ and TaSe$_2$ are even superconducting. Some properties are also dependent on the thickness of the film.
Monolayer MoS$_2$ has a direct gap of 1.8 eV, whereas bulk MoS$_2$ has an indirect band gap of 1.2 eV.

A key aspect for later discussion is the very good absorption coefficient of WS$_2$, to about $10^{-7}$ m$^{-1}$ and for the better part of the visible range, which means that a 300 nm thick film could absorb 95% of the incoming light, similar to crystalline Si used in current solar cell technology. Furthermore, the mean free path of the photo-excited charge carriers in WS$_2$ crystallites is on the order of 1 µm. The reasons and implications of this particular property will be discussed in Chapter 9.

1.6.5 Graphene based heterostructures

The advent of novel 2-D crystals has enabled the possibility to combine their specific properties in vertical stacks called heterostructures as drawn in Figure 1.7 b. Their fabrication was made possible thanks to precise and clean transfer methods which guarantees a contamination free contact between the layers.

Heterostructures are relatively new systems but they have already permitted the observation of intriguing physical phenomena. For instance, graphene/BN/graphene systems proved to be an appropriate system for the observation of charge tunneling and allowed fabrication of tunneling transistors. Coulomb drag between charge carriers between the top and bottom layers has also been reported. Previously, Coulomb drag could only be observed in GaAlAs quantum wells but the effect is much weaker than for graphene. This is explained by the fact that the mean distance between electrons in each graphene plane is larger than the top/bottom plane separation distance. When a current flows in one of the planes, the Coulomb interactions generate a potential difference in the other layer. It is hoped that exciton consisting of electrons and holes in different layers could be observed. Moreover, capacitance measurements of graphene insulated by thin BN film were shown to be a powerful system to probe the DOS of graphene.

Finally the appearance of a moiré pattern in graphene/BN stacks (as shown in Figure...
1.8), resulting from the lattice mismatch between graphene and BN, was identified as the cause of miniband creation in the band structure of graphene at energies as low as 0.2 eV\textsuperscript{87,88} and leads to changes in the Fermi surface topology and Hofstadter quantization in the resistivity of graphene devices in presence of a magnetic field\textsuperscript{89}. Chapter 8 will discuss the characteristics of graphene/BN moiré in more details.

![Figure 1.8: a) Sketch of a moiré pattern obtained by graphene/BN stack b) C-AFM image of such a stack for a mismatch angle of less than 1 degree, courtesy of C. Woods](image-url)
CHAPTER TWO

RAMAN SPECTROSCOPY OF GRAPHENE

This chapter introduces the theoretical background of Raman spectroscopy on crystals with a focus on graphene and details the experimental setups used in the following chapters.

2.1 Theory of Raman spectroscopy

The interaction of light with a medium results in several processes: transmission and reflection for the most part, but, for a tiny fraction of the incoming light, scattering occurs due to inhomogeneities inside the medium. Those can be static for instance due to crystal dislocations, generating elastic scattering (i.e. with no change of wavelength), or dynamic such as atomic vibrations which produces a change in the wavelength. Only a tiny part of the light is inelastically scattered.

Raman spectroscopy is a technique based on the analysis of the inelastically scattered light from the medium, produced by the interaction of the light with the atomic vibrations. Usually, in a Raman spectroscopy experiment, the shift in energy between the incoming and inelastically scattered light is measured. The Raman effect was first observed in molecules by C.V. Raman in 1930, and nowadays Raman spectroscopy is a standard technique for the analysis of molecules, crystals and semiconductors\textsuperscript{90}. In the macroscopic description of the Raman scattering process in crystals, we consider an infinite crystalline medium at finite temperature. The atoms of the structure undergo vibrations, whose normal modes are quantized by quasiparticles called phonons.

The medium displacement $X(r, t)$ at a position $r$ at a time $t$ is the sum of random motions of wave vectors $q$ and frequency $\omega_q$ which vary on a time characteristic for thermal excitation processes:

$$X(r, t) = \sum_q [X(q, \omega_q)e^{i(q\cdot r - \omega_q t)} + X^*(q, t)e^{-i(q\cdot r - \omega_q t)}]$$  \hspace{1cm} (2.1.1)

Atomic displacements change the susceptibility tensor $\chi$ of the medium. Since the displacements are very small compared to the lattice parameter, only the first order Taylor
expansion is considered:

\[ \chi \simeq \chi_0 + \left( \frac{\partial \chi}{\partial X} \right)_{X=0} X(r, t) \]  

(2.1.2)

The polarization \( P(r, t) \) is then

\[ P(r, t) = \epsilon_0 \chi (\omega_1) E_I(r, t) \]  

(2.1.3)

where \( E_I(r, t) \) is the electric field at a position \( r \) and at a time \( t \). It is related to the excitation source of momentum \( k_1 \) and frequency \( \omega_1 \) by:

\[ E_I(r, t) = E_I e^{i(k_1 \cdot r - \omega_1 t)} + E_I^* e^{-i(k_1 \cdot r - \omega_1 t)} \]  

(2.1.4)

The combination of the four equations yields

\[ P(r, t) = \epsilon_0 \chi_0 \left[ E_I e^{i(k_1 \cdot r - \omega_1 t)} + E_I^* e^{-i(k_1 \cdot r - \omega_1 t)} \right] \]  

(2.1.5)

Thus the total polarization of the medium is composed of three components: one in phase with the incoming light (of wave vector \( k_1 \) and frequency \( \omega_1 \)) and the two other ones caused by the interaction with the medium susceptibility. This is the inelastically scattered radiation and has two terms:

i) One of wave vector \( k_S = k_1 - q \) and frequency \( \omega_S = \omega_1 - \omega_q \) corresponding to the so-called Stokes scattered light.

ii) One of wave vector \( k_{AS} = k_1 + q \) and frequency \( \omega_{AS} = \omega_1 + \omega_q \) corresponding to the anti-Stokes scattered light.

In every scattering process, both wave vector and frequency must be conserved. This imposes a condition that in a one-phonon scattering process, the wave vector of the phonon needs to be smaller than twice the photon wave vector. Typically, in a Raman experiment, visible light is used. The wave vector associated with the excitation source and the inelastically scattered light (on the order of \( 2\pi/\lambda \), where \( \lambda \) is either the wavelength of the excitation source or the scattered light) is much smaller than the wave vector associated to the crystal (on the order of \( 2\pi/a \)). Thus, the condition: \( K_{s/as} = k_1 \pm q \) confines the possible phonons involved in such a process to the center of the Brillouin zone around the \( \Gamma \) point, i.e. the wave vector of the phonon is often assumed to be \( q = 0 \). This is the fundamental Raman selection rule. Note that typically only the Stokes component is measured in a Raman spectrum. The Stokes component has a much higher
intensity, compared to the anti-Stokes and most Raman spectrometers are equipped with edge filters (see Section 3.1) that filter out the anti-Stokes component of the spectrum.

A multiple phonon scattering process can also take place: let us consider two phonons involved in the Raman process. By considering the second order Taylor expansion of the susceptibility, the inelastically scattered component of the light now contains new components with frequency \( \omega_0 + \omega_a + \omega_b \) where \( \omega_a \) and \( \omega_b \) stand for the frequency of the two phonons. The wave vector conservation is then satisfied when \( q_a \pm q_b = 0 \). For two identical phonons, the corresponding Raman peak in the spectrum is called an overtone of the peak from the corresponding one-phonon process. In second order overtone scattering, the wave vector conservation indicates that \( q_a = -q_b \). Thus, there is no limitation in the magnitude of the possible wave vectors, i.e. they are no longer limited to the center of the Brillouin zone.

However, the macroscopic description only describes photon/phonon coupling which is rather weak in comparison to electron/phonon coupling. The microscopic description of Raman scattering describes the occurrence of inelastic scattering in a three event process, described in Figure 2.1.

Stokes scattering typically consists of three steps as depicted in Figure 2.2 with \( H_{MR} \) is the Hamiltonian describing material/radiation interaction and \( H_{ep} \), the electron-phonon coupling:

- i) An electron in its initial state \(|i\rangle\) is excited by an incoming photon with energy \( \omega_1 \) to an excited state \(|a\rangle\).
- ii) The electron decays to a state \(|b\rangle\) after interacting with a phonon of energy \( \omega_{ph} \)
iii) The electron returns to its initial state by emitting a photon of a lower energy $\omega_2$.

$$H_{ep} (k_1, \omega_1) (k_2, \omega_2) \rightarrow H_{MR}$$

Figure 2.2: Feynman diagram of the one phonon Raman scattering process.

For anti-Stokes processes, the initial state is an excited state whose population depends on the temperature of the medium and is therefore less populated than the ground states. The anti-Stokes part of the spectrum is therefore weaker than the Stokes one. Comparing the intensity ratio between the Stokes and the anti-Stokes radiation can actually be used as a method to determine the crystal temperature.

In the case where one of the electronic states $|a\rangle$ or $|b\rangle$ is real, the Raman intensity of the peak corresponding to this process is enhanced by several orders of magnitude. This phenomenon is known as resonance and will be discussed in the next Section.

2.2 Raman spectroscopy of graphene

The first characterization of graphene by Raman spectroscopy appears in the work of Ferrari et al. in 2006. Since then, Raman spectroscopy has emerged as a very powerful technique for the investigation of several properties of graphene.

2.2.1 Graphene phonon dispersion

In the previous Section, the role of phonons in the inelastic scattering of light was examined. It is therefore necessary to know the phonon dispersion in the reciprocal space for the crystal under investigation. The phonon dispersion of a crystal can be calculated by ab-initio density functional theory (DFT) or measured experimentally using inelastic X-ray scattering (IXS) measurements or Raman spectroscopy. Figure 2.3 shows the results of the DFT calculation from Ref 96 and the experimental results obtained on graphite by IXS, in excellent agreement with each other.

Since the unit cell of graphene is composed of two unequivalent atoms, the phonon dispersion of graphene is made of six branches: three optical (O) plus three acoustic (A) branches. Within each group, one branch corresponds to an out-of-plane vibration mode while the remaining two branches describe in plane vibration modes, one transverse (T) and one longitudinal (L). The LO and in-plane TO modes near the Brillouin zone center $\Gamma$ are degenerate and, according to group theory, correspond to the in-plane $E_{2g}$ mode, as seen on Figure 2.4. At the $K$ point, the exact position of the branches is still in debate, especially when it comes to the degeneracy of the LO and TO branches. According to group
Figure 2.3: Theoretical and measured phonon dispersion of graphene. Adapted from Ref 96

theory, the Raman active vibration at the \( \mathbf{K} \) point has a \( A_{1g} \) symmetry. Both vibrations will give rise to the G and the 2D peaks (see Section 2.2.2) Note that at the \( \Gamma \) point, the LO phonon branch has kinks, i.e. the derivative of the phonon branch is discontinuous. This is known as a Kohn anomaly\(^{98}\) and corresponds to a sudden decrease of the lattice vibration due to screening from the conduction electrons. The same phenomenon appears at the \( \mathbf{K} \) point for the TO phonon branch.

\[
\text{G: } E_{2g} \text{ mode of sp}^2 \text{ rings and chains} \quad \text{D: } A_{1g} \text{ breathing mode in rings}
\]

Figure 2.4: Vibration modes associated with the G and the 2D peak of graphene

The demonstration of the presence of the Kohn anomalies in graphite was made by Piscanec et al\(^{99}\). The slope of the kinks in the branch gives direct information on the electron phonon coupling (EPC) as \( \text{slope}(X) \propto \text{EPC}^2(X) \), where \( X \) is either \( \Gamma \) or \( \mathbf{K} \). The EPC for the \( E_{2g} \) and \( A_{1g} \) modes at \( \Gamma \) and \( \mathbf{K} \) is therefore much higher than anywhere else in the phonon dispersion of graphene. The Raman peaks corresponding to these modes should then be intense which is indeed the case.
### 2.2.2 Raman spectrum of graphene

The two main features of the Raman spectrum of graphene are the G and 2D peaks at 1580 cm\(^{-1}\) and 2680 cm\(^{-1}\), respectively, as shown in Figure 2.5. Since the in-plane phonon dispersion of graphene closely matches that of graphite, the same peaks are also observed in graphite. The observation and assignment of the G peak to the corresponding vibration was made as early as in 1970 by Tuinstra and Koenig\(^{100}\). The G band corresponds to a single phonon process at the \(\Gamma\) point.

![Raman spectrum of graphene and graphite](image)

**Figure 2.5:** Raman spectrum of graphene and graphite measured at 488 nm.

The Raman process for the G peak can be described with 3 steps as shown on Figure 2.6.a:

i) A photon of energy \(E_{\text{ex}}\) is absorbed by graphene, creating an electron/hole pair with an energy \(E_{k}^{\pi} = E_{\text{ex}}/2\) for the electron and \(E_{k}^{\pi^*} = -E_{\text{ex}}/2\) for the hole (blue arrow). The superscript \(\pi\) and \(\pi^*\) describe a charge carrier in the valence and the conduction band, respectively. This process is more likely at a wave vector \(k\) of the reciprocal space that can guarantee a resonant absorption. This state is labeled \(|a\rangle\)

ii) The electron loses an energy \(\hbar\Omega_{G}\) to a phonon of frequency \(\Omega_{G}\) and wave vector \(q=0\) (black arrow) and is now in a virtual state.

iii) The electron recombines and emits a photon of lower energy (red arrow).

During the whole process, energy and momentum are conserved. This single scattering process would result in the following Raman intensity for the G peak, obtained from the calculation of the Raman cross section using the Fermi golden rule\(^{101}\):
2.2. RAMAN SPECTROSCOPY OF GRAPHENE

\[
I(G) \propto \sum_k \frac{\langle f | H_{MR} | b \rangle \langle b | H_{op} | a \rangle \langle a | H_{MR} | i \rangle}{(E_{ex} - E_{\pi}^k - E_{\pi}^k - i\gamma)(E_{ex} - \hbar \Omega_a - E_{\pi}^k - E_{\pi}^k - i\gamma)}
\]  

where \(|i\rangle, |a\rangle, |b\rangle\) and \(|f\rangle\) are the initial system state, the state of the system at step i), the state of the system at step ii) and the final state of the system, respectively. \(\gamma\) is the energy broadening of the excited state. The term \(2\gamma\) is then the inverse lifetime of the electron. \(\gamma\) can also be seen as the full width at half maximum of the corresponding Raman peak.

This is not however the only possible quantum pathway and many other transitions can occur. For instance, instead of a resonant absorption (step i), the electron can be excited initially to a virtual state, dropping to a real state and then undergoing a resonant reemission instead for a different \(k\). The entire process can also be completely non resonant. Thus a complete description of the intensity should take all possible transitions into account.

From Eq. 2.2.1, one can see the intensity of the G peak is large when electron phonon coupling is large or when the denominator approaches 0, i.e. in case of resonant transitions. Ref. 102 explored the contributions of different quantum pathways to the total G peak intensity by controlling the Fermi energy via a liquid gel ionic gate. Some of the resonant quantum pathways were suppressed by Pauli blocking as the Fermi level shifted and, counter-intuitively, the G peak intensity of doped graphene increased almost four fold for a Fermi energy shift of 0.75 eV, compared to undoped graphene. This is attributed to destructive quantum interferences of the resonant contributions that cancel each other. This means that the G peak intensity is mostly due to non resonant contributions. This problem will be further discussed in Chapter 4.

In contrast, the 2D peak was first observed a decade later\(^{103}\) than the G peak and the mechanism involved in its activation was only explained by a model initially proposed in 2000 by Thomsen and Reich\(^{104}\). Their work together with Ref. 105 described the 2D peak as a two-phonon intervalley double resonant mechanism. D.M. Basko and Venezuela et al. later contributed to this with a triple resonant model\(^{106,96}\). The complete scattering process as shown in Figure 2.6 is:

i) A photon of energy \(E_{ex}\) is absorbed by graphene, creating an electron/hole pair (blue arrow) at energies \(E_{\pi}^k\) and \(E_{\pi}^k\). This process is more likely at a wave vector \(k\) of the reciprocal space that can guarantee a resonant absorption.

ii) The electron loses an energy \(\hbar \Omega_D\) to a phonon of frequency \(\Omega_D\) (black arrow) and wave vector \(q \simeq K\). At the end of this process, the electron energy is \(E_{\pi}^{k+q} = E_{\pi}^k - \hbar \Omega_D\)

iii) The hole loses an energy \(\hbar \Omega_D\) to a phonon of frequency \(\Omega_D\) (black arrow) and wave vector \(q \simeq -K\)
iv) The electron/hole pair recombines and emits a photon of lower energy (red arrow)

\[ E = E_{ex} - 2\hbar \Omega_D \]

The whole process conserves energy and momentum and can only involve real states. The 2D is thus triple resonant. Note that mechanisms involving hole scattering first and then electron scattering are also possible, as well as processes with only electron or only hole scattering. All of these processes contribute to the 2D peak intensity.

\[ I(2D) \propto \sum_k \frac{\langle f|H_{MR}|c\rangle \langle c|H_{sp}|b\rangle \langle b|H_{sp}|a\rangle \langle a|H_{MR}|i\rangle}{(E_{ex} - E_{k+q}^{\pi\pi} - E_{k+q}^{\pi} - 2\hbar \Omega_D - i\gamma/2)} \]

\[ \times \frac{1}{(E_{ex} - E_{k+q}^{\pi\pi} - E_{k}^{\pi} - \hbar \Omega_D - i\gamma/2)} \times \frac{1}{(E_{ex} - E_{k}^{\pi\pi} - E_{k}^{\pi} - i\gamma/2)} \]

Since all transitions are resonant, all terms in the denominator are very close to 0 and the intensity should diverge, explaining why the 2D peak, a two-phonon process is more intense than the G peak which only involves one phonon. Some limitations should however be added to this consideration such as the trigonal warping of the Dirac cones at high energy \(^{108}\). The resonant nature of the 2D peak will be further discussed in Chapter 4.

The triple resonant model in the case of intravalley scattering is responsible for the activation of the 2D’ peak that lies at about 3240 cm\(^{-1}\) as seen in Figure 2.5. It comes from two phonons from the LO branch close to \(\Gamma\).

### 2.2.3 Dispersion of the 2D peak

A direct consequence of the resonant nature of the 2D peak is the dispersive nature of its frequency for both graphene or graphite \(^{103,91}\). In the case of graphene, the linearity of the band structure near the \(K\) point ensures a resonant absorption for a broad range of excitation energies covering the whole visible spectrum, see Chapter 4 and 6. As a
result, the excited electron wave vector is different for different excitation energies and the phonon probed is also different, in other words, the wave vector of the phonon necessary to link the branches of the two cones is different. Since the phonon branch around the $\mathbf{K}$ point is steep and linear (Figure 2.3), the energy of the phonon changes significantly and thus the position of the 2D peak changes, at a rate of about $100 \text{ cm}^{-1}/\text{eV}^{109,96}$.

### 2.2.4 Identification of graphene

![Figure 2.7: a) Band structure of bilayer graphene and sketch of the four possible interband transitions associated to the 2D peak of bilayer graphene, adapted from Ref 91 b) Raman spectrum of bilayer graphene at 514 nm and 633 nm of excitation wavelength, adapted from Ref 91](image)

The resonant nature of the 2D peak is also responsible for one of the largest successes of Raman spectroscopy of graphene: the identification of graphene. Indeed, while the band structure of monolayer graphene near the $\mathbf{K}$ point is composed of the Dirac cones in any given sample, the band structure of AB (or Bernal) stacked bilayer and several layer graphene are different. Bilayer graphene is made of four parabolic bands$^{110}$, Figure 2.7.a. As a result, the 2D peak of bilayer graphene is the superposition of four possible resonant contributions in the scattering process. Consequently the 2D peak of graphene bilayer is the sum of four Lorentzian lineshapes (Figure 2.7.b) while the single layer 2D peak of graphene consists of a single narrow Lorentzian. This consideration can be extended to several layer graphene up to graphite. Figure 2.8 shows the Raman spectrum of single-, bi- and several layer graphene.

The Raman fingerprint of graphene is a symmetric single Lorentzian 2D peak with a FWHM typically below 30 cm$^{-1}$. Another consequence of the double resonance process is the sensitivity of the 2D peak of multiple layers to the stacking order. Indeed the band structure of turbostratic graphite or twisted bilayer graphene (tBLG) differs from that of
AB stacked graphite or bilayer. As a result, the 2D peak of turbostratic graphite is a single Lorentzian with a FWHM of about 50 cm$^{-1}$. A similar shape was observed for tBLG$^{112,113}$ but with FWHM as large as 70 cm$^{-1}$. The Raman spectrum of tBLG will be further discussed in Chapter 8.

### 2.3 Raman spectrum of defective graphene

#### 2.3.1 Defect-activated peaks

As shown in Section 2.2 there is only one single phonon scattering process visible in the Raman spectrum of pristine graphene. Nonetheless the Raman selection rules can be overcome in the presence of scattering centres in the graphene lattice. In other words, Raman modes corresponding to single phonon scattering with a phonon wave vectors $\mathbf{q} \neq 0$ can be activated by defects.

![Figure 2.9: Sketch of the Raman processes involved in the activation of the D and D’ peaks of defective graphene. The blue arrows correspond to the absorption of a photon and the creation of an electron/hole pair. The red arrows represent the radiative recombination of the electron/hole pair. The dashed arrows depict the inelastic charge scattering from phonons or the elastic scattering from defects. Adapted from Ref 107](image-url)
The D and the D’ peaks are the first order intervalley and intravalley scattering process associated with phonons with $q \neq 0$ on the TO phonon branch near the K point and the LO phonon branch near the Γ point, respectively. Their activation processes are exactly the same as that of the 2D and the 2D’ peaks but instead, one of the two phonon scattering is replaced by an elastic scattering by a lattice defect. Consequently, the position of the D and the D’ peaks are roughly half that of the 2D and the 2D’ respectively and appear at 1340 and 1620 cm$^{-1}$ in presence of defects.

![Raman Spectrum of Defective Graphene](image)

Figure 2.10: Raman spectrum of defective graphene.

Defect-activated bands in the Raman spectrum were first observed in nanocrystalline graphite in 1970$^{100,114}$ and further analyzed by by Cançado et al$^{115}$. The defects are predominantly grain boundaries that separate regions of ordered graphite of sizes $L_a$. The famous Tuinstra-Koenig relation was found and corrected for the influence of the excitation energy.

$$\frac{I(D)}{I(G)} = 2 \cdot 10^{-10} \lambda^4 \frac{1}{L_a}$$  \hspace{1cm} (2.3.1)

For instance, near the edge of a graphene flake, the Raman spectrum of graphene shows a D peak$^{116}$, because edges are sensed as defects in the carbon lattice. Methods to introduce defects as well as a literature review on graphene and other carbon based materials are given in Chapter 5, 7 and 6. However, in graphene, the evolution of $I(D)/I(G)$ is more complex, as it will be shown in the next section.

### 2.3.2 Local activation model

Recent work on Ar$^+$ bombardment of single and few layer graphene$^{117–120}$ analyses the amorphization trajectory of graphene. The bombardment was made at an energy such
that single atom vacancies were created in the lattice of graphene. Upon variation of the exposure dose, a careful control on the defect concentration could be achieved\textsuperscript{117}. Similarly to the results presented in Chapter 7 and 6, Lucchese et al. observed a two stage amorphization evolution of the ratio I(D)/I(G), in contrast to what had been observed for nanocrystallite graphite\textsuperscript{100}. The authors proposed a model to fit the evolution of the I(D)/I(G) ratio of defective graphene, so-called local activation model (LAM). It is a phenomenological model that compares the relative amount of defective regions and ordered regions in the graphene sheet.

![Figure 2.11: Graphical description of the local activation model. Adapted from Ref 117](image)

- a) Representation of the electronically disordered area (red) of radius $r_S$ and the activated region of radius $r_A$ (green).
- b), c) and d) Impacted graphene sheet with increasing exposure doses to a beam of Ar$^+$ ions. The impacts progressively cover the whole area. The activated region (area) reaches a maximum area (c) until the disordered area takes over (d). This explains the two-stage evolution of I(D)/I(G) observed in the amorphization trajectory of graphene bombarded by Ar$^+$ ions.

The model is described in Figure 2.11. The impact of an energetic ion removes a carbon atom from the graphene lattice, creating electronically perturbed regions in a disc of diameter $r_s$ that could be observed by scanning tunneling microscopy (STM) measurements. This disc typically has a diameter of 1 nm, in red in Figure 2.11. This region cannot contribute to Raman intensities because Raman scattering only probes sp$^2$ bonded regions. However, the region in the immediate vicinity of the defects is sp$^2$ bonded; thus Raman scattering processes can take place and defect scattering can occur if the electron/hole pair resulting from the absorption of a photon is generated at a distance from the defect smaller than the average distance $l$ traveled by an excited electron/hole before recombination, typically $l \approx v_F/\omega_D \approx 4$nm. This area is represented by the green disc in Figure 2.11 and is responsible for the activation of the D peak.

When the bombardment dose increases, the green area first increases and results in the increase of the D peak intensity (Figure 2.11 b and c) until the discs can no longer be considered as independent. At this point, when the average distance between two defects $L_D$ is close to $l$, the defective red regions take over the ordered green regions and the D peak intensity decreases.

After deriving the expansion rate for both regions, Lucchese et al. proposed the following amorphization equation valid for graphene with vacancies plotted in Figure 2.12:
where $C_A$ is a constant that depends on the excitation energy and $C_S$ a constant that depends on the geometry of the defects. The non-monotonic evolution of $I(D)/I(G)$ with $L_D$ indicates that there are two possible defect concentrations (one in each stage) associated with a value single value of $I(D)/I(G)$.

![Plot of I(D)/I(G) versus L_D with a fit from Eq. 2.3.2. Adapted from Ref 117](image)

The LAM, its parameters and a method to identify stage 1 from stage 2 will be further discussed in Chapter 6.

## 2.4 Raman spectrum of doped graphene

Raman spectroscopy is also sensitive to the level of doping, i.e. the charge concentration of the majority charge carriers in the graphene sheet. The main experiments that permitted its observation are detailed in Ref 121–123 where graphene was deposited on Si/SiOx substrates and a back gate voltage $121,122$ (or top gate voltage $123$) was applied to change the carrier concentration (see Section 1.2). For each incremental change of the charge concentration, a Raman spectrum is taken and it was observed that the position and the FWHM of the G peak was heavily dependent on the charge concentration $121–126$. Up-shifts of the G peak as high as 30 cm$^{-1}$ could be obtained for a charge concentration of $3 \times 10^{13}$ cm$^{-2}$.
An increase in the surface charge concentration in graphene on the order of $10^{13}$ cm$^{-2}$ results in a change of the lattice constant of graphene due to electron-electron interactions on the order of 0.05% and in turn in a frequency shift of the G peak.\textsuperscript{127} This change however is not sufficient to explain such large shifts. Instead, the adiabatic Born Oppenheimer approximation (ABO) usually used to describe lattice motion in metals was questioned\textsuperscript{127,121}. It states that the motion of the electrons with respect to the nuclei is adiabatic during a lattice vibration event, i.e. electrons follow the nuclei without delay. Ref\textsuperscript{127} showed in a dynamic model beyond the ABO that such shifts could be expected because the Kohn anomaly at the $\Gamma$ point shifts away from $\Gamma$ and the phonon probed by the G peak has a higher energy, i.e. the G peak blue-shifts.

![Raman spectra of graphene](image)

Figure 2.13: Two spectra taken on separate flakes with different levels of doping. Strong doping was found here on a flake prepared by micromechanical exfoliation on a substrate that was previously cleaned by O$_2$ plasma.

The decrease of the FWHM of the G peak can be explained by Pauli blocking of the decay channels of the phonons into electron/hole pairs because of the exclusion principle\textsuperscript{121}.

The 2D peak of graphene is also affected in the following ways: the intensity decreases for increasing charge concentration and the position increases for electron doping and decreases for hole doping\textsuperscript{123} at high doping levels ($\geq 2 \times 10^{13}$ cm$^{-2}$). The position changes are attributed to the softening/stiffening of phonons due to the lattice expansion/contraction that occur with electron/hole doping\textsuperscript{123}. The decrease in intensity of the 2D peak can be understood thanks to the calculations of Ref 106,107, which takes into account the electronic scattering rates. This is further confirmed by the ab-initio DFT calculations in Ref 96.
\[ I(2D) = \frac{A}{B + (\gamma_{ep} + \gamma_D + \gamma_{ee})^2} \] (2.4.1)

where A and B are constants and \(\gamma_{ep}\) is the electron-phonon scattering rate at K. \(\gamma_D\) is the defect scattering rate and increases for increasing defect concentration as the probability to scatter with a defect is higher. \(\gamma_{ee}\) is the electron-electron scattering rate and increases for increasing doping level as the probability to scatter with a phonon is higher when the electron concentration is higher. The sum of the three terms \(\gamma_{tot} = \gamma_{ep} + \gamma_D + \gamma_{ee}\) is the inverse lifetime of the electron involved in the scattering process mentioned in section 2.2.2.

From Eq. 2.4.1, it is straightforward to see that \(I(2D)\) decreases for increasing doping level as well as for increasing defect concentration. Figure 2.13 shows two spectra taken on a pristine and a doped graphene flake and shows the dramatic changes that occur in presence of doping.

### 2.5 Conclusion

To conclude this Chapter, Raman spectroscopy of graphene is rich and versatile and allows the acquisition of both qualitative and quantitative data on the properties of graphene. Chapter 4 will discuss the intensities of the G and the 2D peaks and give a measure of their scattering cross section. Further, it is shown that the level of doping could be estimated and the distinction between p and n doping can be made. Finally the defect activated peaks allow the quantification of defects. It will be used to discuss the production of graphene and the introduction of defects in several configurations in Chapters 5 to 7. Chapter 6 will also show that the Raman spectrum of graphene is sensitive to the type of defects while Chapter 8 will discuss the new features appearing when graphene is embedded in superlattices. Finally Chapter 9 will present photocurrent results obtained on graphene based heterostructures.
3.1 Raman spectrometers

All the Raman spectra presented in this thesis have been measured by three different spectrometers. The WITec alpha 300S and the In-via Renishaw belong to the category of the confocal single monochromator spectrometer and are equipped with a scanning stage (either piezo-stage or motorized stage) that allowed Raman mapping. The Dilor relies on a triple monochromator that allows multiwavelength measurements that are presented in the next chapters. A full list of the lasers available on all three spectrometers is presented in table 3.1.

<table>
<thead>
<tr>
<th>Laser type and spectrometer</th>
<th>Excitation wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>He-Ne (WITec)</td>
<td>633 nm</td>
</tr>
<tr>
<td>Ar⁺ (WITec)</td>
<td>488, 514 nm</td>
</tr>
<tr>
<td>Innova 70C Ar-Kr (Dilor XY)</td>
<td>457, 472, 476, 488, 502, 514, 532, 568, 647 nm</td>
</tr>
<tr>
<td>UV He-Cd (Renishaw In-Via)</td>
<td>325 nm</td>
</tr>
<tr>
<td>Ar⁺ Multi line Stellar (Renishaw In-Via)</td>
<td>457, 488, 514 nm</td>
</tr>
<tr>
<td>HP-NIR (Renishaw In-Via)</td>
<td>785 nm</td>
</tr>
</tbody>
</table>

Table 3.1: List of the lasers equipping the three spectrometers used in the thesis, WITec, Renishaw and Dilor

3.1.1 Confocal single monochromator spectrometer

A typical confocal Raman spectrometer is sketched in Figure 3.1. It is composed of three major parts: a laser, a microscope and a spectrum analyser. The microscope directs the laser beam onto the sample and redirects the back-scattered light to the analyser that measures the energy spectrum of the scattered light. More specifically, the laser passes through a beam splitter and is focused onto a sample by an objective. The sample can be mounted on a scanning XYZ piezo-stage and thus allows Raman mapping. In a XY Raman map, a rectangle frame and a mesh is defined around a region of interest on a
sample. The density of the mesh is defined by the scan step in both X or Y direction. A Raman spectrum is then recorded at each position defined by the mesh and the list of spectra can be analyzed in batch in order to plot the spatial variations of a Raman fit parameter such as the position, FWHM or intensities of the Raman peaks. This is used in Chapter 7.

As the laser enters the sample, inelastic and elastic scattering occurs. Figure 3.1 depicts the reflected light path scattered at two different depths of the sample, one in the focal plane of the objective and the other one out of focus. After re-entering the microscope through the objective, both beams hit the beam splitter which now acts as a mirror. A filter cuts out the Rayleigh emission, i.e. the elastically scattered light as it constitutes the major part of the beam and could risk damaging the light detector. The beam splitter and edge filter can be realized by a specific single optical element called a dichroic mirror. It is transparent for light with a given energy until a certain threshold value after which it acts as mirror. After removal of the Rayleigh beam, another lens focuses the beam on a pinhole which cuts out the rays coming from different layers of the sample that are not in the focal plane of the objective. This is an important feature of a confocal spectrometer. It allows information to be obtained at a specific depth in the sample. The beam is then diffracted by a grating and re-focused onto a CCD sensor in the focal plane of the last lens. The CCD sensor converts the incoming photons into an electrical signal and accumulates counts between each read out on request from the software. The result is a spectrum with a number of counts assigned to each resolvable energy.
3.1.2 Spectral and energy resolution

From this short description of the Raman beam path, the definition of the numerous resolutions can be given. First the spatial resolution in XY is defined as half the size of the probe on the sample, i.e. the minimum laser spot size diameter after the objective. The minimum spot size that can be achieved is diffraction limited and is related to the diameter of the first Airy disc \( d = 1.22 \frac{\lambda}{NA} \), where NA is the numerical aperture of the objective and \( \lambda \) the excitation wavelength. Thus the resolution obtained with a 100x/NA=0.9 objective and a 514 nm laser, is \( \sim \frac{700}{2} = 350 \) nm. The depth resolution is limited by the size of the pinhole. A smaller pinhole enhances the depth resolution but also decreases the total intensity of the signal. The value of the depth resolution greatly depends on the optical path and therefore on the spectrometer. Finally the spectral resolution is related to the ability of the spectrograph to resolve small changes of photon energy. Thus it depends on the grating’s diffraction capability and can be improved by increasing the groove density. It also depends on the optical path of the refracted light. Typically for a WITec spectrometer and a grating of 1800 grooves/mm, the spectral resolution is of the order of 3 cm\(^{-1}\).

3.1.3 Triple monochromator spectrometers

The configuration of the single monochromator spectrometer works only at a specific wavelength because of the edge filter. It is possible to overcome this issue by designing a specific filter unit for each wavelength or by replacing the edge filter with two more gratings that allow selection of a particular energy spectrum simply by grating rotation. The Dilor spectrometer uses the latter solution. The combination of a grating, mirror and lenses is called a monochromator and the Dilor spectrometer therefore belongs to the category of triple-monochromator spectrometers as depicted on Figure 3.2. The first monochromator diffracts the inelastic light onto a slit (S4 on Figure 3.2) that filters the desired energy range. The second monochromator recombines what remains of the diffracted beam and directs it onto the third monochromator that analyze the Raman light, as described in Section 3.1.1.

3.1.4 Photovoltage setup

The WITec Raman spectrometer is a modular system that permits more complex measurements. In our case, it was modified in order to record photovoltage and photocurrent maps. They will be presented in Chapter 9. This was made possible by combining the scanning stage and the laser of the spectrometer together with a Keithley Nanovoltmeter 2182A that provides an external measure of the current.

Figure 3.3 shows a sketch of the experimental setup. The optics of the spectrometer was used to focus a laser on a sample embedded on a chip carrier and contacted by gold wires. A sample holder ensured the connection between the chip carrier and the break
out box enables connections with coaxial cables. The Sourcemeter is used to apply a gate voltage as previously discussed in Section 1.3. Here the silicon substrate is contacted to the pin numbered 15 and the graphene sample is grounded on the pin 4. The photocurrent resulting from the laser illumination is recorded by the Nanovoltmeter between two contacts of the sample, here between pins 4 and 12 and is sent to the spectrometer controller via an analog/digital converter provided by WITec GmbH. Thus the synchronization of the stage motion with the current measurement was done through the spectrometer controller and allowed photocurrent mapping in a similar way as Raman mapping. The scattered light from the sample could be analyzed at the same time in exactly the same way as for the standard spectrometer configuration.

3.2 Substrate engineering

Chapter 7 makes use of structured substrates to investigate the chemical reactivity of graphene. Section 7 uses a bilayer membrane for double sided functionalization of bilayer graphene. Si/SiOx substrates were engineered by a combination of photolithography and reactive ion etching following a Bosch process. The total step by step method is shown...
3.2. SUBSTRATE ENGINEERING

Figure 3.3: Sketch of the photocurrent setup composed of the WITec Spectrometer, one Sourcemeter and one Nanovoltmeter. The dashed circle is a zoom on the sample embedded in a chip carrier, resting on the XY stage of the spectrometer.

in Figure 3.4.

1 A double sided polished Si/SiOx substrate is covered with a layer of Ma-N negative photoresist provided by Microchem.

2 After a soft bake, a flood exposure of the masked photoresist was performed for 10 s on a mask aligner system and the photoresist developed in Ma-D533S leaving pillar-like structures on the surface.

3 A 50 nm thin film of Cr is deposited on the surface by e-beam evaporator (Moorfield).

4 The remaining Ma-N photoresist is removed in Ma-REM660 (Microchem) giving access to the SiOx surface through holes in the Cr film.

5 The substrate undergoes plasma etching for 2 h in a reactive ion etcher following the Bosch\textsuperscript{129} procedure.

6 The substrate is flipped and another 50 nm layer of Cr is deposited on its backside. The geometry of the Cr layer is such that some large parts (several mm across) of the silicon surface are left unprotected.

7 We perform another etching phase similar to step 5 for another 3 h.
Figure 3.4: Step by step description of the substrate engineering process in the case of a through hole preparation.

8 The substrate is left for a couple of minutes in a solution of Cr etcher and rinsed in DI water

Figure 3.5 shows a section of a trench etched with the Bosch recipe. The etch yielded vertical walls thanks to a highly anisotropic etch rate.

### 3.3 Hydrogenation and fluorination of graphene

Several examples of chemical functionalization of graphene are given in Chapters 7 and 6. The hydrogenation of graphene is performed in an Edwards 306A vacuum chamber in which electrodes generate a plasma from a gaseous mixture of Ar and H\textsubscript{2} as described in Ref. 63 and sketched in Figure 3.6. The sample is left on the sample holder at a distance of about 30 cm from the electrodes and the chamber is pumped to a typical pressure of 10^{-6} mbar by a combination of a rotary and a diffusion pump. The rotary pump allows a rough pumping (roughing mode) of the chamber and a pre-pumping of the diffusion pump which is used to reach high vacuum levels (high vacuum mode). Once the chamber
3.3. HYDROGENATION AND FLUORINATION OF GRAPHENE

Figure 3.5: Scanning electron microscopy image of a section of a trench etched by the Bosch process.

is pumped out, the system is left in backing mode: all valves are closed except the backing valve. At this point, a needle valve allows the introduction of the gaseous mixture with 10% H\textsubscript{2} and 90% Ar at a pressure of typically 0.15 mbar. A high DC voltage is then applied between the Al electrode and a purple plasma appears. The graphene sample is exposed to such plasmas for about 1 h in 15 min cycles before the system is vented to take out the sample.

Hydrogenation is a reversible reaction, meaning that H atoms can desorb upon annealing. Typically, annealing was done in a furnace with a controllable Ar/H\textsubscript{2} atmosphere at 300°C for 2 h.

Fluorination and oxidization of graphene were performed in similar conditions in a Plasmalab 80Plus from Oxford Instruments except that the plasma was obtained by RF at a frequency of 13.56 MHz in CF\textsubscript{4} and O\textsubscript{2} gases, respectively. Soft fluorination was also achieved following the protocol presented in Ref. 64. Graphene flakes deposited on quartz substrates are left in the vicinity of a XeF\textsubscript{2} crystal which is unstable upon exposure to light or at elevated temperatures. F\textsuperscript{−} radicals coming from the crystal eventually chemisorb on the graphene scaffold. In all cases, the concentration of adatoms is controlled by varying the exposure time.
Figure 3.6: Sketch of the hydrogenation setup. Adapted from the instruction manual of the AUTO 306 Vacuum Coater.
Part II

Experimental results
CHAPTER
FOUR

RAMAN SCATTERING EFFICIENCY OF GRAPHENE

My contribution

I produced graphene samples on three different substrates, took the multiwavelength Raman measurements, measured the calibration curve of the Dilor spectrometer, analyzed the data and participated in the preparation of the manuscript and the Figures.
Raman scattering efficiency of graphene

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We determine the Raman scattering efficiency of the G and 2D peaks in graphene. Three substrates are used: silicon covered with 300 or 90 nm oxide, and calcium fluoride (CaF₂). On Si/SiO₂, the areas of the G and 2D peak show a strong dependence on the substrate due to interference effects, while on CaF₂ no significant dependence is detected. Unintentional doping is reduced by placing graphene on CaF₂. We determine the Raman scattering efficiency by comparison with the 322 cm⁻¹ peak area of CaF₂. At 2.41 eV, the Raman efficiency of the G peak is \( \sim 200 \times 10^{-5} \text{ m}^{-1} \text{Sr}^{-1} \), and changes with the excitation energy to the power of 4. The 2D Raman efficiency is at least one order of magnitude higher than that of the G peak, with a different excitation energy dependence.

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PACS number(s): 78.30.–j, 78.67.Wj, 81.05.ue

I. INTRODUCTION

Graphene attracts enormous interest because of its unique properties.1–7 Near-ballistic transport at room temperature and high mobility make it a potential material for nanoelectronics,12–16 especially for high frequency applications. Furthermore, its optical and mechanical properties are ideal for micro- and nanomechanical systems, thin-film transistors, transparent and conductive composites and electrodes, and photonics.17–24

Besides these practical applications, Raman spectroscopy in graphitic systems is interesting per se because it involves resonant conditions, defect-induced processes and strong electron-phonon coupling.42–47

The determination of the Raman scattering efficiency in carbon-based materials has not been thus far the subject of many investigations. The dependence of the Raman efficiency on the excitation energy was studied in diamond,48,49 graphite,50,51 nanographites,52 fullerene solutions,53 hydrocarbonized amorphous carbon,54–56 nanodiamond films,57 and carbon nanotubes.58,59 The absolute value of the Raman scattering efficiency of highly oriented pyrolytic graphite (HOPG) was reported in two seminal works: the one of Wada et al.,51 who used diamond as a reference scatterer, and that of Sinha et al.,50 who used silicon as a reference scatterer. They found the G peak Raman scattering efficiency measured at 2.41 eV to be \( \sim 200 \times 400 \times 10^{-5} \text{ m}^{-1} \text{Sr}^{-1} \) and \( \sim 800 \times 10^{-5} \text{ m}^{-1} \text{Sr}^{-1} \), respectively.50,51

Knowledge of the Raman scattering efficiency is of great importance because it can provide detailed information on the electron-phonon interaction, such as the deformation potentials,60 the two phonon absorption cross section,61 electro-optic coefficients,62 electron-phonon interaction under hydrostatic pressure,63,64 to cite a few. Furthermore, the Raman efficiency dependence on excitation energy can probe singularities in the dielectric constant,60 since an enhancement in the Raman efficiency is expected whenever the incident or scattered energy approaches these resonances.65–71 In the case of carbon-based materials, a quantitative knowledge of Raman efficiency would allow one to evaluate the relative amount of graphitelike to diamondlike bonds in amorphous and disordered carbons.34,57,72 In the case of carbon nanotubes, this would allow one to use Raman spectroscopy as a fully quantitative tool to evaluate the abundance of each chirality.73 However, an accurate determination of the Raman efficiency faces various hurdles, such as corrections for sample absorption, collection angle, spectral sensitivity, and surface conditions.60 These have not been explicitly discussed in most previous works on graphite and amorphous carbons.50,54,57 In particular, the spectrometer sensitivity can strongly affect the apparent Raman efficiency dependence on excitation energy.

All \( sp^2 \) bonded carbons show common features in their Raman spectra, the so-called G and D peaks, around 1580 and 1360 cm⁻¹.73 The G peak corresponds to the \( E_{2g} \) phonon at the Brillouin zone center (\( \Gamma \) point). The D peak is due to the breathing modes of six-atom rings and requires a defect for its activation.45,74,75 It comes from \( TO \) phonons around the \( K \) point,74,75 is active by double resonance (DR),45 and is strongly dispersive with excitation energy due to a Kohn anomaly at \( K \).33 The activation process for the D peak is intervalley: (i) a laser induced excitation of an electron/hole pair; (ii) electron-phonon scattering with an exchanged momentum \( q \sim K \); (iii) defect scattering; (iv) electron-hole recombination. DR can also happen as an intravalley process, i.e., connecting two points belonging to the same cone around \( K \) (or \( K' \)). This gives the so-called \( D' \) peak, which is at \( \sim 1620 \text{ cm}^{-1} \) in defect-free graphite measured at 514 nm. The 2D peak is the second order of the D peak. This is a single peak in single layer graphene (SLG), whereas it splits in four in bilayer graphene (BLG), reflecting the evolution of the band structure.25 The 2D' peak is the second order of the D' peak. Since both 2D and 2D' originate from a process where momentum conservation is satisfied by two phonons with opposite wave vectors \( q \) and \(-q\), they do not require defects for their activation, and are thus always present. Indeed, high quality graphene shows the G, 2D, and D', but not D and D'.25 The 2D and 2D' peaks are triple resonant.42,46,47 This means that all intermediate electronic states are real. As a consequence,
two-phonon Raman spectroscopy is sensitive to the dynamics of the photoexcited electron-hole pair, in particular, to the scattering processes it can undergo.\textsuperscript{44,47} Note that one-phonon modes in defect-free samples can be Raman active only if their symmetry is correct and their wave vector is zero (i.e., obey the fundamental Raman selection rule). In SLG only the $G$ peak satisfies these requirements.\textsuperscript{42} The energies of the intermediate states are given by the difference in energies of electrons in the empty $\pi^*$ and filled $\pi$ bands, $\epsilon_k^* - \epsilon_k$ (with $k$ the electronic wave vector), with or without the phonon energy, $\hbar\Omega_{0q}$.\textsuperscript{42} The decay rate of the intermediate states is given by the sum of the scattering rates of the electron in the $\pi^*$ band, $2\gamma_k^*/\hbar$, and of the hole in the $\pi$ band, $2\gamma_k^*/\hbar$. The contribution from the phonon decay is typically smaller.\textsuperscript{42} Counterintuitively, the electronic wave vectors $k$ mostly contributing to the matrix element for the $G$ peak are not just such that the excitation energies $\epsilon_k^* - \epsilon_k$ lie within an interval $\gamma - \gamma$ from $\hbar\omega_1$ or $\hbar\omega_1 - \hbar\Omega_{0q}$, with $\hbar\omega_1$ being the incident laser photon energy. Instead, they are such that $|\epsilon_k^* - \epsilon_k|$ can be of the order of $\hbar\omega^1$, and there are strong cancellations in the sum over $k$.\textsuperscript{76} These cancellations correspond to destructive quantum interference. In fact, this interference can be controlled externally. Indeed, occupations of electronic states can be changed by doping and, since transitions from an empty state to or to a filled state are impossible due to Pauli blocking, doping can effectively exclude some regions of $k$ from contributing to the matrix element.\textsuperscript{42} Due to suppression of destructive interference, this leads to an increase of the $G$ peak intensity at high doping levels, as was predicted in Ref. 76 and observed in Refs. 77 and 78. Thus, unlike the $2D$ peak, in undoped or low-doped samples, the $G$ peak arises from nonresonant processes, and only at extremely high doping, not dealt with in this paper, and anyway difficult to achieve in any standard experiment, do resonant contributions have a role.

In graphic materials the intensity of the Raman features strongly depends on the amount of disorder.\textsuperscript{52,72,74,75,79-84} Single-crystal graphite and exfoliated graphene can have negligible $D$ peak intensities, and thus be structurally nearly perfect. Therefore, these are ideal for an accurate investigation of their Raman scattering efficiency. Here we determine the Raman scattering efficiency of single-crystal graphite (SCG) and SLG. We find that the Raman intensity of SLG on Si/SiO$_2$ is modulated by the substrate, reaching a maximum at $\sim$530 nm excitation under our experimental conditions, when graphene is placed on 300 nm silicon oxide. This is due to interference enhanced Raman effects. This is confirmed by measuring SLG on a transparent substrate (CaF$_2$), where no intensity modulation with the excitation energy is found. Therefore, we use the Raman intensities of graphene measured on CaF$_2$ to determine the Raman efficiency by the sample substitution method (Sec. II). We find that the Raman scattering efficiency of the $G$ peak $[dS/d\Omega(G)] \sim 200 \times 10^{-5}$ m$^{-1}$ Sr$^{-1}$ at 2.41 eV. In our samples, the $2D$ peak Raman scattering efficiency $[dS/d\Omega(2D)]$ is much higher than the Raman scattering efficiency of the first order line of silicon and gallium arsenide, measured at 2.41 eV. This is quite unusual, since normally the overtones intensities are much smaller than the first order peaks.\textsuperscript{97} This large value for the Raman scattering efficiency of the $2D$ peak, compared with other overtones efficiencies, clearly shows that the area of the $2D$ peak is given by resonant contributions.\textsuperscript{44,46,85,86}

This paper is organized as follows. Section II describes the experimental setup. Section III presents background concepts on the Raman scattering efficiency and the sample substitution method. Section IV discusses the Raman scattering efficiency dependence on substrate and excitation energy and gives the absolute Raman efficiencies of $G$ and $2D$ peaks, measured at 2.41 eV.

II. EXPERIMENT

Graphene flakes are produced by micromechanical cleavage of SCG (Nacional de Grafite LTDA) using Nitto tape.\textsuperscript{53} Three substrates are used: silicon covered with 300 nm and 90 nm silicon oxide (IDB Technologies LTD) and CaF$_2[111]$ (crystal GmbH). The number of layers is estimated by a combination of Rayleigh and Raman scattering.\textsuperscript{25,26} The oxide thickness of the silicon substrates used here allows graphene to be optically visible,\textsuperscript{26} while the optical contrast of graphene on CaF$_2$ is very weak, but enough to identify single graphene layers by optical microscopy and Raman spectroscopy.\textsuperscript{26,88} Fresh and clean SCG surfaces are prepared by cleaving SCG flakes by Nitto tape before measuring the spectra.

Raman spectroscopy is performed with various spectrometers: a Renishaw single monochromator, equipped with 488, 514, and 633 nm excitation energies, a Dilor triple monochromator (Horiba-Jobin Yvon), equipped with excitation lines from 647 nm to 457 nm, and a HORIBA XploRA Confocal Raman Spectrometer, equipped with 785 nm laser wavelength. In all cases the microscope objective has a numerical aperture (NA) of 0.9. Raman maps are taken with a Witec single monochromator, equipped with 633 nm excitation. This spectrometer features also an atomic force microscope (AFM), used here to study the surface properties of graphene deposited on CaF$_2$. All Raman spectra are recorded in backscattering, with incident light normal to the sample surface.

The Raman spectrum of graphene consists of a set of distinct peaks. Each characterized by its position, width, and area. We use the following notation: $I$ for peak height, $A$ for peak area, Pos for peak position, FWHM for the full width at half maximum. So, e.g., $I(G)$ is the height of the $G$ peak, $A(G)$ its area, FWHM($G$) the full width at half maximum and Pos($G$) its position. The frequency-integrated area under each peak represents the probability of the whole process. It is more robust with respect to various perturbations of the phonon states than width and height.\textsuperscript{44} The measured peaks are fitted with Lorentzians. For BLG, four Lorentzians are used to fit the 2D peak, while in thicker layers the 2D peak is fitted with two Lorentzians, with the sum of the integrated areas of the subpeaks taken to represent the overall 2D strength. Several measurements are performed both on the same spot and different spots on the same sample. We only consider flakes much larger than the laser spot size ($\sim1 \mu$m$^2$), to avoid edge effects.\textsuperscript{33} All measurements are performed with power on the sample below 0.6 mW. Sometimes peaks at $\sim$1350, 1450, and 1530 cm$^{-1}$ are seen; see Fig. 1. We attribute them to glue and tape residuals, as confirmed by performing Raman spectroscopy directly on the tape used to exfoliate SCG. In this case, the peak at
The Raman scattering efficiency $dS/d\Omega$ has dimensions of an inverse length, and is defined as the ratio between scattered and incident power, for a unit solid angle and optical probe depth ($L$):\(^{60}\)

$$
\frac{dS}{d\Omega} = \frac{I_{\text{ins}}}{\Delta \Omega_{\text{ins}}} \frac{h\omega}{P_{\text{ins}}L},
$$  

where $I_{\text{ins}}, \Delta \Omega_{\text{ins}},$ and $P_{\text{ins}}$ are the number of photons, solid angle collection, and laser power inside the crystal. $L$ is (i) for a transparent sample, either the focal length or the thickness of the sample, whichever is smaller\(^{60}\), and (ii) $L = 1/(\alpha_r + \alpha_s)$, if the sample is opaque, where $\alpha_r$ and $\alpha_s$ are the absorption coefficients measured at incident and scattered energies.\(^{60,71,94-96}\) However, the signal measured in a Raman experiment is the number of scattered photons outside the crystal, within a solid collection angle $\Delta \Omega$. Thus, to get the Raman scattering efficiency from the peak’s area, Eq. (1) needs to be corrected for light refraction, and reflection losses incurred when light enters and leaves the crystal:\(^{57}\)

$$
A = I_{\text{ins}}(1 - R_s),
$$

$$
P_{\text{ins}} = P_0(1 - R_r),
$$

$$
\Delta \Omega_{\text{ins}} \approx \Delta \Omega/n_s^2,
$$

where $R_s$ and $R_r$ are the reflectance measured at the incident and scattered frequency, $n_s$ the refractive index at the scattered frequency, and $P_0$ is the laser power. Inserting Eqs. (2)–(4) into Eq. (1), we get:

$$
A = \frac{(1 - R_s)(1 - R_r) P_0 \Delta \Omega L}{\hbar \omega} \frac{dS}{d\Omega}.
$$

This is the relation between Raman peak area and scattering efficiency. Within a microscopic description, the Raman scattering efficiency is given by:\(^{58}\)

$$
\frac{dS}{d\Omega} = \frac{2\hbar N^2}{pc \omega_{ph}} (n_{ph} + 1) \sum_j |\mathbf{e}_i \cdot \mathbf{R}_j|^2,
$$

where $c$ is the light speed, $\rho$ is the density, $N$ is the number of primitive cells per unit volume, $\omega_{ph}$ is the phonon frequency, and $n_{ph}$ is the phonon occupation number. We approximated $(\omega - \omega_{ph}) \sim \omega$. $\mathbf{e}_i$ and $\mathbf{e}_j$ are the unit vector representing the polarization of the incident and scattered light. $\mathbf{R}_j$ is the Raman tensor of the phonon $j$, containing the tensor element $a$ (the Raman polarizability), with:\(^{60}\)

$$
a^2 = V \frac{d^2 \chi(\omega)}{d\xi^2},
$$

where $V$ is the volume, $\chi$ is the susceptibility, and $\xi$ is the normal mode coordinate.

For a second order overtone process, Eq. (6) has the following form:

$$
\frac{dS}{d\Omega} \sim \omega^4 \sum_{\mathbf{q}} \left| \mathbf{e}_i \cdot \frac{d^2 \chi}{d\mathbf{q}^2}(-\mathbf{q}) \mathbf{e}_j \right|^2.
$$

By putting Eqs. (6) and (8) into Eq. (5), the first order and overtone Raman peak area can be described directly as a function of the excitation energy and the Raman tensor, respectively. Note the dependence of the Raman scattering efficiency on the excitation frequency (e.g., energy) to the power of 4 in Eqs. (6) and (8). Since all the other parameters in Eqs. (6) and (8) are not expected to vary with the excitation energy, then the Raman efficiency should increase with $\omega^4$. However, this is not always true: the dependence of the Raman efficiency on excitation frequency over and above $\omega^4$ is expected to be small or null only if the excitation energy is far from any singularity of the dielectric function, i.e., only when the process is nonresonant. Under resonance conditions, the

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**FIG. 1.** (Color online) Raman spectra of SLG with Nitto tape residuals and Nitto tape, measured at 633 nm.

$\sim1350$ cm$^{-1}$ cannot be attributed to the $D$ peak. Note that the $D$ peak changes position with excitation energy, moving to $\sim1320$ cm$^{-1}$, when measured at 633 nm,\(^{39}\) unlike the tape peaks.

The typical approach to measure the Raman efficiency is to compare the Raman intensity of the sample under study with that of another sample used as a reference (substitutional method).\(^{60}\) A commonly used standard scatterer is liquid benzene, since its Raman efficiency and its dependence on excitation energy are well known.\(^{89}\) However, several corrections are needed, such as those to account for the solid angle and reflection losses, and spectrometer sensitivity. An alternative method compares the Raman and Brillouin spectra from the same sample, measured at the same time in the same setup, and uses the Brillouin data as reference.\(^{90-93}\) This approach relies on the fact that Brillouin scattering cross sections can be expressed in terms of elastic-optic coefficients and other macroscopic quantities, which in turn can be determined using independent techniques.\(^{91}\) This was used to measure the Raman efficiency of the first order silicon peak\(^{91}\) and the second order of strontium titanate (SrTiO$_3$),\(^{93}\) potassium iodide (KI),\(^{93}\) potassium bromide (KBr),\(^{93}\) and potassium chloride (KCl).\(^{58}\) Here, we employ the substitutional method, using CaF$_2$ as a reference scatterer (Sec. III).
Raman tensor element strongly changes with the excitation frequency, so the Raman efficiency does not follow the $\omega^4$ law. In semiconductors this is typically observed when the excitation energy is close to the optical gap of the material: under this condition a strong enhancement of the Raman peaks areas is observed. The resonance intensity profile was indeed used in the past to study the electronic structure of several semiconductors.

B. Substitutional method

The absolute value of the Raman scattering efficiency can be measured from the Raman peaks areas by using Eq. (5). However, a Raman peak area strongly depends on the experimental setup, such as type and numerical aperture of the objective, power, integration time, and on surface conditions. E.g., Ref. 51 reported that the silicon intensities increased a factor of 2 after polishing the surface. Thus, the direct use of Eq. (5) does not provide accurate values for the Raman efficiency.

In order to measure the absolute value of the Raman scattering efficiency, we use the substitutional method. This consists in normalizing the Raman peak area of the sample to that of the substitutional scatterer (indicated by $^*$ in the following equations) and correcting this ratio by the optical constants of the two materials. From Eq. (5), we have

$$\frac{A}{A^*} = \frac{(1 - R_s)(1 - R_s)}{(1 - R_t^*)(1 - R_t^*)} \frac{n_s^2}{n_t^2} \frac{L}{L^*} \frac{dS/d\Omega}{dS^*/d\Omega^*}.$$  (9)

Thus we can get the Raman scattering efficiency simply measuring the Raman peaks areas ratio between the two materials.

The advantage of this method is that $A/A^*$ is automatically corrected for the $\omega^4$ dependence and for the spectrometer and detector sensitivity, which strongly varies with the excitation energy. Every Raman spectrometer has its own sensitivity curve, depending on the type of detector, gratings, and optics used. This can be measured with a calibration lamp. In our case, we used a quartz tungsten halogen (QTH) lamp (Oriel, Newport Corp.) with a calibrated spectral irradiance between 250 and 2400 nm. The sensitivity curve for our triple monochromator spectrometer is shown in Fig. 2. Note that the spectrometer response varies by almost one order of magnitude between 2.2 and 2.7 eV.

In order to use the substitutional method, we need to choose as a reference scatterer a material whose optical properties and Raman efficiency are very well known in the visible range. One could then use the first order of the silicon peak. However, silicon is resonant in the visible, so the silicon peak area needs to be corrected for the dispersion of its dielectric function. Thus the simplest way to get the absolute value of the Raman scattering efficiency and its energy dependence is to use a material which is not resonant in the energy range investigated. In this way any residual energy dependence of $A/A^*$ can be ascribed totally to the Raman tensor, since spectrometer sensitivity and $\omega^4$ dependence are automatically corrected and the Raman tensor of the reference material is constant, i.e.,

$$\frac{A}{A^*} \sim \frac{dS/d\Omega}{dS^*/d\Omega^*} \sim \frac{\sum_j |\mathbf{e}_i \cdot \mathbf{R}_j \cdot \mathbf{e}_s|}{\sum_j |\mathbf{e}_i \cdot \mathbf{R}_j \cdot \mathbf{e}_s^*|} \sim \sum_j |\mathbf{e}_i \cdot \mathbf{R}_j \cdot \mathbf{e}_s|.$$  (10)

By choosing a reference material which is not resonant under the energy range investigated, the energy dependence of $A/A^*$ directly describes that of the Raman tensor of the material under investigation. This is a different approach with respect to the experiments based on cyclo-hexane, where the measured Raman peaks areas include also the $\omega^4$ dependence.

Here we use as reference material CaF2: this crystal shows only one first order line at $\sim 320$ cm$^{-1}$, and its gap is $\sim 11$ eV, well above any of our excitation energies. This allows one to consider the CaF2 Raman tensor constant in the range 1.8–3.8 eV, within a 16% error bar. The substitutional method with CaF2 was previously used to measure the Raman efficiency of other materials, such as diamond, silicon, CdS, and ZnO.

Using CaF2 as a reference scatterer, we have $1 - R_s^* = 1 - R_t^* = 0.97$ and $n_s^* = 1.437$ in the visible range. The Raman scattering efficiency $dS/d\Omega$(CaF2) is $\sim 4.935 \times 10^{-7}$ m$^{-1}$Sr$^{-1}$ at 2.41 eV. Being a transparent material, we assume that the CaF2 probe length corresponds to our focus length ($\sim 1000$ $\mu$m). Thus Eq. (10) gives

$$\frac{A}{A^*} = \frac{4479 L}{\mu m} \frac{(1 - R_s)(1 - R_s)}{(1 - R_t^*)(1 - R_t^*)} \frac{n_s^2}{n_t^2} \frac{L}{L^*} \frac{dS/d\Omega}{dS^*/d\Omega^*},$$  (11)

where $L$ is in nm and $dS/d\Omega$ in m$^{-1}$Sr$^{-1}$.

To be effective, the substitutional method requires the measurements to be performed on the sample and on CaF2 under exactly the same conditions. For this reason we placed SLG directly on CaF2 by micromechanical exfoliation.

Note that the position of the CaF2, G, and 2D peaks span over a $\sim 0.4$ eV range, so the ratio between G, 2D, and CaF2 areas needs to be corrected for the spectrometer sensitivity. As an example, we consider in detail the correction performed for an excitation energy of 2.18 eV (568 nm). The 2D peak lies at $\sim 2650$ cm$^{-1}$. This corresponds to an energy shift of 0.33 eV. Since we measure the Stokes line, the 2D peak position corresponds to an absolute energy of 2.18 $\pm$ 0.33 $= 1.85$ eV. The G peak absolute energy is then 2.18 $- 0.2 = 1.99$ eV.

![FIG. 2. (Color online) Sensitivity curve of our Dilor Raman spectrometer setup (detector, grating, and optics).](image-url)
The CaF$_2$ peak, used as a reference, lies at $\sim$325 cm$^{-1}$, i.e., at an energy of $\sim$2.14 eV. Thus Fig. 2 shows that the measured $A(2D)$ is underestimated, when compared to $A(G)$. Figure 2 gives a correction factor of $\sim 0.81/0.7 = 1.14$.

We now apply the substitutional method to SLG on CaF$_2$. Equation (11) requires transmittance, penetration length, and the refractive index of SLG. Transmission measurements on suspended SLG have shown that reflectance is negligible, while absorbance and transmittance in the visible range are constant and equal to 0.023 and 0.977, respectively. Since the light penetration length cannot be smaller than the SLG effective thickness (0.33 nm), for SLG we use $L = 0.33$ nm. The refractive index of SLG was measured by ellipsometry. This showed that one can use for graphene the refractive index in the basal plane of graphite. 

The refractive index in the basal plane of graphite can be taken as almost constant in the visible range. For SCG, we also need to consider interference effects produced by the Si/SiO$_2$ substrate. 

As we will show in the next section, $A_{SLG}/A_{SCG}$ can be strongly modulated by the excitation energy because of the interference effects produced by the Si/SiO$_2$ substrate.

IV. RESULTS AND DISCUSSION

A. Si/SiO$_2$ substrate

Figure 3 plots $A(G)$ for graphene deposited on Si/300SiO$_2$ as a function of the number of layers ($N$) of a flake, measured at (a) 633 nm, (b) 514.5 nm, and (c) 488 nm, showing that $A(G)$ has a different dependence on $N$ for different excitation energies. In particular, at 488 and 514 nm, $A(G)_{SLG}$ is similar to $A(G)_{SCG}$, while at 633 nm, $A(G)_{SLG}$ is $\sim 0.01$ times smaller than $A(G)_{SCG}$.

Figure 4 plots $A(2D)$ as a function of $N$ deposited on Si/300SiO$_2$, measured at (a) 633 nm and (b) 488 nm. Note the effect of doping on $A(2D)$. Indeed, one needs to be very careful when evaluating $dS/d\Omega(2D)$. Pristine graphene samples on Si/300SiO$_2$ are usually doped by charged impurities and $A(2D)$ strongly changes with doping. Also, Fig. 4 implies that the $A(2D)$ dependence on $N$ changes with the excitation energy. In particular, $A(2D)_{SLG}/A(2D)_{SCG} = 0.37$ and $A(2D)_{SLG}/A(2D)_{SCG} = 3.3$, when measured at 633 and 488 nm, respectively.

We attribute this different behavior with excitation energy to interference enhanced Raman scattering. We use the transfer matrix method (TMM) to evaluate the effect of substrate interference effects and sample absorption on the overall
Raman signal. This proceeds in two steps. First, we calculate the incident amplitude $E(x)$ in the sample as a function of depth $x$. The Raman absorption at depth $x$ is proportional to $|E(x)|^2$. Next we calculate the emissivity $\gamma_R(x)$ from depth $x$ at the corresponding Stokes-shifted frequency. The Raman intensity is then proportional to

$$I \propto \int_{x=0}^{d} |E(x)|^2 |\gamma_R(x)|^2 dx.$$  

(14)

In the case of a nonzero NA, we perform the TMM calculation for every angle of incidence and both polarizations, so that

$$I \propto \int_{x=0}^{d} E(x) \bar{\Gamma}_R(x) dx,$$

(15)

with:

$$E(x) = \sum_{s,p} \int_{\theta=0}^{\pi/2} |E_{\theta}(x)|^2 S_p f(\theta) \sin \theta d\theta,$$

$$\bar{\Gamma}_R(x) = \int_{\theta=0}^{\pi/2} |\gamma_{R,\theta}(x)|^2 f(\theta) \cos \theta \sin \theta d\theta,$$

(16)

(17)

where the angle $\theta$, inside the sample is related to the incident angle $\theta^0$ through Snell’s law $\sin \theta = \sin \theta^0 / n_g$, with $n_{g}$ the graphene’s index of refraction and $\gamma_{R,\theta}(x)$ is 1 or $|\cos \theta|^2$ for s- or p-polarized incidence, respectively. In Eq. (16), we assumed for simplicity that the emitting dipole is parallel to the surface and that the emission is s-polarized. The extra cosine in the emission integral is to enforce a Lambertian distribution, and the angular weight $f(\theta)$ is determined by the NA: $f(\theta) = e^{-2 \sin^2 \theta \gamma R / \pi^2}$. Our measurements are done with NA = 0.9. For comparison, we also plot results for NA = 0 and NA = 0.6. The indexes of refraction of SiO$_2$ and Si are those used in Ref. 26.

We then calculate $A(2D)$ and $A(G)$ as a function of $N$, for three different excitation wavelengths, each for three different NA. $A(G)$, normalized to the corresponding graphite signal, is plotted in Fig. 5. We note that for NA = 0.6 the calculations reproduce well our experimental results. This could mean that the laser does not completely fill our objective, giving an effective NA = 0.6. Under our experimental conditions, at 488 and 514 nm $A(G)_{\text{SLG}}$ is slightly less than $A(G)_{\text{SCG}}$, with a maximum enhancement (compared to graphite) of 2.5 and 4 for $N = 15$ layers. In contrast, at 633 nm $A(G)_{\text{SLG}}$ is smaller than $A(G)_{\text{SCG}}$, with at least eight layers required for the signal to reach it, and a maximum enhancement of 2.5 for $N \sim 35$ (not shown in the experimental data).

We get a similar result for $A(2D)$, as indicated in Fig. 6. We find that at 633 nm and NA = 0.6 we need $N \sim 10$ to reach $A(2D)_{\text{SCG}}$, with a maximum enhancement of a factor 1.5 for $N \sim 38$ layers. However, our calculation cannot reproduce the fine features observed for SLG and FLG, as for Fig. 6. It does, however, reproduce well the results for large $N$.

One striking effect is the different trend as a function of NA that we observe at different excitation wavelengths: at 488 nm there is a large increase of $A_{\text{SLG}}/A_{\text{SCG}}$ with increasing NA, while the opposite is found for 633 nm. At 532 nm, on the other hand, there is very little variation with NA. This is seen for both $G$ and $2D$ peaks. In order to understand this behavior, we plot in Fig. 7 the normalized $A(G)$ and $A(2D)$ as a function of excitation wavelength and NA. Note that for the $2D$ peak in Fig. 7(b) we scaled the graphene results by $A_{\text{expt}}^{2D}(1)/A_{\text{expt}}^{2D}(1) = 4.18$ so that a direct comparison with experiments can be made. At NA = 0 the enhancement reaches 0.88 at 560 nm for $G$ and 2.9 at 545 nm for $2D$. At NA = 0.9, however, the maxima shift to 515 nm and 500 nm, respectively, with peak values 0.82 and 2.8. Thus, for excitation close to the maximum (where there is little slope...
with wavelength), no significant change is observed as NA increases (as is the case for the 514 nm excitation in Fig. 7).

On the other hand, below the peak (large positive slope with wavelength) we observe significant increase in enhancement (e.g., at 488 nm), while above the peak (large negative slope with wavelength) significant decrease (e.g., at 633 nm). This is expected, since in all interference phenomena, as the angle increases, the resonant wavelength decreases. This underlines the crucial role of NA to fully understand the measurements.

Figure 8 plots $A(G)$ and $A(2D)$ of SLG on Si/90SiO$_x$ measured at different excitation wavelengths. The intensities are higher than on Si/300SiO$_x$ and they do not show a strong dispersion with excitation wavelength and NA. The different behavior of the intensity is expected since interference enhancement strongly depends on the oxide thickness. Figure 8 implies that Si/90SiO$_x$ is indeed a better substrate in order to quickly measure a Raman spectrum, since it gives up to eight times higher intensity, depending on the excitation wavelength, compared with Si/300SiO$_x$.

### B. CaF$_2$ substrate

Figure 9 shows (a) the AFM picture and (b) the Raman map of graphene on CaF$_2$; here, the green color corresponds to regions of the sample without a $D$ peak, the blue area shows regions with a $D$ peak, and the red area corresponds to the Raman spectrum of graphite. This figure implies that there are only small regions with $D$ peak, and no contamination is detected by AFM.

Figure 10 plots the Raman spectra of SLG on CaF$_2$, measured at different excitation energies. The Raman fit parameters do not show strong variations from sample to sample, or within the same sample, and are comparable with those measured on suspended SLG. Thus CaF$_2$ can be used as a substrate in order to measure the Raman efficiency of SLG, since doping, defects, and interference effects do not affect the measured Raman peaks areas, in contrast to when Si/SiO$_x$ is used as substrate.

Figure 11 plots the Raman peaks areas of SLG, compared to CaF$_2$, as a function of excitation energy. This figure shows that $A(G)_{SLG}/A(CaF_2)$ and $A(2D)_{SLG}/A(CaF_2)$ have a very different energy dependence. This is ascribed to the Raman tensor (Sec. III): that of the $G$ peak is constant, so the Raman scattering efficiency follows the $\omega^4$ law. This is an indication that the $2D$ peak area is ruled by resonant contributions. In contrast, the Raman tensor of the $2D$ peak is not constant in the energy range investigated here, so the corresponding Raman scattering does not follow the $\omega^4$ law. This agrees with previous results obtained for nanocrystalline graphite.
The different energy dependence between the $G$ and $2D$ peaks is a fingerprint of their different activation mechanisms: the $2D$ peak involves resonant contributions, in agreement with recent measurements on intercalated graphite $^{86}$ while the $G$ peak cannot be described by a single-resonance model, in agreement with recent results $^{77,78}$ Note that the exact form of a resonance is determined by the phase and functional dependence of the matrix elements and the frequencies of the resonances $^{60}$

By using the data in Fig. 11, we can now calculate the Raman scattering efficiency of the $G$ and $2D$ peaks for SLG, by using Eq. (12). At 2.41 eV $A(G)_{SLG}/A(CaF_2) \sim 0.4$ and $A(2D)_{SLG}/A(CaF_2) \sim 3.2$, so from Eq. (12) we get $dS/d\Omega(G)_{SLG} \sim 200 \times 10^{-5}$ m$^{-1}$Sr$^{-1}$ and $dS/d\Omega(G)(2D)_{SLG} \sim 1580 \times 10^{-5}$ m$^{-1}$Sr$^{-1}$.

We then consider SCG. Figure 12 plots $A(G)_{SCG}/A(CaF_2)$ and $A(2D)_{SCG}/A(CaF_2)$. The energy dependence of the Raman peaks areas of SLG and SCG is the same, i.e., the $G$ peak Raman tensor is constant in the visible range, in contrast to the $2D$ Raman tensor, in agreement with previous measurements on disordered graphite $^{52}$ For SCG we get $A(G)_{SCG}/A(CaF_2) \sim 4 \pm 1.2$ at 2.41 eV, so $dS/d\Omega(G)_{SCG} \sim 100 \times 10^{-5}$ m$^{-1}$Sr$^{-1}$. This value is smaller than that reported in Ref. 51. However, taking into account that Ref. 51 measured HOPG and no spectrometer sensitivity correction was mentioned, we think that this difference is reasonable.

FIG. 10. (a) First and (b) second order Raman spectra of graphene on CaF$_2$, measured at different excitation wavelengths.

FIG. 11. (Color online) Areas of $G$ and $2D$ peaks of graphite measured at different excitation energies and normalized to the CaF$_2$ Raman peak area.

FIG. 12. (Color online) Areas of $G$ and $2D$ peaks of graphite measured at different excitation energies and normalized to the CaF$_2$ Raman peak area.
TABLE I. Raman scattering efficiency of the $G$ peak of graphene and graphite, measured at 2.41 eV, compared to the Raman cross section measured for other materials. The units of $S$ are $10^{-5}$ m$^2$ Str$^{-1}$. Note that $dS/d\Omega$ depends on the scattering geometry and temperature.

<table>
<thead>
<tr>
<th></th>
<th>Graphene</th>
<th>Graphite</th>
<th>CaF$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>2.69</td>
<td>2.69</td>
<td>1.437</td>
</tr>
<tr>
<td>$L$ (nm)</td>
<td>0.33</td>
<td>15</td>
<td>1000</td>
</tr>
<tr>
<td>$dS/d\Omega(G)$</td>
<td>$\sim 200$</td>
<td>$\sim 100$</td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega(G)$</td>
<td>300–400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega(G)$</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega$(diamond)$^{71}$</td>
<td>1332 cm$^{-1}$</td>
<td>6–5</td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega$(silicon)$^{51}$</td>
<td>521 cm$^{-1}$</td>
<td>500–700</td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega$(c-BN)$^{71}$</td>
<td>1332 cm$^{-1}$</td>
<td>0.1 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega$(h-BN)$^{71}$</td>
<td>1332 cm$^{-1}$</td>
<td>20 ± 10</td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega$(GaAs)$^{65}$</td>
<td>267 cm$^{-1}$</td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega$(KI) second order$^{93}$</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega$(KBr) second order$^{93}$</td>
<td>0.088</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$dS/d\Omega$(SrTiO$_3$) second order$^{93}$</td>
<td>172</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In any case, the order of magnitude is the same. Table I compares $dS/d\Omega$ of the Raman peaks of graphene with the values reported for graphite and other materials.

Note the polarization dependence of the $G$ and 2$D$ peaks. The $G$ peak corresponds to a phonon with $E_{2g}$ symmetry. Then, from group theory, we expect its intensity not to change with polarization.$^{104}$ In contrast, the 2$D$ peak, being an overtone, always contains an $A_1$ symmetry. Then, from group theory we expect $A(2D)$ to strongly change with polarization, i.e.,

the maximum area should be obtained in the configuration which measures the diagonal components of the Raman tensor.$^{79}$ We rotated CaF$_2$, SLG, and SCG, but we did not observe any change in $A(G)$ and $A(2D)$. This shows that the Raman peaks areas do not depend on the angle between the incident polarization and the crystal lattice, as discussed in Ref. 104. $A(2D)$ depends only on the relative angle between incident and scattered polarization, no matter the incident polarization angle. We then used a Fresnel rhomb in order to rotate the polarization of the incident light. Now, we have to take into account that the whole spectrometer (grating and beam splitter) is sensitive to the polarization direction. Figure 13(a) shows the dependence of the spectrometer on polarization, obtained by measuring the CaF$_2$ intensity as a function of the incident polarization. Figure 13(b) plots $A(G)$ and $A(2D)$ as a function of the polarization angle, after correction for the spectrometer sensitivity. This shows that the beam splitter acts as an analyzer. This explains why, even after correcting $A(G)$ and $A(2D)$ for the polarization dependence, $A(2D)$ changes with polarization. Indeed, in order to avoid effects arising from the spectrometer sensitivity on polarization it is necessary to insert a half-$\lambda$ plate before beam splitter and detector, as done in Ref. 104. Figure 13 shows that under our configuration, i.e., without introducing any external polarizer/analyzer, our spectrometer measures the maximum $A(2D)$.

It is also interesting to compare the relative intensity of the two-phonon lines, such as 2$D$, 2$D'$, and $D + D''$, measured for SLG on CaF$_2$ as a function of excitation energy. The $D + D''$ peak lies at $\sim 2450$ cm$^{-1}$, and it is a combination between $D$ and the $D''$ peak at $\sim 1100$ cm$^{-1}$.$^{42,105–109}$ The relative areas of these peaks shows a peculiar dependence on excitation energy: $A(2D')/A(2D)$ decreases for increasing excitation energy, while $A(D + D'')/A(2D)$ increases, see Fig. 14. This further confirms the importance of resonant processes on the two-phonon lines area.

V. CONCLUSIONS

We presented a detailed analysis of the Raman intensities of graphene. We measured the absolute Raman efficiency...
of graphene and graphite in the visible range by sample substitution. We showed how the Raman scattering efficiency of graphene changes with the number of layers, the type of substrate, and the incident laser frequency. In particular, we showed that the Raman intensity of graphene is strongly modulated by the Si/SiO\textsubscript{2} substrate, as confirmed by depositing graphene on a different substrate (CaF\textsubscript{2}).

By using the sample-substitution method, we measured the absolute Raman efficiency of graphene. The $G$ peak Raman scattering efficiency is $\sim 200 \times 10^{-5}$ m\textsuperscript{-1}S\textsuperscript{-1}. For the $2D$ peak the Raman scattering efficiency is one order of magnitude bigger than that of the $G$ peak, at 2.41 eV. Furthermore, its absolute value strongly depends on light polarization. The high Raman scattering efficiency of the $2D$ peak and its dependence on the excitation energy further confirm the resonant nature of the Raman process giving rise to this peak.

**ACKNOWLEDGMENTS**

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CHAPTER
FIVE

HIGH-YIELD PRODUCTION AND TRANSFER OF
GRAPHENE FLAKES OBTAINED BY ANODIC
BONDING

My contribution

I produced some samples, performed the flake transfers, participated in the deposition parameter optimization, took some Raman measurements, analyzed the data and participated in the redaction of the paper and the preparation of the Figures.
High-Yield Production and Transfer of Graphene Flakes Obtained by Anodic Bonding

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Graphene is a two-dimensional hexagonal lattice of carbon atoms. Several graphene sheets stacked give ordinary three-dimensional graphite crystals. Graphene attracts enormous interest because of its unique properties.1–7 Near-ballistic transport at room temperature and high mobility6–11 make it a potential material for nanoelectronics,12–16 especially for high-frequency applications. Furthermore, its optical and mechanical properties are ideal for micro- and nanomechanical systems, thin-film transistors, transparent and conductive composites and electrodes, and photonics.17–22

The most used technique to produce graphene flakes is based on the micro-mechanical exfoliation (MME) of graphite.2,23 This is a very simple and cheap method that requires only some graphite flakes and adhesive tape. However, the graphene yield is very low: graphene flakes are rare, while few graphene layers and thick pieces of graphite mostly cover the whole substrate. Thus, identification of graphene is time-consuming and relatively difficult, in particular when graphene is deposited on transparent substrates. Furthermore, the graphene flakes produced by MME are relatively small, typically with a lateral size of 10–20 μm. It is possible to strongly increase the graphene size by using some special cleaning treatment of the substrate: flakes up to 1 mm lateral size have been produced. However, the yield still remains very low: fewer than three to four large flakes per substrate are typically produced. Furthermore, often the large flakes are covered by bubbles,24 whose origin is still unknown.

Alternative techniques have been developed in order to produce graphene wafers such as epitaxial growth on SiC25 and chemical vapor deposition on metals.26,27 They all require a complex, relatively expensive setup and careful control of the deposition parameters in order to grow graphene of high quality.

Finally, a different approach is based on the anodic bonding technique, typically used to bond borosilicate glass and silicon wafers.28,29 Anodic bonding is achieved by pressing borosilicate glass on a silicon wafer at high temperatures (above 200 °C), while a high electrostatic field is applied perpendicular to the layers. Due to heating, the Na2O impurities in the glass decompose into Na+ and O2− ions. The Na+ ions are lighter and have a higher mobility compared to the O2− ions. The polarity of the voltage is chosen so that the Na+ ions move away from the silicon–glass interface to the back contact.30 The O2− ions remain at the interface, causing a strong electric field there, which allows bonding between silicon and glass. Covalent Si–O–Si bonds are formed at the interface. This method can be used also to deposit graphene, where graphene replaces the silicon in the original technique.31,32 This method allows quick and cheap production of graphene layers in high yield: under optimum parameters an area comparable with the size of the graphitic flake is covered by

**ABSTRACT**

We report large-yield production of graphene flakes on glass by anodic bonding. Under optimum conditions, we counted several tens of flakes with lateral size around 20–30 μm and a few tens of flakes with larger size. About 60–70% of the flakes have a negligible D peak. We show that it is possible to easily transfer the flakes by the wedging technique. The transfer on silicon does not damage graphene and lowers the doping. The charge mobility of the transferred flakes on silicon is on the order of 6000 cm2/V s (at a carrier concentration of 1012 cm−2), which is typical for devices prepared on this substrate with exfoliated graphene.

**KEYWORDS:** graphene · transfer · anodic bonding · Raman spectroscopy

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graphene and a few graphene layers, with a typical size well above 10 μm, some up to 1 mm. The flakes have been studied by Raman spectroscopy, atomic force microscopy, scanning tunneling microscopy, and transport. Despite the simplicity of the setup, this method has been rarely adopted mainly because the anodic bonding technique allows depositing graphene on substrates with relatively mobile ions. Thus, the most used substrate has been borosilicate glass. This substrate is useful to study the optical properties of graphene, but it is not suitable for transport measurements because of the higher complexity in the lithography process and lack of backgate. Furthermore, the optical visibility of graphene on glass is extremely low, so the flake is very difficult to spot on the substrate. However, by using the anodic bonding method the location of the flakes on glass is straightforward: after anodic bonding, the glass surface is no longer smooth; that is, the area of the coverslip that was treated by high voltage and temperature becomes opaque, so it is well visible by eye (Figure 1a in the Supporting Information). Furthermore, this area is mostly covered by single-layer flakes among bilayers and very few thick layers. This makes graphene flakes produced by anodic bonding the perfect samples for optical spectroscopy and near-field measurements.

Previous works also report electrostatic deposition of graphene on oxidized silicon by applying a voltage well above 3 kV. However, under these conditions, the control of the thickness is very difficult: few layers are generally deposited, and the quality of the flakes is very low, since the Raman spectrum shows a very intense D peak. No information on the yield of single layers is reported. This method has been used for electrostatic printing of few-graphene-layer arrays and nanoribbons.

In this work we show an extensive analysis of the properties of graphene produced by anodic bonding. Raman spectroscopy has been used to identify single-layer graphene and to probe doping and disorder. The peaks have been fitted with a single Lorenzian line shape, and we analyzed the position (Pos), full width at half-maximum (fwhm), and intensity (I) of the G and 2D peaks (here intensity is the integrated area of the peak).

We show that anodic bonding is a valid alternative to MME, since it allows producing high-yield and defect-free graphene flakes with a very simple setup. We show that the flakes can be easily transferred with no damage to other substrates, such as silicon (Si/SiO₂), by the wedging technique.

RESULTS AND DISCUSSION

In the anodic bonding a single crystal flake of graphite is pressed on glass, and a high voltage of
0.5–2 kV is applied between the graphite and a metal back contact, while heating the glass at about 200 °C for 10–20 min. In case of the positive electrode applied to the top contact, a negative charge concentration occurs in the glass at the side facing the positive electrode. A few layers of graphite, including single layers, stick on the glass by electrostatic interaction. The anodic bonding is a simple technique because there are only two deposition parameters: temperature and voltage. Thus, in order to determine the optimum conditions to have high-yield and high-quality single-layer graphene, we made several samples at different temperatures (between 160 and 260 °C) and voltage (between 0.4 and 3 kV).

First, we investigated the samples by optical microscopy. Figure 1a shows a sample obtained at 220 °C and 0.4 kV: the substrate is mostly empty, and the bonding efficiency is very low. Figure 1b shows a sample obtained at 220 °C and 0.9 kV: the substrate is well covered by graphene flakes, and a few layers of graphene are visible also. Figure 1c shows a sample obtained at 220 °C and 1.5 kV: the large single-layer sheets are broken into small flakes, with no defined edges. At higher voltage disruptive discharges through the glass can be observed: 3 kV is the upper limit for the applied voltage, under our experimental conditions. Thus, we found that the bonding efficiency of graphene on glass is maximum between 0.6 and 1.2 kV: moving to higher voltage strongly damages the largest flakes. Figure 1d shows a sample obtained at 260 °C and 0.9 kV: only a few graphitic particles and thick flakes are visible on the glass surface, which is no longer smooth, but shows circular spots and lines. Our results show that the bonding is starting to be efficient above 180 °C, but above 260 °C many thicker flakes and particles are visible. Thus, we can conclude that at low temperature the mobility of ions in the glass is not high enough for achieving a strong electrostatic

![Figure 2](image-url)  
**Figure 2.** (a) Raman spectra of the flakes obtained under different conditions; (b,c) Raman map of the fwhm of the 2D peak (the scale bar is in cm⁻¹) and intensity ratio between the D and G peak (scale bar is in arbitrary units) of a sample deposited at 0.9 kV and 220 °C. The flake in the center of (b), with a lateral size of about 0.1 mm, is a graphene, as indicated by the fwhm(2D) of about 30 cm⁻¹. The D peak is localized only at the edges of this flake. Other single-layer flakes are visible.

![Figure 3](image-url)  
**Figure 3.** Schematic of the properties of most of the flakes obtained with different deposition parameters with our anodic bonding setup.

![Figure 4](image-url)  
**Figure 4.** Raman fit parameters for the G peak and 2D peak of graphene deposited on glass by anodic bonding, compared with the Raman fit parameters of exfoliated graphene deposited on Si/SiOₓ. The data of gated graphene are taken from ref 41. The dotted lines are only a guide for the eyes.
interaction between graphene and glass. In contrast, if the temperature is too high, then the efficiency of the bonding is high, allowing even thick graphite to bond to the glass and thinner flakes are damaged.

Under our experimental conditions, we found that the highest yield of graphene is obtained in the range 180–240 °C and 0.6–1.2 kV. Under these conditions, we counted several tens of flakes with a lateral size around 20–30 μm and a few tens of flakes with larger size. A few flakes with a lateral size of about 100 μm have been observed also. Note that the optimum voltage and temperature strongly depends on the type of substrate.32 Since the process involves high temperature and voltage, it is fundamental now to investigate the quality of the flakes. Figure 2a shows the typical Raman spectra measured on flakes obtained in the range 180–240 °C and 1.1–1.4 kV. First, we can note that the 2D peak is a single and sharp peak, which confirms that the flakes are single layers.39 Second, we can see that some of the Raman spectra show defect-activated peaks, D and D0.39 We found that the D peak intensity strongly depends on temperature and voltage: the higher these parameters, the higher the probability that the flake will have a strong D peak. Most of the single layers deposited at 0.6 kV and 220 °C do not show any D peak. For increasing voltage, the D peak starts to appear in some of the flakes: at 1.1 kV most of the flakes have a D peak, although its intensity is usually up to 10–20% of the G peak intensity. At higher voltage all the flakes have a large D peak; sometimes disordered carbon is also observed.

Figure 2b,c shows a Raman map of the fwhm(2D) and intensity ratio between D and G peaks, I(D)/I(G), of some flakes deposited under optimum conditions. A flake with a lateral size of about 100 μm is visible. This is a single-layer graphene, as indicated by its fwhm(2D) of about 30 cm−1.39 The D peak is visible only at the edges. Smaller single layers and bilayers are visible too.

Figure 3 gives a schematic overview of the quality of the graphene flakes obtained under different deposition parameters. Finally, we can observe that even in the absence of a D peak, the Raman spectra show variations in the peak positions and fwhm. This can be well attributed to doping. Doping is expected in these samples because there are charges involved in the anodic bonding method.32 In order to confirm that the samples can be doped, we compared the Raman fit parameters of the G and 2D peaks with the ones measured in pristine graphene on Si/SiOx and gated graphene,40–42 Figure 4: a very good agreement in the variation of the G and 2D peak shape is observed. A high Pos(G) and large fwhm(G) correspond to low doping, while the Pos(2D) can be used to distinguish between n- and p-doping.40–42 Figure 4 shows that anodic bonding graphene can be doped and that the doping is p-type, as observed from Pos(2D) measured on the samples with high doping.

We transferred two graphene flakes deposited under the same conditions on two glass coverslips to: (i) a new glass coverslip, in order to check if the doping is related to the glass substrate; (ii) on Si/SiOx, for transport measurement. Figure 5a,b shows a graphene

Figure 5. Optical micrograph of graphene as deposited on glass (note the change in the topography of the coverslip, bottom of the figure). (b) Optical picture of the same sheet transferred to a new and clean coverslip. (c) Raman spectra of the flake before and after transfer. No D peak is visible after transfer. The scale bar in (a) and (b) is 10 μm. (d) Optical picture of another as-deposited graphene flake on glass. (e) Optical picture taken after transferring the flake on Si/SiOx. (f) Raman spectra of the graphene sheet before and after transfer.
Methods

Materials. Single-crystal graphite flakes (National de Graphite) 1.7 mm in size have been used to produce graphene. Few depositions have been performed with very large single-crystal graphite flakes, with a size of 5 mm. The graphite flake is cleaved once using sticky tape in order to achieve a clean and fresh surface. The flake is then placed on a microscope coverslip, with a thickness of 120 μm (Menzel-Gläser). The coverslip is cleaned before deposition by sonication in acetone and then 2-propanol.

Anodic Bonding Setup. This is composed of a grounded metal block used as back electrode and can be heated to 300 °C using a temperature feedback controlled heating plate. The glass coverslip is placed on the grounded electrode. The top electrode, a cylindrical metal rod with a diameter of 2 mm, mounted vertically above the back gate, is pressed on the graphite flake, while applying a dc voltage for 20–30 min. The setup allows dc voltages of up to 10 kV. After the deposition, thick graphite material is removed from the coverslip by using sticky tape.

Monochromatic Filter. The contrast of a graphene sheet on glass illuminated in reflection mode is 7%. However, the flakes were hardly visible under the microscope. We found that it is possible to steadily increase the contrast of the flake by converting the RGB image into a monochromatic image.

Conclusions

Micromechanical exfoliation of graphite is the most used method to produce graphene flakes on a substrate. Despite being simple and cheap, this technique can produce only few flakes. Furthermore, the identification of graphene can be very time-consuming when the single layer is deposited on transparent substrates. Here, we show that it is possible to deposit a large yield of graphene flakes on glass by anodic bonding. Under optimum conditions, 60–70% of the flakes have a negligible D peak. The flakes can be easily transferred onto other substrates, without damage, by the wedging technique. The charge mobility measured after transfer on silicon is on the order of 6000 cm²/(Vs) (at carrier concentration 10¹² cm⁻²), which is typical for devices prepared with exfoliated graphene on Si/SiO₂.
Transfer and Transport. The graphene flakes produced by anodic bonding have been transferred to other substrates by using the wedging technique. We transferred graphene flakes from the coverslip to a silicon substrate covered with 90 nm silicon oxide (IDT Technology) for transport measurements. Electron beam lithography and e-beam evaporation were used to prepare a set of contacts (5 mm × 50 mm Au). A Hall bar mesa structure has been prepared by reactive plasma etching.

Raman Spectroscopy. We used a WITEC alpha300 Raman spectrometer, equipped with 488, 514, and 633 nm laser lines. The laser power was kept as low as 500 mW in order to avoid damage by laser heating. The spectral resolution is 2–3 cm⁻¹. The instrument is equipped with a piezostage, which allows doing Raman mapping with a spatial resolution down to 10 nm. Further measurements have been taken with a HORIBA XploRA confocal Raman spectrometer, equipped with 532 nm laser wavelength. The theory of the Raman spectrum of graphene is described in the Supporting Information.

Acknowledgment. The authors thank S. Reich for the use of the XploRA Raman spectrometer and F. Mauri for useful discussions.

Supporting Information Available: Pictures of the flakes and details on the monochromatic filter, transfer technique, and Raman spectroscopy background are available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

Supporting information

1) Optical detection

The area covered with flakes is visible by naked eyes, Fig. 1(a). A quick inspection on the coverage and size of the flakes can be done directly with the optical microscope. However, under normal conditions, the thinnest flakes are hardly optically visible, Fig. 1(b). It is possible to increase the colour contrast of the flake on glass by applying a monochromatic filter to the image taken with our camera. The monochromatic filter transforms a 3 channels (RBG) image into one channel image. After this transformation, the flakes are optically visible, Fig. 1(c). Our microscope is equipped with a piezostage, thus we performed the optical inspection in the following way: we programmed the stage to scan an area of 240x240 μm², and then the monochromatic filter is applied to the pictures of the scanned area. The thinner layers (mostly single layers and few bilayers, including few folded graphenes) are identified by colour contrast and Raman spectroscopy. Figure 2 shows some images of graphene flakes produced by anodic bonding.

2) Transfer technique

The following steps were performed in order to transfer the graphene sheets from the glass coverslip:

Figure 1 (a) Glass coverslip after anodic bonding: the area covered by the flakes is visible by eyes, so it is straightforward to locate the flakes on the substrate; (b) Optical micrograph taken with our camera under normal illumination conditions: the flakes are hardly visible; (c) Same image after applying a monochromatic filter: graphene flakes are now clearly visible.
first, we prepared a solution of cellulose acetate butyrate in ethylacetate with a concentration of 30 mg/ml. We used a pipette to place a drop of about 5 μℓ on the surface. The solvent evaporates at ambient conditions and a solid cellulose film encapsulated the graphene sheets. Then, the sample is put into water, the water goes at the cellulose/glass interface so that the graphene flakes, embedded in the cellulose film, float on the top of the water. By placing the desired new substrate under the cellulose film, one can carefully deposit the encapsulated graphene on the new substrate. The final step is to dissolve the cellulose film by using ethyl-acetate and to heat the sample in order to remove water residuals. Graphene is further cleaned with acetone and isopropanol and then dried with nitrogen.

3) Raman Spectroscopy: background

All $sp^2$ bonded carbons show common features in their Raman spectra, the so-called G and D peaks, around 1580 and 1360 cm$^{-1}$. The G peak corresponds to the $E_{2g}$ phonon at the Brillouin Zone (BZ) center. The D peak is due to the breathing modes of six-atom rings and requires a defect for its activation. The 2D peak is the second order of the D peak. This is a single peak in single layer graphene, whereas it splits in four in bilayer graphene, reflecting the evolution of the band structure. Since the 2D peak originates from a process where momentum conservation is satisfied by two phonons with opposite wavevectors ($\mathbf{q}$ and $-\mathbf{q}$), it does not require defects for its activation. Indeed, high quality

Figure 2 Images of some graphene flakes obtained by anodic bonding. Average lateral size is 30 μm, but larger flakes can be found too.
graphene shows the G and 2D peaks, but not D peak.\(^1\) Thus, Raman Spectroscopy can easily probe disorder in graphene. Raman Spectroscopy is very sensitive to doping.\(^3\) In particular, doping affects both the G and 2D peaks in the following way:

(i) Pos(G) increases for increasing charge concentration and saturates for high doping. The FWHM(G) decreases for increasing doping and saturates when the electron-hole gap becomes higher than the phonon energy.\(^3\)

ii) Pos(2D) increases for p-doping, while it decreases for n-doping, for increasing charge concentration. However, this is visible only at relatively high doping.\(^4\)-\(^5\)

iii) The ratio between the peaks intensity, I(2D)/I(G), decreases for increasing charge concentration.\(^4\)-\(^6\)-\(^7\) In the framework of a fully Raman resonant process for the second-order 2D peak, the intensity dependence on the doping is due to the electron-electron scattering contribution, which increases for increasing charge concentration.\(^6\)-\(^7\)

These variations have been also observed in the Raman spectrum of pristine graphene samples, produced by MME and deposited on Si/SiO\(_x\) substrate, and attributed to charged impurities.\(^5\)


6.1 Probing the nature of defects in graphene by Raman spectroscopy

My contribution

I produced most of the samples, took most of the Raman measurements, analyzed the data, prepared all the figures and wrote the manuscript.
Probing the Nature of Defects in Graphene by Raman Spectroscopy

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ABSTRACT: Raman spectroscopy is able to probe disorder in graphene through defect-activated peaks. It is of great interest to link these features to the nature of disorder. Here we present a detailed analysis of the Raman spectra of graphene containing different types of defects. We found that the intensity ratio of the D and D’ peak is maximum (∼13) for sp3-defects, it decreases for vacancy-like defects (∼7), and it reaches a minimum for boundaries in graphite (∼3.5). This makes Raman Spectroscopy a powerful tool to fully characterize graphene.

KEYWORDS: Graphene, Raman spectroscopy, defects, conductive AFM

Since its first experimental observation, graphene has triggered enthusiasm in the world’s scientific community due to its outstanding properties.1,2 In particular, near-ballistic transport at room temperature and high carrier mobilities3–6 make it a potentially attractive material for nanoelectronics.

Despite being praised for being inert, ultrathin, and impermeable to any gaseous material,7 realistic graphene structures always contain defects.8 One generally refers to defects in graphene as anything that breaks the symmetry of the infinite carbon honeycomb lattice. Thus, different types of defects can be defined such as edges, grain boundaries, vacancies, implanted atoms, and defects associated to a change of carbon-hybridization, for example, from sp2 into sp3. The amount and nature of defects strongly depend on the production method and may change from sample to sample. Both the amount and the nature of defects can have a strong influence on the properties of graphene samples.9 For example, resonant scatterers, atomic-sized defects that introduce midgap states close to the Dirac point, have been identified as the major limitation of electron mobility for graphene deposited on substrates.10,11 On the other side, the control of the location of defects and their arrangement into ordered and extended structures allows making preparation of new graphene-based materials with novel properties.12 Extended line defects could be used to guide charge as well as spin, atoms, and molecules.13 Defects also have strong influence on the chemical reactivity.14 This makes defective graphene a prospective catalyst.14 It is therefore of fundamental importance to be able to probe defects and to establish the precise nature of disorder.

Raman spectroscopy is a well-established technique for investigating the properties of graphene.15,16 This technique is able to identify graphene from graphite and few-layers graphene and it is sensitive to defects, excess charge (doping), strain and to the atomic arrangement of the edges.15–24 Raman spectroscopy is able to probe defects in graphitic materials because, along with the G and 2D (also called G’, being symmetry allowed) peaks that always satisfy the Raman selection rule, the Raman-forbidden D and D’ bands appear in the spectrum.25 They are activated by a single-phonon intervalley and intravalley scattering process, respectively, where the defect provides the missing momentum in order to satisfy momentum conservation in the Raman scattering process.26–29

Graphene is an ideal material to study defects because its two-dimensional nature makes it easy to add, remove or move carbon atoms, that is, to introduce only a specific type of defect, in contrast to graphite or carbon nanotubes. Graphene is then the perfect target to investigate the sensitivity of the Raman spectrum on the nature of defects and finally build up a complete theory linking the Raman peak intensities to the number and type of defects.

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The study of the evolution of the intensities of the Raman peaks for increasing disorder has been recently reported for vacancy-type defects but no analogue experimental work has been done on graphene with other types of defects. Here we study the Raman spectrum of a large amount of defective graphene samples, where different type and amount of defects have been introduced. The sp$^3$-defects were introduced by fluorination and mild oxidation and compared to vacancy-like defects produced by Ar$^+$-bombardment. Pristine defective graphene produced by anodic bonding were also analyzed. Note that little is known about defects produced by this method.

We will show that the evolution of the Raman spectrum for increasing disorder depends on the type of defect and this is reflected in the defect-activated Raman intensities. In particular, our results clearly show that the intensity ratio between the D and D' peak is able to probe the nature of the defects for moderate amount of disorder. We then applied our new finding to defective graphene produced by anodic bonding; we found that these samples mainly contain vacancy-like defects. Thus, defective graphene produced by anodic bonding is very different from graphene’s chemical derivatives obtained by partial fluorination or oxidation. This has been further confirmed by using atomic force microscopy (AFM) in tapping and conductive mode.

Chemical derivatives obtained by partial oxidization, hydrogenation, and fluorination of graphene were used to investigate sp$^3$-type defects. Pristine graphene samples were prepared by micromechanical exfoliation of single-crystal graphite flakes (Nacional de Graphite LTDA) on Si/SiO$_2$. The flakes were placed in a purpose-built chamber where they undergo an inductively coupled plasma at RF of 13.56 MHz. The plasma treatments were performed at a power of 10 W and a pressure of 0.1 Torr. The amount of defects was tuned by changing the treatment time (between 2 and 300 s). A controlled flow of oxygen, dihydrogen, and tetrafluoromethane inside the chamber enabled partial oxidation, hydrogenation, or fluorination of graphene, respectively. In addition, partial fluorination was realized on separate exfoliated flakes, using the technique described in ref 36. Exfoliated flakes with no initial D peak were used. Anodic bonding onto glass substrate was used to prepare pristine graphene with defects. The quality of such flakes depends on the deposition parameters; we purposely choose deposition parameters that yield flakes with high D peak.

Micro Raman measurements were performed with a confocal Witec spectrometer equipped with a 514.5 nm (2.41 eV) laser in backscattering configuration. We used a 100× objective giving a laser spot size of about 400 nm. The laser power was kept well below 1 mW to avoid damage or heating, which could induce desorption of the adatoms from graphene. The spectral resolution is ≃3 cm$^{-1}$. The spectrometer is equipped with a piezoelectric stage that allows Raman mapping of area up to $200 \times 200 \mu$m$^2$. Because of the inhomogeneity of the fluorinated and anodic-bonded flakes, we used Raman mapping to collect a large amount of spectra with different amount of disorder. The D, G, and 2D peaks are fitted with Lorentzian functions and the D' peak by a Fano line shape. Here, we refer to peak intensity as the height of the peaks and it will be denoted as I(D), I(G), I(D'), and I(2D) for the D, G, D', and 2D peaks, respectively.

We used AFM to further investigate the nature and morphology of defects. Tapping mode AFM was used to study anodic bonded samples, while conductive AFM was utilized to gather information on defects in fluorinated and oxidized graphene. Topography and current images were obtained with Atomic Force Microscope NanoScope Dimension V (Bruker) in contact mode with conductive Pt/Ir-coated cantilevers PPP-CONTPt (Nanosensors). This technique provides information on local conductivity and can be used to distinguish the patches of sp$^3$ carbon (typically insulating) within a perfect graphene matrix. Current was measured at fixed bias of 0.1 V applied to the tip via Keithley2400 source-meter. The fluorinated graphene substrate was grounded through 1 MΩ limiting resistor and the voltage drop across this resistor measured by 2184A Nanovoltmeter (Keithley) was measured as a function of tip position. Images were obtained in ambient conditions with scan rate 0.2 Hz and applied force of about 5 nN.

Figure 1a shows the Raman intensities measured on an oxidized graphene flake for increasing plasma treatment time. At short exposure time, that is, for small defect concentrations, I(G) is practically constant, while I(D) and I(D') strongly increase with exposure time. At a certain defect concentration, I(D) reaches a maximum and then starts decreasing. On the other side I(D') stays constant. Note that at high defect
concentration the D′ peak starts to merge with the G peak, so it is difficult to separate the individual contribution of the G and D′ peak. Our observations agree with the results reported for graphene and multilayer graphene bombarded with Ar+ ions.30–32 By using the same terminology introduced in disordered carbons,38 the authors of these works have shown that the ratio \( I(D)/I(G) \) follows a two-stage evolution. By introducing a typical length \( L_d \), representing the mean distance between two defects, they observed the following: (i) at low defect concentration, \( I(D)/I(G) \approx 1/L_d^2 \) (Stage 1); (ii) at high defect concentration, \( I(D)/I(G) \approx 1/L_d^2 \) (Stage 2). The transition between Stage 1 and 2 is usually observed at \( I(D)/I(G) \approx 3 \) at 2.41 eV (corresponding to \( L_d \approx 2-5 \) nm).25 In our case, the transition is observed at about 60 s, corresponding to \( I(D)/I(G) \approx 4 \) (at 2.41 eV). What exactly happens to the Raman intensities for \( L_d \approx 0 \) still remains an open question. Reference 32 proposes \( I(D)/I(G) \approx 0.8 \) for \( L_d \approx 0 \), while ref 31 claims that \( I(D)/I(G) \approx 0 \) for \( L_d \approx 0 \). They both analyzed samples with vacancies. In the case of sp³-defective graphene, for example, obtained by fluorination, the intensity of the D peak is never null, even in the most fluorinated samples.36 In this case, both the D and G peak intensities strongly decrease, so that the minimum \( I(D)/I(G) \) measured in stage 2 is \( \approx 0.8 \). This disagrees with the theory presented in refs 31 and 32, where the authors claim that this number should be dependent on the geometry of the defect. On the other side, in the highly disordered regime the defects should be so close to each other and so many that the information about the geometry of the single defect should be lost. Thus, this regime needs further investigation.

Note that in some cases the integrated area (A) is used as intensity. It is then interesting to compare the evolution of \( I \) and \( A \) for increasing disorder. Figure 1b shows that in Stage 1 both the Raman fit parameters follow the same evolution. Thus, in this range the use of integrated area or amplitude is equivalent. This has been already observed for the G and D peaks in ion bombarded graphene.39 A difference is observed only in stage 2 because the decrease in intensity is compensated by an increase in the fwhm.38 Here we show that this observation is also valid in the case of D′ type defects. Since our results mainly concern the low defect concentration range, in the following we will always refer to intensity as amplitude.

Figure 1b shows that there is a fundamental difference between the integrated intensity of defect-activated D and D′ peaks and the two-phonon Raman line (2D). The theory predicts the double-resonant peaks to be strongly sensitive to the dynamics of the photoexcited electron–hole pair,28 that is, to the scattering process it can undergo. In particular, any increase of defects will affect the electron lifetime, which translates in a decrease of the intensity. This is valid for D, D′, and 2D peaks. However, in the case of the D and D′ peaks, there is a further dependence: the D and D′ intensities are also directly proportional to the defects concentration \( n_d \).28 This gives rise to differences in the evolution of the Raman peak intensities; in Stage 1, the D and D′ peak intensity increase with increasing amounts of defects, while the 2D intensity stays almost constant. Thus, we expect D and D′ to be proportional to each other. In stage 2, the effect of the reduced electron lifetime dominates, so the integrated intensity of the peaks changes compared to Stage 1. Note that the D′ peak integrated intensity does not decrease as seen for the D peak, which is in contrast to what expected by the resonant theory. This leads to a more complicated relation between \( I(D) \) and \( I(D′) \), which are no longer proportional to each other as in Stage 1. On a microscopic picture, the intensity of the defect-activated peaks starts decreasing when the average length an electron/hole travels in between two scattering events with a defect becomes smaller than the average length an electron/hole couple travels before scattering with an optical phonon.30,31

Figure 2 shows two representative Raman spectra of a fluorinated flake and pristine defective graphene, obtained by anodic bonding. The difference between the two spectra is visible at first sight: both spectra show well visible D and D′ peaks and their combination mode (D+D′ peak). In both cases \( I(D)/I(G) \) is \( \approx 2.3 \) and the G peak fwhm \( \approx 24 \text{ cm}^{-1} \), that is, the two defective graphene samples belong to Stage 1. The D, G, 2D, and D+D′ peaks intensity almost perfectly match between the two spectra. In contrast, the D′ peak intensity is very different; fluorinated graphene has a higher \( I(D)/I(D′) \), compared to pristine defective graphene. Figure 2 suggests that \( I(D)/I(D′) \) could be used to identify the nature of defects. We then performed a systematic analysis of the Raman spectra of all our samples, by including also some data from literature: oxidized graphene from ref 40, ion-bombarded graphene from refs 30–32, and polycrystalline graphite from ref 41. Figure 3 plots \( I(D)/I(G) \) versus \( I(D′)/I(G) \) for all the samples. If we follow a disordering trajectory, that is, we move from Stage 1 to Stage 2, we can observe that in Stage 1 \( I(D)/I(G) \) and \( I(D′)/I(G) \) always increase. Taking into account that in this stage \( I(G) \) is constant, \( I(D′) \) is simply proportional to \( I(D) \), inset Figure 3, as expected. However, Figure 3 shows that the proportionality factor depends on the type of samples: all the sp³-type defective graphene (partially hydrogenated, fluorinated and oxidized graphene) share the same slope in the plot \( I(D)/I(G) \) versus \( I(D′)/I(G) \), that is, they have the same \( I(D)/I(D′) \). In contrast, defective graphene samples produced by ion-bombardment show a smaller \( I(D)/I(D′) \). Finally, polycrystalline graphite, where the defect is given by the grain boundaries, shows an even smaller \( I(D)/I(D′) \) (inset Figure 3).

Our results can be easily explained by following the resonant Raman theory: in Stage 1, \( I(D) \sim A_D n_d \) and \( I(D′) \sim B_D n_d \) where \( A_D \) and \( B_D \) are two constants, which both depend on the type of perturbation introduced by the defect in the crystal lattice, that is, they depend on the nature of the defect.25 Consequently, \( I(D)/I(D′) \sim A_D/B_D \) this parameter should not depend on the
defect concentration, but only on the type of defect. By fitting the data in Figure 3, we found that \( \frac{I(D)}{I(D')} \) is maximum (\( \approx 13 \)) for defects associated with sp\(^3\) hybridization, it decreases for vacancy-like defects (\( \approx 7 \)) and reaches a minimum for boundary-like defects in graphite (\( \approx 3.5 \)). This shows that \( \frac{I(D)}{I(D')} \) can be used to get information on the nature of defects. This makes Raman spectroscopy a powerful tool to fully characterize disorder in graphene.

Note that only a few works paid attention to the D’ peak.\(^{29,42} \) In general this peak is not much studied because of its relatively small intensity compared to the D peak; often the peak appears just as a small shoulder of the G peak. However, at moderate defect concentration, the D’ peak can be clearly distinguished from the G peak and it can have relatively large intensity (up to 1/3 of the intensity of the G peak). A few examples are provided in the Supporting Information.

It is now interesting to compare our results with recent ab initio calculations which simulate graphene with specific type of defects.\(^{29} \) In particular, the following three idealized defects have been simulated: (i) hopping defects, produced by the deformation of the carbon-bond; (ii) on-site defects, which describe out-of-plane atoms bonded to carbon atoms (namely sp\(^3\) hybridization); (iii) charged impurities, describing any charged atom or molecule adsorbed over the graphene sheet. These defects are not expected to give detectable D and D’ peaks.\(^{29} \)

The calculations show that in Stage 1 hopping defects should have \( \frac{I(D)}{I(D')} \sim 10.5 \), while on-site defects should be characterized by \( \frac{I(D)}{I(D')} \sim 1.3. \)^{29} Hopping defects should describe defective graphene containing vacancies, while on-site defects should describe sp\(^3\)-defective graphene. However, experimentally, we found not only different numbers, but also that \( \frac{I(D)}{I(D')} \) should be larger for hopping defects than on-site defects. The discrepancy between theory and experiments can be attributed to the idealized description of defects in the ab initio calculations. It is well-known, for example, that a real sp\(^3\)-defect cannot be described as a on-site defect only. This defect is expected to have both on-site and hopping components since the out-of-plane bonding with the atom also introduces distortions in the crystal lattice.\(^{36,43} \) Furthermore, this type of defect is usually not isolated (as assumed in the ab initio calculations), but it appears in form of dimers or clusters.\(^{44} \)

In Stage 2, the Raman fit parameters do not show a clear dependence on the type of defect. This is probably because the defect concentration is so high that any information about the nature of the defect is lost. Note that the exact transition between Stage 1 and 2 seems to slightly change with the type of defect: the higher \( \frac{I(D)}{I(D')} \), the higher \( \frac{I(D)}{I(G)} \) at which the transition from stage 1 to stage 2 is observed. This agrees with the theory of ref 29, where “less damaging” defects should have higher “critical” defect concentration, at which the D line intensity starts to decrease. This could explain why Stage 2 cannot be achieved by grain boundaries in graphite.\(^{50,51} \)

Interestingly, Figure 3 also shows that pristine-defective graphene produced by anodic bonding have the same \( \frac{I(D)}{I(D')} \) of ion-bombarded graphene. This should indicate the presence of vacancy-like defects in these samples. Thus, we do expect to see different defects in partially fluorinated graphene and defective graphene produced by anodic bonding. Therefore, we investigated topography and conductive AFM images of these two type of samples.

Figure 4a,b shows two AFM topography images of defective graphene produced by anodic bonding. Figure 4a evidences the presence of holes distributed in a random pattern. The typical size of the holes is found to be \( \approx 80 \) nm, as can be seen in Figure 4b.

Figure 3. \( \frac{I(D)}{I(G)} \) versus ratio \( \frac{I(D')}{I(G)} \). Data from literature (open symbols) have been included: ion bombarded graphene,\(^{30,31} \) oxidized graphene\(^{30,42} \) and graphite with different grain sizes.\(^{41} \) The dotted lines are only a guide for the eyes. The inset shows the linear dependence between the two parameters at low defect concentration, giving different \( \frac{I(D)}{I(D')} \) for different type of defects.
Figure 4c,d shows topography and conductive AFM images, respectively, taken on partially fluorinated graphene. The current scale shows the variation of the current compared to an average current value obtained from the whole scan. The dark spots correspond to low conductivity areas while the bright spots show high conductivity.

Figure 4. (a,b) Topography AFM images of pristine defective graphene produced by anodic bonding. (c) Topography and (d) conductive AFM image on the same area of a fluorinated flake. The current measured between the conductive AFM tip and the contacted graphene sample deposited on an insulating substrate clearly indicates the presence of regions with lower conductivity (dark spots in Figure 4d). Several scans taken on the same area revealed that the pattern was reproducible (Figure S3, Supporting Information). This observation rules out noise as the cause of conductivity variations. Comparison with the topography scan of the same area (Figure 4c) showed no strong correlation between height and conductivity. Thus, the low-conductivity “patches” can be attributed to fluorinated clusters. The typical size of the sp² clusters were ≃20–30 nm. The nonzero conductivity of the fluorinated clusters can be accounted for by their small size compared to the size of the tip and probably by the presence of tunneling current. The AFM analysis shows that defective graphene produced by anodic bonding is characterized by the presence of holes with sizes typically below 100 nm, while fluorinated graphene exhibits sp² clusters of 20–30 nm in size.

To conclude, this work offers a detailed analysis of the Raman peak intensities in defective graphene. By comparing samples with different amounts and type of defects, we have shown that I(D)/I(D') can be used experimentally to get information on the nature of defects in graphene. This makes Raman Spectroscopy a powerful tool to fully characterize disorder in graphene.

**ASSOCIATED CONTENT**

Supporting Information: Further measurements by conductive AFM and Raman spectra with corresponding fit lines of graphene containing different amount and type of defects. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Supporting Information

Figure S1 – Examples of two fits (in green) realized on the same spectrum (in red) with a) 3 Lorentzians line-shape and b) 2 Lorentzians and 1 Fano line-shape for the D’ peak. c) Results of the fits for the D, G and D’ peaks. We can observe that the Fano-line gives better fit for the D’ peak. However, the peak intensity is the same.

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Figure S2 – Examples of three fits (green) realized on the three representative spectra (red) with different defect concentrations at a), b) Stage 1 (I(D)/I(G)=0.9, I(D)/I(D')=15), (I(D)/I(G)=4.5, I(D)/I(D')=11) respectively and c) at the beginning of Stage 2 (I(D)/I(G)=4.0, I(D)/I(D')=4.9).
Fig. S3 – Several images of partially fluorinated graphene, obtained sequentially: topography (top row) and current maps (bottom row). The thermal drift causes the images to be slightly shifted. These images show the same features, thus excluding contributions of electrical or mechanical noise to the fine structure visible in the current maps. The scale bars are the same as on Figure 4.c and 4.d, respectively.
6.2 A Raman study on defective graphene: effect of the excitation energy, type and amount of defects

My contribution

I produced most of the samples, took most of the Raman measurements, analyzed the data, prepared all the figures and wrote the manuscript.
A Raman study on defective graphene: effect of the excitation energy, type and amount of defects

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We present a detailed Raman study of defective graphene samples containing specific types of defects. In particular, we compared sp³-sites, vacancies and substitutional Boron atoms. We find that the ratio between the D and G peak intensities, I(D)/I(G), does not depend on the geometry of the defect (within the Raman spectrometer resolution). In contrast, in the limit of low defect concentration, the ratio between the D and G peak intensities is higher for vacancies than sp³-sites.

By using the local activation model, we attribute this difference to the term C_S, representing the Raman cross section of I(x)/I(G) associated to the distortion of the crystal lattice after defect introduction per unit of damaged area, where x= D or D'. For the defects considered in this study we observed that C_SD = 0, while C_SD' of vacancies is 2.5 times larger than C_SD of sp³-sites. This makes I(D)/I(D') strongly sensitive to the nature of the defect. We also show that the exact dependence of I(D)/I(D') on the excitation energy may be affected by the nature of the defect.

These results can be used to obtain further insights into the Raman scattering process (in particular for the D' peak) in order to improve our understanding and modeling of defects in graphene.

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Keywords: Raman Spectroscopy, graphene, defects, implantation, doping

I. INTRODUCTION

Graphene has attracted enormous interest because of its unique properties.¹-³ Near-ballistic transport at room temperature and high mobility⁴,⁵,⁸ make it a potential material for nanoelectronics.⁶,⁹,¹³ Furthermore, its optical and mechanical properties, combined to its high charge mobility, allows the use of this material for other applications, such as thin-film transistors, transparent and conductive composites and electrodes, and optoelectronics.¹⁴-²¹

Graphene is usually considered as a perfect honeycomb crystal. However, real samples may contain defects: the amount and nature of defects strongly depend on the production method and may change from sample to sample.¹⁶,²²-³⁰ Defects can also be introduced in pristine graphene through ion bombardment,³¹-³⁶ e-beam irradiation,³⁷,³⁸ soft X-ray irradiation,³⁹ covalent modification,⁴⁰-⁵³ and implantation of substitutional atoms.⁵⁴-⁵⁷ The possibility of introducing only well defined defects and carefully control their amount allows fine tuning of the properties of graphene: defects lines can be used as metallic wire inter-connectors for nanoelectronics,⁵⁸,⁵⁹ while sp³-sites defects can be used to turn the electronic properties of graphene from metallic to insulating, leading to the creation of stoichiometric graphene-based derivatives.⁶⁰,⁶¹ These can be easily obtained by exposing the crystal to a plasma. This method is very attractive for industrial applications because it is a simple, fast and scalable process. Depending on the plasma gas used, various species such as oxygen, fluorine, nitrogen and chlorine can be grafted at the graphene scaffold. The bonding with the out-of-plane atom changes the carbon hybridization from sp² to sp³, leading to a change in the electronic and optical properties.⁶²,⁶³

Raman Spectroscopy is a fast and non-destructive technique for investigating the properties of graphene.⁶⁴-⁶⁶ This is able to identify graphene from graphite and few-layer graphene,⁶⁷ and to probe doping level,⁶⁸,⁶⁹ strain,⁵⁸,⁶⁹,⁷⁰,⁷¹ disorder,⁵⁸,⁶⁹ chemical derivatives,⁷²-⁷⁴ and the atomic arrangement at the edges.⁷²-⁷⁵

Due to its sensitivity to defects, Raman spectroscopy has been used since the '70s to study disorder in carbon-based materials, from nano-crystalline graphite (nc-G),⁷⁴-⁸² to disordered carbons⁸³-⁸⁵ and to carbon nanotubes.⁸⁶-⁸⁸ These works provided important advances in understanding disorder in sp²-bonded carbon materials and they strongly contributed to the widespread use of Raman spectroscopy for general characterization of these samples. However, the correlation between defect-activated Raman features and geometry of defects is still missing. We do not know if Raman spectroscopy is sensitive to every type of defect, i.e. if and how the disorder-activated Raman intensities depend on the nature of the defects. For instance, Raman spectroscopy could be more sensitive to certain defects rather than others. If so, then a Raman spectrum without a D peak would not be necessarily associated with a defect-free material.

To answer these questions, one needs to be able to carefully introduce defects in the material and control their nature, in order to compare the corresponding Raman spectra. In the case of a 3-Dimensional (3-D) material such as graphite, this is extremely challenging; the only defect that can be carefully controlled is the grain boundary, which depends on the size of the crystalline grains. Other 3-D materials such as disordered carbons...
do not appear as ideal material for this kind of study because they contain different types of defects: here, disorder is associated not only to the sp$^3$ sites, but also to the different types of sp$^2$ configuration and amount of sp$^2$ clustering.\textsuperscript{83–85} In general, these types of disorder are not correlated with each other (e.g., two disordered carbons films may have the same sp$^3$ content, but different degree of sp$^2$ clustering) and they strongly depend on the deposition conditions.\textsuperscript{83–85} This makes the Raman spectrum of disordered carbon rather difficult to analyze and correlate with the specific nature of disorder. Moving to low-dimensional carbon forms, nanotubes are difficult to manipulate and characterize, due to their 1-D nature. In contrast, graphene is an ideal material to study the Raman sensitivity to defects because its 2-D nature makes it easy to add, remove or move carbon atoms, i.e., to carefully introduce only specific type of disorder.

Here we present a detailed analysis of the evolution of the Raman spectra of graphene samples containing specific defects, such as sp$^2$ sites, substitutional atoms and vacancies. We show that the general trend of the Raman spectrum of defective graphene does not depend on the nature of defects: a two-stage disordering evolution is always observed, no matter the geometry of the defect. In each stage the Raman fit parameters have a different dependence on the excitation energy. By comparing the Raman spectra of graphene containing sp$^3$ sites, substitutional atoms and vacancies, we found that in the limit of small defect concentration the D peak is not sensitive to the defect geometry, but only to the amount of disorder (at least within the Raman resolution and for the type of defects studied here). In contrast, the D’ peak shows a strong dependence on the type of defect introduced in the lattice, e.g., the D’ peak intensity is higher for vacancies than sp$^3$ sites. Within the local activation model,\textsuperscript{33} we attribute this to the term $C_S$, representing the Raman cross section of $I(x)/I(G)$ associated to the distortion of the crystal lattice after defect introduction per unit of damaged area, where $x = \text{D or D’}$. Thus, this parameter is expected to strongly depend on the nature of the defect.\textsuperscript{33} We found that for the D peak $C_S \sim 0$, no matter the nature of the defect; while for the D’ peak, $C_S = 0.33$ for sp$^3$ sites, and $C_S = 0.82$ for vacancies. This makes the D’ peak more sensitive to vacancies than sp$^3$ sites.

This paper is organized as follows: Section II presents the Raman scattering background, while Section III describes the experiential setup and the sample preparation. Section IV shows the evolution of the Raman spectrum with the amount of defects, its dependence on the excitation energy and on the nature of defects.

II. BACKGROUND

The Raman spectrum of graphene is composed of two main features, the G and the 2D peaks, which lay at around 1580 and 2680 cm$^{-1}$, respectively, when taken at an excitation energy of 2.4 eV (514 nm).\textsuperscript{64} The G peak corresponds to the $E_{2g}$ phonon at the Brillouin Zone (BZ) center ($\Gamma$ point).\textsuperscript{74} The 2D peak is an overtone peak, associated to the breathing modes of six-atom rings.\textsuperscript{64} It comes from TO phonons in the vicinity of the K point\textsuperscript{74} and it is activated by a resonant intervalley scattering process.\textsuperscript{89,90}

Raman spectroscopy is able to probe defects in graphitic materials because, in addition to the G and 2D peaks that always satisfy the Raman selection rule,\textsuperscript{91} the otherwise forbidden D and D’ band appear.\textsuperscript{74,78} They correspond to single phonon intervalley and intravalley scattering events, respectively, where the defect provides the missing momentum in order to satisfy momentum conservation during the Raman scattering process.\textsuperscript{89,90,92} Another (weak) defect-activated peak is observed at about 3000 cm$^{-1}$, corresponding to the combination mode of the D and D’ mode. It is therefore called D+D’ peak.

The activation mechanism of the defect-activated features, their overtones and combination modes involve resonant electronic transitions.\textsuperscript{89,90,92} Hence the frequency of these peaks are intimately correlated to the electronic band structure making the peaks dispersive with the excitation energy.\textsuperscript{80,89,93,94}

Previous works on defective graphene introduced the local activation model in order to explain the evolution of the Raman spectrum for increasing amount of defects.\textsuperscript{31–33} Within this model the intensity of any defect activated peak $I(x)$, where $x = \text{D or D’}$, as compared to the G peak intensity $I(G)$, is given by\textsuperscript{33}:

$$I(x) \approx \frac{I(x)}{I(G)} = C_A \left( \frac{r_A^2 - r_S^2}{r_A^2 - 2r_S^2} \right) \left[ e^{-\pi r_S^2/L_2^2} - e^{-\pi (r_A^2 - r_S^2)/L_2^2} \right] + C_S \left[ 1 - e^{-\pi r_S^2/L_2^2} \right].$$

(1)

This equation shows that the intensity of the defect-activated peak depends on two length scales, $r_S$ and $r_A$, which are the radii of two circular areas measured from the defect site. The first length, $r_S$, is the radius of the structurally disordered area around the defect, so it is expected to change from defect to defect.\textsuperscript{33} For distances larger than $r_S$ but shorter than $r_A$, the lattice structure is preserved, but the proximity to a defect causes a mixing of Bloch states near the K and K’ valleys of the graphene Brillouin zone, thus causing a breaking of selection rules, and leading to an enhancement of the D band.\textsuperscript{31,33} $r_A$ defines the disc where the D peak scattering takes place and it defines the activated area.\textsuperscript{33} From a microscopic point of view, an electron/hole excitation will only be able to “see” the structural defect if it is created sufficiently close to it and if the excited electron (or hole) lives long enough for the defective region to be probed by Raman spectroscopy.\textsuperscript{31,33} Therefore, the distance $r_A - r_S = l_z$ represents the length traveled over the lifetime of the electron-hole pair, roughly given by $v_F/\omega_F$, where $v_F$ is the graphene Fermi velocity and $\omega_F$...
is the peak frequency of either the D or D' peak.\textsuperscript{31,33} 

$C_A$ depends only on the Raman mode, being roughly given by the ratio between the electron-phonon coupling between the two phonons considered.\textsuperscript{31,33} $C_S$ is a factor assumed to depend only on the geometry of the defect for a fixed phonon mode.

Note that Eq. 1 can also be used for the intensity measured as integrated area. In any case, in the limit of low defect concentration, the use of intensity or integrated area is equivalent.\textsuperscript{31,34,71} Only in the high disorder regime it is more informative to decouple the peak intensity from the full width at half maximum.\textsuperscript{12}

There are also physical models based on first principles and quantum mechanics that calculate the intensities of the Raman resonant features. In particular, a recent work\textsuperscript{92} has been able to successfully reproduce numerous features of the Raman spectrum of graphene. We will then compare our experimental data with the results presented in Ref. 92, in particular for the dependence of the Raman features with the excitation energy and amount of defects. However, we will make use only of the activation model to explain the dependence of the Raman features on the geometry of the defects, since it has been shown\textsuperscript{71} that the simple on site and hopping perturbation used in Ref. 92 are not suitable to describe real defects such as sp\textsuperscript{3} sites.

### A. Dependence on the amount of defects

The only parameter that changes with defect concentration ($n_D$) in Eq. 1 is $L_D$, being $n_D = 10^{14}/\pi L_D^2$.\textsuperscript{32} This equation gives a non-monotonic evolution of $I(x)/I(G)$. This is the result of two competing mechanisms for the increase and decrease in the defect-activated bands. The increase in the activated area gives rise to an increase of the defect activated peak intensities; on the other side, an increase in the defect activated area produces a decrease of the intensities. Therefore, one can identify two stages, where one mechanism dominates the other.\textsuperscript{31,33} The transition from Stage 1 to Stage 2 is typically observed when the mean distance between two defects ($L_D$) is comparable to $L_x$.\textsuperscript{31} Note that the stage terminology was first introduced for disordered carbons.\textsuperscript{83–85}

Within the two-stage model, $C_S$ is the value of $I(x)/I(G)$ measured in the highly disordered limit.\textsuperscript{33} This is difficult to measure since both the D and D' peak intensities decreases in Stage 2 and the D' peak, being close to the G peak, merges with this peak.

If we now focus on Stage 1 (i.e. low defect concentration), the model shows that both the D and D' peak intensities increase with increasing amount of defects. In particular, in the limit of low defect concentration, a Taylor expansion of Eq. 1 to the first order gives:

$$
\frac{I(x)}{I(G)} = C_A \frac{\pi (r_A^2 - r_S^2)}{L_D^2} + C_S \frac{\pi r_S^2}{L_D^2} \tag{2}
$$

The defect concentration for this stage is then:

$$
n_D (\text{cm}^-2) = \frac{10^{14}}{\pi^2 [C_A (r_A^2 - r_S^2) + C_S r_S^2]} \frac{I(x)}{I(G)} \tag{3}
$$

### B. Dependence on the geometry of the defect

By looking at Eq. 2, the dependence of the peak intensities on the nature of the defects is given by $r_S$ and $C_S$, being $r_A = r_S + l_x$, where $l_x$ is fixed by the phonon mode and the excitation energy.

The only experimental works reporting data for those parameters are based on vacancies.\textsuperscript{31–33} In these works, the D peak was extensively studied. The following parameters were reported for intensity measured as height: $r_A \sim 3 \text{nm}$, $r_S \sim 1 \text{nm}$, $C_A = 4.2$. $C_S$ has been reported being 0 or 0.87 in Refs 32 and 33, respectively. Ref 32 claims that $C_S = 0$ for the ideal case where the defect is the breakdown of the C-C bonds. However, $C_S$ may be different for other type of defects such as sp\textsuperscript{3} sites, which do not break the network, but just produce a different arrangement of the carbon atoms. In any case, one should observe that the term $C_S$ has a minor influence in Stage 1, in particular in the limit of very low defect concentration. A change in $C_S$ from 0 to 0.87 produce variations well smaller than 10% on $I(D)/I(G)$ at the beginning of Stage 1. Therefore, if we focus on the low defect concentration regime, it is correct to assume $C_S \sim 0$, so Eq. 2 becomes:

$$
\frac{I(D)}{I(G)} \simeq \frac{\pi C_A (r_A^2 - r_S^2)}{L_D^2} \tag{4}
$$

which shows that the only dependence on the defect geometry for the D peak is given by $r_S$.

In this work, we analyze sp\textsuperscript{3} sites, vacancies and implanted atoms, so we do not expect $r_S$ to strongly change with the type of defect. Consequently, we expect the D intensity not to be able to probe differences in the geometry of the defects here analyzed: the Raman spectrometer is not enough sensitive (the typical error bar on a Raman intensity ratio is 10-15%). Thus, we will use Eq. 1 to find the defect concentration from $I(D)/I(G)$.

In the case of the D' peak, its intensity follows qualitatively the same behavior of the D peak, i.e. it increases in Stage 1 and decreases in Stage 2. However, the exact dependence on defect concentration is different.\textsuperscript{71} Indeed Ref. 31 shows that $C_S$ cannot be neglected for the D' peak, and that small variations on $C_S$ can produce strong changes in $I(D')/I(G)$, even at low defect concentrations.

In this work we aim at comparing the results obtained for vacancies with other type of defects, such as Boron substitutional atoms and sp\textsuperscript{3} sites. In particular, we will investigate the intensity dependence of the D and D' peak on the parameter $C_S$, which we will refer to as $C_{S,D}$ and $C_{S,D'}$, respectively.
III. EXPERIMENTAL METHOD

We studied three types of defects in graphene:

i) sp³ defects. Pristine graphene samples were prepared by micro-mechanical exfoliation of single-crystal graphite flakes (Nacional de Graphite LTDA) on Si/SiO₂ substrates. The flakes were then placed in a purpose-built chamber, where they underwent an inductively coupled plasma at RF of 13.56 MHz.² Defects were introduced by exposing pristine graphene to a mild O2 and CF₄ plasma.Δ The plasma treatments were performed at a power of 10 W and a pressure of 0.1 Torr. The amount of defects was tuned by changing the treatment time (between 5 s and 300 s). More details of the process are described in Refs 42. In addition, we fluorinated some exfoliated flakes by using the technique described in Refs 41. In all cases, chemical modification was performed on pristine samples with no detectable D peak.

ii) vacancy-like defects: the samples were produced by anodic bonding, as reported in Refs 24,71. We also used the results reported in Ref 31–33, where graphene was exposed to Ar⁺ ion bombardment.

iii) substitutional atoms: we used B-doped graphene samples, as reported in Ref 54.

In the following discussion, we will group our data based on the nature of defects, so we will refer as “vacancies” the data obtained by anodic bonding and ion bombardment, while we will refer as “sp³” the data obtained for oxidized and fluorinated samples. The nature of the defects in these samples have been verified in Refs 33,42,71.

Raman measurements were performed in backscattering configuration with a confocal WITec spectrometer equipped with 2.54 eV, 2.41 eV and 1.96 eV laser lines. The WITec spectrometer is also equipped with a piezoelectric stage that allows Raman mapping of areas up to 200 × 200 µm². Because of the inhomogeneity of the fluorinated and anodic bonded flakes, we used Raman mapping to collect a large amount of spectra with varying I(D)/I(G) ratios, typically between 0.5 to 4. Multi-wavelength analysis was performed with a Dilor triple-monochromator Raman spectrometer, equipped with an Ar-Kr laser with excitation lines between 647 and 457 nm. In all cases we used a 100x objective giving a laser spot size of about 400 nm. The laser power was kept well below 1mW to avoid damage or heating, which could induce desorption of the adatoms from graphene. The spectral resolution was ∼2 cm⁻¹. The D, G and 2D peaks were fitted with Lorentzian functions and the D’ peak by a Fano line-shape. A Fano line-shape was indeed preferred to a Lorentzian because for a defect concentration close to the transition between Stage 1 and Stage 2 and beyond this point, the G and the D’ peak start to merge. This does not allow using a fully symmetric line for fitting the G peak. In any case, the use of Fano or Lorentzian line does not change the results relying on the peaks’ amplitude as the peak height is the same for the two lines. We analyze the following Raman fit parameters: Position (POS) and Full Width at Half Maximum (FWHM), and intensities. Here, we refer to peak intensity as the height of the peaks and it will be denoted as I(D), I(G), I(D’), I(2D) for the D, G, D’ and 2D peaks, respectively. The integrated areas will be labeled A(D), A(G), A(D’) and A(2D).

Note that the D’ peak has a small intensity compared to the D peak; often the peak appears just as a small shoulder of the G peak. However, at low and moderate defect concentration, the D’ peak can be clearly distinguished from the G peak and it can have relatively large intensity (up to 1/3 of the intensity of the G peak).

IV. RESULTS AND DISCUSSION

A. Evolution of the Raman spectrum with the amount of defects

Let us start by looking at the evolution of the Raman spectrum of graphene for several types of defective graphene with increasing defect concentration.

Figures 1a and b show a collection of first and second order Raman spectra, measured at 2.41 eV of graphene containing sp³ sites obtained by partial fluorination (a) and oxidation (b). Figures 1c shows a collection of first and second order Raman spectra for increasing defect concentration (from bottom to top), measured at 2.41 eV of graphene with vacancy-like defects obtained by anodic bonding as described in Ref 24.

The defect-activated features (D, D’ and D+D’ peaks) appear in all the spectra. Qualitatively, one can see that as the defect concentration increases, the D peak increases at first and then decreases while broadening. The D’ peak increases and eventually merges with the G peak and the 2D peak monotonously decreases until it almost disappears. The D+D’ peak increases in intensity and broadens. The same general evolution is observed in ion-bombarded graphene.³¹–³⁴ In the following discussion, we will group our data based on the nature of defects, thus we will refer as vacancies to the data obtained by anodic bonding and ion bombardment, while we will refer as “sp³ sites” to the data obtained for oxidized and fluorinated samples. The defects in these samples have been verified in Refs 33,42,71.

Figure 2 shows the evolution of the Raman fit parameters against exposure time for the oxidized samples. Although we do not know the exact relation between plasma exposure time and defect concentration, we expect the amount of defects to increase for increasing time.

If we focus on the D peak intensity (Figure 2.a (top)), we can clearly see a two-stage evolution: at low defect concentration (between 0 and 40s), I(D) and I(D’) increase for increasing time. This corresponds to Stage 1. In contrast, I(G) and I(2D) show very little variation. At higher defect concentration (between 40 and 300s), I(D) decreases with time. This corresponds to Stage 2. Furthermore, I(G) decreases, but more slowly than I(D)
FIG. 1: Representative spectra of: a) fluorinated graphene, b) oxidized graphene and c) anodic bonded graphene, with increasing defect concentrations (from bottom to top). All measurements are taken at 2.41 eV.

and I(2D) strongly decreases. The transition between the two stages corresponds to the maximum I(D)/I(G) (~5). This two-stage evolution agrees with the experimental results obtained in vacancy-defective graphene.\textsuperscript{31–33}

A two-stage evolution is also visible when looking at the peaks’ FWHM (Figure 2a (bottom)). In Stage 1, the FWHM of all peaks remains constant, while it strongly increases in Stage 2. The FWHM of any peak can consequently be used to distinguish between the two stages. Conclusions drawn about the defect concentration when only considering the ratio I(D)/I(G) is indeed ambiguous since a given D peak intensity (or I(D)/I(G) ratio) may correspond to two different defect concentrations.

The introduction of disorder also changes the peak positions, as shown in Figure 2b (top). In order to better visualize these changes, we plotted the shift of the position with respect to the positions measured on the pristine graphene, Figure 2b (bottom). This figure shows that the D, D', and 2D peak positions down-shift for increasing defects concentration, where Pos(2D) experiences the largest shift, (well above 15 cm\(^{-1}\) at 300s). In contrast, the G peak shifts to higher wave numbers, up to 10 cm\(^{-1}\) at 300s. We expect the G peak to shift with disorder: this effect is well reported for disordered carbons.\textsuperscript{83–85} Changes in the G peak position occur because the introduction of defects relaxes the Raman selection rule (q ~ 0). Due to the Kohn anomaly,\textsuperscript{95} the phonon energy strongly increases with the phonon wave vector, resulting in a blue-shift of the G peak position for increasing disorder in the hexagonal rings. Note that at 300s, the D' and the G peak have merged, so the uncertainty related to the fit is large. The down-shift of both the D and 2D peaks is assigned to the TO phonon dispersion branch in the vicinity of the K point while Pos(D') decreases due to the LO phonon branch dispersion near
Γ.31 These observations agree with the results from Refs 31,47.

It is now interesting to compare the disordering trajectory of the Raman spectrum in disordered graphene and disordered carbons, i.e. to compare disorder in 2-D and 3-D carbon-based materials.

Figure 3 plots the ratio A(D)/A(G) against FWHM(G). This allows to decouple the amount of defective hexagonal rings from the overall disorder.85 Indeed, the FWHM always increases for increasing disorder because this parameter is sensitive to all types of defects, either in the sp² rings or chains; in contrast, A(D)/A(G) is sensitive only to defects in the rings. Note that we decided to plot the ratio A(D)/A(G) because it allows comparison of a large sets of data available in literature, which are reported in area only.

The 2-D materials group includes fluorinated graphene (defect = sp³ site), ion bombarded graphene (defect = vacancies),31 and graphene oxide (GO) and reduced graphene oxide (rGO).27,28,96,97 These last two materials have been selected because in contrast to hydrogenated and fluorinated graphene which contain only sp³ sites, GO and rGO contain different type of defects, whose nature and corresponding amount is not completely known. From this point of view, GO and rGO can be seen as the 2-D equivalent of disordered carbons. For the 3-D materials group, we used the data reported for disordered carbons in Ref 85.

Figure 3 shows that both 2-D and 3-D disordered materials have a similar "bell-like" disordering trajectory, in agreement with the two-stage evolution described in Section II. However, disordered carbon materials extends into a third stage (for FWHM(G) > 200 cm⁻¹), which corresponds to the conversion of the rings into sp² chains.83–85 It does not seem to happen for graphene, even in highly fluorinated samples, so the defects may stretch the rings but do not open them into chains. In the following discussion, we will use Eq. 1 to calculate the defect concentration from I(D)/I(G) for all defective 2-D samples based on the fact that they observe the same disordering trajectory, as seen in Figure 3.

In conclusion, we have observed a similar two-stage evolution of the Raman fit parameters for graphene containing vacancy and sp³ sites. Neither the position nor the FWHM of the peaks are strongly sensitive to the type of defects.

B. Multi-wavelength Raman analysis

The previous analysis was performed at a fixed wavelength of 2.4 eV. We now extend the analysis to other excitation lines in the visible range. We select two oxidized graphene samples with two different defect concentrations: one sample shows I(D)/I(G) = 4 and FWHM(G) = 20 cm⁻¹ at 2.4 eV, it therefore belongs to the onset of the stage transition but still in Stage 1, while the other sample shows I(D)/I(G) = 2.5 and FWHM(G) = 43 cm⁻¹ at 2.4 eV. Thus, it is representative of Stage 2. Figures 4, 5, and 6 compare the evolution of several Raman fit parameters of these two stage-reference samples.

Figure 4 shows that at Stage 1, FWHM(D), FWHM(2D) and FWHM(G) do not significantly change with excitation energy. However, at Stage 2, the FWHM of the first and second order D peak strongly decrease with increasing excitation energy at a rate of -18 and -43 cm⁻¹/eV for the D and the 2D peak, respectively. In contrast, FWHM(G) is constant in Stage 2. For any of the three peaks the FWHM in Stage 2 is larger than the FWHM in Stage 1, as already shown in Figure 2a. In comparison, Ref 32 reported -20 cm⁻¹/eV and -53 cm⁻¹/eV for the D and the 2D peak, respectively, for a Stage 2 ion bombarded sample. The same behaviour has been observed also for the D peak of disordered carbons,83–85 and it has been attributed to the resonant mechanism in presence of a broad distribution of defects,83–85: by changing the excitation line we will be resonant to different defects. This is possible only in stage 2, where the hexagonal crystal lattice becomes strongly deformed, i.e. can be seen as a disordered network containing small graphitic islands of different size. Thus, attention to the laser line must be paid when comparing the FWHM of the peaks measured at Stage 2.

Figure 5 shows the dispersion of the D, 2D and D’ peaks. This is caused by the combination of the resonant scattering mechanism and the Kohn anomaly close to the K point.89,95 The slopes obtained for the D peak is 48 cm⁻¹/eV and 50 cm⁻¹/eV for Stage 1 and 2, respectively. For the 2D peak, we found a slightly different slope between the two stages: 101 cm⁻¹/eV and 112 cm⁻¹/eV, for Stage 1 and 2, respectively. These slopes for the D and the 2D peaks for both Stage 1 and 2 are similar to reported values.92,98 The red shift of both the D and 2D
an E\(^{-4}\)L relation, while the red line is a linear fit. Due to the confinement of ordered sp\(^{2}\) regions whose size

peaks in stage 2 has been observed and attributed to changes in the phonon dispersion and the band structure of graphene\(^{199,100}\) until a band gap eventually opens up as expected for both hydrogenated or oxidised graphene.

The D’ peak also shows dispersion with the laser excitation, but its dependence is weaker compared to the D peak, as previously observed\(^{92,101}\). We do not show the position of the D’ peak at Stage 2 because here the G and the D’ peaks merge and their positions are therefore not reliable.

Figure 6 compares the dependence of the ratio I(D)/I(G) with excitation energy. I(D)/I(G) strongly depends on the excitation energy for both stages. In Stage 1, since I(G) is constant, the increase of I(D)/I(G) with the excitation energy \(E_L\) has to be attributed to I(D) only. In the model used in Refs 31–33 to describe defects obtained by ion bombardment, I(D)/I(G) was found to be proportional to \(E_L^{-4}\) for Stage 1. The same trend is observed here with oxidised graphene and I(D)/I(G) could be fitted well with the same equation. However, the evolution of I(D)/I(G) for Stage 2 is different: this parameter depends linearly on the excitation energy. The breakdown of the \(E_L^{-4}\) dependence at high defect concentration has already been shown in Ref 47. This is due to the confinement of ordered sp\(^{2}\) regions whose size

FIG. 4: Evolution of the FWHM of the a) D peak, b) 2D peak, c) G peak versus excitation energy for stage 1 and 2 samples. The solid lines are fits of the experimental data.

FIG. 5: Evolution of the Position of the a) D peak, b) 2D peak, c) D’ peak versus excitation energy for stage 1 and 2 samples. The solid lines are linear fits of the experimental data.

FIG. 6: Evolution of the intensity ratio I(D)/I(G) versus excitation energy for stage 1 and 2 samples. The black line is a fit following an \(E_L^{-4}\) relation, while the red line is a linear fit.
become comparable to the average distance an electron hole travels before being scattered by a phonon. The same behaviour was observed in graphitic foams in the same energy range. Our linear fit gives a slope of \(-0.27eV^{-1}\), which is in excellent agreement with the result \((-0.31eV^{-1})\) obtained in Ref 102. The same behaviour was observed for fluorinated graphene samples.

To summarize, we have shown that FWHM and relative intensities have a different behaviour with excitation energies depending on the disordering stage. Furthermore, the \(E_L^{A}\) dependence for \(I(D)/I(G)\) in Stage 1 is the same both for graphene with vacancies or \(sp^3\) sites.

C. Dependence on the nature of defects

We now compare the dependence on the defect concentration of the Raman intensities of two different types of defective graphene in Stage 1, one containing \(sp^3\) sites, and the other with vacancies, Figure 7. In this case, we also added the calculation from Ref 92, which only reports the Raman intensities as integrated area.

In the previous Section we have shown that it is possible to extend the use of Eq. 1 to all the type of defects analyzed in this work. Thus, in the following discussion, we report the defect concentration as calculated from \(I(D)/I(G)\) by using Eq. 1.

Figure 7 shows an overall good agreement between the calculations and the experimental data: \(A(D)\) increases with defect concentration, while \(A(2D)\) decreases due to the increasing of the electron-defect scattering rate.\(^{30,92}\)

It is striking to observe that within the Raman resolution, the disordering trajectory for the 2D and the D peak areas for \(sp^3\) sites and for vacancies overlap quite well, further suggesting that the Raman spectrometer is not sensitive enough to probe small changes in \(r_s\), at least for the type of defects here analyzed. Therefore, \(I(D)/I(G)\) can be used to derive the amount of disorder (Eq. 1), but it cannot provide any additional information on defects.

As highlighted in Section II, the data of Ref 31 suggests for the D’ peak a stronger dependence on the geometry of the defects, as compared to the D peak, since \(C_{S,D'}\) cannot be neglected. Therefore, let us focus on the D’ peak in the limit of low defect concentration, where Eq. 2 is valid.

![FIG. 7: Evolution of the integrated area of the 2D and the D peaks as a function of the defect concentration for graphene flakes with either vacancies or \(sp^3\) sites. The solid lines are taken from the calculations of Ref 92.](image)

Figure 8 compares \(I(D')/I(G)\) as a function of \(L_D\) for our samples, containing \(sp^3\) sites, and the ones reported in Ref 31, which contain vacancies. This figure shows that for the same defect concentration, \(I(D')/I(G)\) is higher for vacancies than \(sp^3\) sites. The solid lines are fits obtained using Eq. 1. In the fit we took \(C_{A,D'}\) equal to the ratio between the electron phonon coupling between the D’ and the G peaks optical phonons.\(^{33}\) By using the GW electronic band structure of Ref. 92 and scaled the electronic gap at the M point to 4.6 eV obtained by Ref 103, we found that \(C_{A,D'} \sim 0.5\).

The fit for graphene samples containing vacancies gives: \(C_{S,D'} = 0.82\), \(r_{A,D'} = 2.6\) nm and \(r_{S,D'} = 1.4\) nm. Note that the values of \(r_{A,D'}\) nm and \(r_{S,D'}\) are in good agreement with the parameters found from the D peak intensity (Section II).

If we now move to \(sp^3\) sites, in order to find \(C_{S,D'}\) we fit the data with \(r_{A,D'} = 2.6\) nm and \(r_{S,D'} = 1.4\). We found \(C_{S,D'} = 0.33\). Thus, \(C_{S,D'}\) for vacancies is almost 3 times larger than \(C_{S,D'}\) for \(sp^3\) sites, i.e. the D’ peak is more sensitive to vacancies than \(sp^3\) sites.

In our previous work,\(^{71}\) we showed that the intensity ratio between the D and D’ peak can be used to identify the nature of defects at low defect concentration (\(n_D <\)}}
vacancies and \( \approx 13 \) for sp\(^3\) sites (measured at 2.41 eV). We will show now that this dependence is strictly related to \( C_{S,D'} \). By using Eq. 2, we have:

\[
\frac{I(D)}{I(G)} \approx \frac{\pi [C_{A,D}(r_{A,D}^2 - r_{S,D}^2)]}{L_D^2}
\]  \hspace{1cm} (5)

\[
\frac{I(D')}{I(G)} \approx \frac{\pi [C_{A,D'}(r_{A,D'}^2 - r_{S,D'}^2) + C_{S,D'}r_{S,D'}^2]}{L_D^2}
\]  \hspace{1cm} (6)

By dividing Eq. 5 for Eq. 6, we have:

\[
\frac{I(D)}{I(D')} \approx \frac{C_{A,D}(r_{A,D}^2 - r_{S,D}^2)}{C_{A,D'}(r_{A,D'}^2 - r_{S,D'}^2) + C_{S,D'}r_{S,D'}^2}
\]  \hspace{1cm} (7)

This shows that \( I(D)/I(D') \) strongly depends on \( C_{S,D'} \), making it sensitive to the geometry of the defect. Note that if \( C_{S,D'} = 0 \), then \( I(D)/I(D') \) would be constant within the Raman resolution, no matter the geometry of the defects, in contrast to the results presented in Ref. 71.

FIG. 9: Plot of \( I(D)/I(D') \) as a function of \( C_{S,D'} \) according to Eq. 7.

Figure 9 plots Eq. 7, obtained by plugging in the values obtained by Ref 33 for the D peak (\( r_{S,D} = 1 \) nm, \( r_{A,D} = 3 \) nm, \( C_{A,D} = 4.2 \)), and \( r_{S,D'} = 1.4 \) nm, \( r_{A,D'} = 2.6 \) nm for the D' peak. This plot shows that the higher \( C_{S,D'} \), the more sensitive is the D' intensity to the defect. From Figure 9 we found that: \( C_{S,D'} \approx 0.1 \) for sp\(^3\) sites and \( C_{S,D'} \approx 1.2 \) for vacancies, in relatively good agreement with the values obtained by fitting the data in Figure 8. Note that in the case of B-doped graphene, we found that \( I(D)/I(D') \approx 9 \), which gives \( C_{S,D'} \approx 0.68 \).

V. CONCLUSIONS

In conclusion, we have presented a detailed analysis of the Raman spectrum of defective graphene by focusing on the effect of the excitation energy, amount and type of defects. The overall evolution of the Raman spectrum for increasing disorder is similar to that one observed for...
disordered carbons, although a third stage has not been observed in the case of graphene. By comparing the Raman intensities measured for defective graphene samples containing specific defects, we observed that $I(D)/I(G)$ is not sensitive to the nature of the defects (at least within the spectrometer resolution and for the defects analyzed in this work). Thus, the relation between $I(D)/I(G)$ and defects concentration found for vacancies$^{31}$ can be extended to other defects. In contrast, $I(D')/I(G)$ shows a strong dependence on the type of defect. By using the local activation model, we attribute the different sensitivity of the D and D' peak to the nature of defects to the parameter $C_S$: this is negligible for the D peak, for any defect; in contrast, $C_S$ is not null for the D' peak, in particular this is larger for vacancies than sp$^3$ sites. This makes $I(D')/I(G)$ more sensitive to vacancies than sp$^3$ sites. As a consequence, the ratios $I(D)/I(D')$ or $I(D)/I(G)$ are especially useful to determine the type of defects at a given wavelength. Finally, we have shown that also the energy dependence of $I(D)/I(D')$ may be affected by the nature of the defects.

In conclusion, this work offers a full insight into the defect activated Raman scattering process, which will be useful to improve our understanding and modelling of defects in graphene.

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CHAPTER
SEVEN

SINGLE- AND DOUBLE-SIDED CHEMICAL FUNCTIONALIZATION OF BILAYER GRAPHENE

My contribution

I prepared some of the samples. In particular, I have made the suspended bilayer graphene for double-sided functionalization.
1. Introduction

Graphene and few-layer graphene have recently been proposed as one of the basic building blocks for future nano-electronics.\textsuperscript{[1]} The ultimate 2-dimensional character and the sp\textsuperscript{2} configuration of the carbon network indeed leads to exceptional electronic, mechanical, and optical properties.\textsuperscript{[2–5]}

An experimental study on the interaction between the top and bottom layer of a chemically functionalized graphene bilayer by mild oxygen plasma is reported. Structural, chemical, and electrical properties are monitored using Raman spectroscopy, transport measurements, conductive atomic force microscopy and X-ray photoelectron spectroscopy. Single- and double-sided chemical functionalization are found to give very different results: single-sided modified bilayers show relatively high mobility (200–600 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} at room temperature) and a stable structure with a limited amount of defects, even after long plasma treatment (>60 s). This is attributed to preferential modification and limited coverage of the top layer during plasma exposure, while the bottom layer remains almost unperturbed. This could eventually lead to decoupling between top and bottom layers. Double-sided chemical functionalization leads to a structure containing a high concentration of defects, very similar to graphene oxide. This opens the possibility to use plasma treatment not only for etching and patterning of graphene, but also to make heterostructures (through single-sided modification of bilayers) for sensors and transistors and new graphene-derivatives materials (through double-sided modification).
In order to develop graphene-based electronics, various approaches have been used to carefully tune and control the properties of graphene. In particular, chemical functionalization has been shown to be a facile and effective way for the modification of graphene. For example, chemisorption of hydrogen and fluorine has been reported. Depending on the amount of bonded hydrogen or fluorine, it is possible to carefully tune the electronic properties of graphene from metallic to insulating. Furthermore, by exposing both surfaces of a suspended graphene, it is possible to achieve full hydrogenation or fluorination, leading to the creation of stoichiometric graphene-based derivatives, called graphane and fluoro-graphene, respectively. Similarly to hydrogenation and fluorination, it has been shown that the covalent bonding with oxygen can induce a conversion of the carbon atoms from sp² to sp³ hybridization, which produces changes in the optical and electronic properties of graphene. The opening of a band gap, which should increase for increasing oxygen functionalization, has been predicted in such materials. Chemical modification of graphene can be easily obtained by exposing the material to a plasma. This method is very attractive for industrial applications because it is simple and fast scalable process. Depending on the plasma gas used, various species such as oxygen, fluorine, nitorgen and chlorine can be grafted to the graphene surface. In addition, plasma methods are already used for patterning and etching of graphene.

Whereas covalently modified monolayer graphene has been extensively studied in the literature, little is known about the possible tunability of the properties of bilayer graphene by chemical modification. Usually, bilayer graphene is shown to be less reactive than a single layer graphene sheet, i.e. its optical and electronic properties change slower than the ones of graphene exposed to the same conditions. For example, Dong et al. have modified bilayer graphene using bromophenyl groups derived from diazonium salts. They showed that bilayer has smaller reactivity compared to monolayer. However, they also evidenced that the modification was occurring only at defects sites. Because of it they were able to observe only slight p-doping and no change in the resistance. Plasma treatment, in contrast, is a very different process which allows fast and large modification of graphene and does not depend on the defect concentration. Nourbakhsh et al. compared experimentally and theoretically the plasma modification of mono- and bilayer graphene. Their calculations showed that oxidized bilayer graphene, unlike monolayer, retains its semimetallicity even at oxygen densities as high as 50%.

In the case of plasma treatment, modification strongly depends on the ion energy involved in the process. Nevertheless, under mild energetic conditions, it is normally assumed that chemical functionalization of graphite and few-layer graphene by oxygen plasma exposure happens layer by layer. In the case of a bilayer graphene, it is normally assumed that only the top layer would be chemically functionalized, while the bottom layer is unperturbed. This opens the possibility to use plasma treatment to protect graphene from the environment by passivating the top layer of a bilayer. This is particularly important in sensing devices, where the sensitivity of graphene to environmental conditions, such as doping and charge transfer, strongly affects the reliability of the device. In addition, chemical functionalization by oxygen plasma allows having epoxy and hydroxyl groups on the surface, which can be used to anchor chemical and biological objects to graphene. The possibility to produce an insulating layer on top of graphene could be further used to develop in-situ gate dielectrics in field-effect transistors and hetero-structures based transistors.

In this work we aim at studying the interaction between the top and bottom layer of a chemically functionalized bilayer graphene by mild oxygen plasma. We are challenging the suggestion that chemical functionalization by plasma happens layer-by-layer: in contrast to previous studies where a lack of data and statistics did not allow to give a clear picture of the evolution of the bi-layer under plasma treatment, structural, chemical and electronic properties are monitored at different stages of the plasma exposure by Raman spectroscopy, transport measurements, conductive AFM and X-ray photoelectron spectroscopy. For a better understanding, comparison between mono- and bilayer graphene is also shown. Our study reveals a peculiar behavior for one-sided chemically functionalized bilayer: while the monolayer becomes insulating upon increasing oxygen plasma exposure, the bilayer retains its ambipolar behavior with carrier mobility between 200–600 cm² V⁻¹ s⁻¹, even after long plasma treatment. We attribute this to the chemically functionalized graphene top-layer. In order to further confirm this result, double-sided chemical functionalization of bilayer has been performed: in the framework of the layer-by-layer functionalization, this process should allow chemisorption to take place on both layers. This material is very attractive because it is expected to have a four-layer structure such as dopant/carbon/carbon/dopant and an optical gap of 2.12 eV, in case of hydroxyl groups. Raman spectroscopy clearly shows that double-sided chemical functionalization leads to a strongly distorted structure, compared to single-sided functionalized bilayer, in agreement with the theoretical predictions of ref. 23.

2. Results and Discussion

Figure 1a,b shows optical micrographs of a mono- and a bilayer graphene flakes in a 2-probe device configuration with source-drain electrodes separated by 4 μm. The number of layers has been determined by optical contrast and Raman spectroscopy. Both flakes were mechanically exfoliated on the same SiO₂ substrate and are separated by less than 1 nm ensuring identical plasma treatment conditions. The devices were exposed to repeated oxygen plasma treatments followed each time by Raman and electrical characterization. The plasma experiments were carried out at very low power (5 W) and short treatment exposure (5–120 s). Figure 1c,d shows the optical micro-graphs of the mono- and bilayer graphene corresponding to Figure 1a,b after 80 s exposure to oxygen plasma. We observe that the monolayer disappeared.
while the bilayer is still optically visible. Raman spectroscopy is a fast, non-destructive and powerful technique for the characterization of graphene,\textsuperscript{[24]} it allows to unambiguously identify graphene,\textsuperscript{[25]} probe doping and charged impurities,\textsuperscript{[26,27]} as well as characterize disorder and defects.\textsuperscript{[28–30]} The evolution of the Raman spectra of mono- and bilayer graphene measured for increasing exposure time to oxygen plasma is shown in Figures 2a and b, respectively. The pristine spectrum shows the two main Raman peaks of graphene: the G band around 1580 cm\textsuperscript{-1} and the 2D band around 2700 cm\textsuperscript{-1}. The 2D band acts as a fingerprint to assign the number of layers in graphene; a monolayer can be fitted with one Lorentzian exhibiting a full width at half maximum (FWHM) between 20–30 cm\textsuperscript{-1}, while a bilayer is composed by four components.\textsuperscript{[24]}

Figure 2 shows that after oxygen plasma exposure, new features corresponding to defect activated bands appear in the Raman spectra. The most prominent ones are the so called D and D' band at \(\sim 1340\) cm\textsuperscript{-1} and \(\sim 1620\) cm\textsuperscript{-1}, respectively.\textsuperscript{[31]} The Raman spectrum of the monolayer graphene shows drastic changes upon increasing oxygen plasma exposure. After 5 s of exposure, an intense D peak is already observed. Its intensity first increases and then rapidly decreases for increasing plasma exposure. After 10 s, a broadening of all peaks is observed (see Figure S1 in SI for quantitative data), followed by the suppression of the 2D band intensity, and a merging of the G and D' bands into one single peak. At 80 s the Raman signal is largely attenuated and finally disappears after longer treatment time, suggesting complete etching of the monolayer. This is confirmed by the optical image in Figure 1c where no optical contrast is seen at the supposed flake position. The changes in the Raman spectra of modified bilayer graphene are less drastic. From 5 to 60 s, the D and D' bands intensities increase slowly while the 2D band decreases. From 60 to 120 s, very little variation is observed.

![Figure 1](image1.png)

**(a,b)** Optical micrographs of pristine mono- and bilayer graphene devices, respectively. **(c,d)** Optical images of the same devices after 80 s oxygen plasma treatment. The scale bar (bottom left) is 5 \(\mu\)m and it is the same in all the figures.

![Figure 2](image2.png)

**(a)** Raman spectra evolution of (a) monolayer and (b) bilayer graphene for increasing exposure to oxygen plasma. **(c)** D and G band integrated intensity ratio, \(I(D)/I(G)\), of mono- and bilayer graphene for increasing exposure time to oxygen plasma. **(d)** 2D Raman spectra of a pristine monolayer, pristine bilayer and oxygen plasma treated bilayer graphene (5 W, 120 s). The excitation wavelength is 514 nm.
in the spectra. As shown in Figure 1d, bilayer graphene is still optically visible after 80 s of treatment and the optical contrast slightly decreases from 23% for the pristine flake to 21% after 80 s plasma exposure. These results point out that the bilayer is less affected by the plasma treatment than the monolayer and that a stable configuration is reached after 40 s. The higher resistance of the bilayer towards oxygen plasma could be attributed to its smaller intrinsic roughness (ripples)[32] and/or its better screening of the substrate charge puddles.[33,34]

The difference between the Raman spectral evolution of monolayer and bilayer graphene is quantified in Figure 2c by plotting the integrated height ratio of D and G band intensities, I(D)/I(G), as a function of the plasma exposure. I(D)/I(G) has been widely used in the literature to quantify the defect density in sp²-bonded carbons: it is well known that at low defect concentrations I(D)/I(G) increases for increasing amount of disorder, while I(D)/I(G) decreases with disorder for high defect concentrations.[30,31,35] In the case of monolayer graphene, I(D)/I(G) clearly increases at short plasma-exposure time. This likely corresponds to the introduction of defects into the sp² lattice. The intensity ratio then decreases at high plasma-exposure time which is attributed to amorphisation of graphene due to the high density of defects. Amorphisation also becomes evident by the massive increase in the FWHM of all peaks and the disappearance of the 2D band.[36]

A similar qualitative evolution of the I(D)/I(G) ratio is observed for the bilayer (Figure 2c). However the bilayer has a much slower linear increase and reaches a maximum I(D)/I(G) of ~4 after 60 s, whereas the monolayer reaches a maximum ratio of ~5 after only 10 s, i.e. the bilayer does not achieve high defect concentration. In Figure 2c, we multiplied the calculated I(D)/I(G) of the bilayer by 2 since its G peak intensity is twice the one of graphene. Note that in the case of bilayer I(D)/I(G) does not strongly change after 60 s plasma exposure. In the initial regime, differences between monolayer and bilayer graphene are very pronounced with an intensity ratio up to 12 times higher for the monolayer. In the case of bilayer I(D)/I(G) clearly increases at short plasma-exposure time. This likely corresponds to the introduction of defects into the sp² lattice. The intensity ratio then decreases at high plasma-exposure time which is attributed to amorphisation of graphene due to the high density of defects. Amorphisation also becomes evident by the massive increase in the FWHM of all peaks and the disappearance of the 2D band.[36]

Figure 2d compares the 2D Raman spectra of pristine monolayer, pristine bilayer and oxidized bilayer graphene. The 2D peak of the monolayer graphene is fitted using one Lorentzian component of FWHM ~30 cm⁻¹ centered at 2684 cm⁻¹. Due to its two pairs of conduction and valence bands allowing four double-resonance processes,[34] the bilayer graphene 2D band is best fitted using four Lorentzian components. The oxygen plasma treatment progressively transforms the 2D band of the bilayer into the one of a monolayer. After 120 s it can be fitted with one Lorentzian of FWHM ~46 cm⁻¹ centered at 2689 cm⁻¹. The larger FWHM is attributed to the lose of the AB-stacking configuration after introduction of defects.

Figure 3. (a,c) Contact mode topographic AFM image of pristine and oxygen plasma treated bilayer graphene. (b,d) current map obtained with bias of 5 mV. Scale bar = 60 nm. Regular pattern in (b) is a measurement artifact.
less pronounced in the case of oxidized graphite (blue curve) due to the penetration depth of electrons which probes around 20 graphitic layers while only the first layer is functionalized by the plasma. The C1s spectrum of the oxidized bilayer is then fitted using five components corresponding to sp² C/H, sp³ C/H, hydroxyl C/H, carbonyl C/O or epoxy C/O, and carboxyl COOH groups (Figure 4c). The relative amount of these components corresponds respectively to 36.4%, 32.3%, 12.7%, 13.9% and 4.3%. These numbers should be treated with care because of the uncertainty inherent to the peak fitting. However, they show the complexity of the surface chemistry of the bilayer. Presence of carboxyl groups is of particular interest since they are commonly used as attachment points for molecules and biological objects. As an example, covalent attachment of DNA on plasma modified bilayer graphene is shown later in the discussion.

Transport measurements were carried out to study the electronic properties of oxidized graphene. The graphene transistors were fabricated on Si/SiO₂ substrate using conventional electron beam lithography followed by metal sputtering (1 nm Ti and 50 nm Pd). The measurements were performed in air and at room temperature. Figure 5a,b plots the resistance of the mono- and bilayer graphene devices as a function of the back gate voltage for increasing plasma duration. The source-drain voltage was set to 10 mV. The pristine sheets are slightly p-doped with hole mobilities of ∼6700 and ∼2300 cm² V⁻¹ s⁻¹ for graphene and bilayer graphene, respectively.

The electronic properties of plasma treated monolayer graphene are drastically degraded even after short oxygen plasma exposure. The film resistance increases by 1 order of magnitude after 10 s and additional 4 orders of magnitude after 20 s. For longer treatment time, the device resistance increases beyond the measurement range of the semiconductor parametric analyzer. These results are consistent with Raman measurements where an exposure of 20 s corresponds to the beginning of the high defect density regime. Rapid degradation of the structural and electrical
properties shows that, even at very low power and short time processes, oxygen plasma is very aggressive toward single graphene sheets, in agreement with previous results.\cite{Liang,10,18,40}

Bilayer graphene, on the contrary, shows a very peculiar behavior upon plasma oxidation (Figure 5b). For short plasma exposure, the device resistance slightly increases with a very large shift of the Dirac point to a positive gate voltage beyond 80 V. A positive shift of the Dirac point can be explained by hole doping from oxygen species.\cite{Liang} From 5 to 40 s, electron conduction cannot be induced. At 60 s we observe a slight decrease in the resistance which surprisingly is accompanied by a downshift of the Dirac point to \(-50\) V. After 120 s, the resistance further decreases while the Dirac point has been shifted up again to \(>80\) V. It is worth noting that the total resistance of the bilayer device at zero gate voltage never exceeds 6 k\(\Omega\). We analyzed four devices and observed similar behavior (Figure S5 in SI). A possible explanation for this intriguing electrical behavior is that the oxygen plasma induces a mechanical deformation of the top layer. After 60 s of treatment the oxygen coverage may be high enough to induce a relatively strong wrinkling of the top layer, which may lead to decoupling of the two layers. In this situation, the decoupled bottom layer will mainly contribute to the current transport which may explain why the total resistance of the device is decreasing and the Dirac point is downshifting.

These results can be compared with recent works on modified bilayer. Dong et al.\cite{Dong} have shown that modification of the bilayer using bromophenyl groups leads only to a p-doping of the bilayer with no changes in the resistance and mobility of the device. This different behavior compared to our results could be attributed to the different modification process with diazonium salts, which involves grafting only at pre-existing defect sites. In their study, Nourbakhsh et al.\cite{Nourbakhsh} have shown that the electrical properties of the bilayer after one short exposure to an O\(_2\) plasma stay constant. Since no evolution of the electrical properties was presented, this result may correspond to our samples modified with 60–80 s plasma, where the resistance of the bilayer is decreased and the Dirac point is down-shifted.

To determine the mobility of the bilayer graphene, the \(R(V_G)\) curves were fitted using the formula:\cite{Liang}

\[
R = R_c + \frac{L/W}{\mu e ((C_g|V_G-V_D|)^2 + n_0^2)}
\]

where \(R_c\) is the contact resistance, \(V_G\) the back gate voltage, \(V_D\) the Dirac point, \(\mu\) the mobility, \(C_g\) is the back gate capacitance and \(n_0\) represents the density of carriers at the minimum conductivity. We only fitted the hole-conduction branch of the curves since the data covers a wider range for gate voltages below the Dirac point. Figure 6 shows the mobility of mono- and bilayer for increasing plasma duration. The mobility of the bilayer quickly decreases from \(-2300\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for pristine device to \(-200\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) after 20 s of treatment. After 40 s this trend is reversed and \(\mu_h\) increases to \(-600\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). This observation is surprising since an increase in defect density should induce a rapid and irreversible drop of the mobility as observed for graphene.

However, bilayer graphene does not follow the same trend presumably due to preferential chemisorption on the top layer. Once the maximum coverage is achieved on the top layer, then the material will be stable even under long plasma exposure preventing amorphization and decrease of mobility. A further explanation could be related to distortion induced by the chemisorption: the conversion of the bond from sp\(^2\) to sp\(^3\) induces strong distortion of the top layer. We speculate that at high coverage the top layer could “shrink” and decouple from the bottom layer. In this case, the relatively high mobility observed, should be attributed entirely to the bottom layer. Note that the calculated hole mobility of plasma oxidized bilayer graphene is 4–10 times lower than that of the pristine bilayer sample, it is comparable to the mobility of bilayer graphene grown by chemical vapor deposition (350–580 cm\(^2\) V\(^{-1}\) s\(^{-1}\)), and it is higher than the mobility of reduced monolayer graphene oxide (0.5–200 cm\(^2\) V\(^{-1}\) s\(^{-1}\)).\cite{Liang,41,42,43}

We now move to double-sided oxygen plasma functionalization. In this case, the plasma treatment was performed on a suspended bilayer by exposing each side one after the other to the plasma under exactly the same conditions (Figure 7a). The non-exposed side is directly facing the surface of the electrode which therefore prevents its modification by the plasma gas. The bilayer membrane broke down after 120s exposure (60 s on each side), while measuring the Raman spectrum. Figure 7b compares the Raman G, D and D’ peaks of suspended and supported bilayers after 120 s of oxygen plasma treatment. The spectrum of the supported bilayer after 60 s and monolayer after 40 s are also shown for comparison. The two spectra of suspended and supported bilayer exposed for 120 s are clearly different with the suspended one presenting a spectrum very similar to graphene oxide,\cite{Dong,41,42,43} i.e. merging of G and D’ peaks and much broader FWHM of the D peak (79.3 cm\(^{-1}\) compared to 40.3 cm\(^{-1}\) in the supported bilayer). Figure 7c shows the evolution of the D band FWHM.
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for monolayer, and single- and double-sided functionalized bilayer. Similar FWHM are first observed for single- and double-sided treated bilayer graphene which suggests that, for short treatment time, the introduction of defects by the oxygen plasma is similar in both type of functionalization. It is only after 80 s of treatment (40 s on each side) that the D band width strongly increases, reaching values observed in the monolayer. The double-sided chemical functionalization thus results in a new material which becomes highly disordered, in agreement with the theoretical predictions of ref. [23]. The oxygen treatment strongly changes the interaction between the two layers and it is likely that the pristine layered structure is lost in double-sided bonding because of the formation of interlayer bonds.

Finally, we show that covalent attachment of DNA to the single-sided functionalized bilayer is possible, leading the way to the fabrication of new graphene-based chemical and biological sensors. The DNA experiment was performed in 2 steps. First, the plasma treated bilayer was exposed to an amino- and FAM (carboxy fluorescein)-modified single strand DNA (NH2-CAGAACCATAGCCATAATTACT-FAM). In presence of carboxyl groups, the amino-terminated end of the DNA will react to form a covalent amide bond. The attachment of the DNA to the graphene could then in principle be visualized by fluorescence microscopy. Unfortunately, successful bonding of the DNA cannot be immediately confirmed due to drastic fluorescence quenching induced by the graphene.[47] In order to restore the fluorescence, a second step consisting in the hybridization with the complementary strand DNA was needed. Indeed, it has been shown that upon formation of the duplex, (i) physisorbed DNA strands are removed from the surface[48,49] and (ii) the fluorescein dye to graphene distance is increased for covalently attached DNA, hence restoring fluorescence.[47] Figure 8 shows the fluorescent microscopy image of a plasma treated bilayer graphene after exposure to the amino- and FAM-modified DNA and its complementary strand. The fluorescence observed on the graphene confirms successful covalent attachment. In addition, a control experiment using non plasma functionalized graphene bilayer showed no fluorescence (see Supporting Information) which corroborates our results. These findings validate single-sided functionalized bilayer as a new building block in the fabrication of biosensors. Furthermore, the

Figure 7. (a) Schematic representation of the double-side functionalization. The bilayer is sitting on a hole. First the top layer is exposed (i), then the sample is turned around and the bottom layer is exposed through the hole under otherwise identical conditions (ii). (b) Comparison of the G, D and D' Raman bands of supported and suspended bilayer graphene after 120 s exposure to oxygen plasma. The spectrum of the supported bilayer after 60 s and monolayer after 40 s are also shown for comparison. (c) Evolution of the D band FWHM for the monolayer, and single-side and double-side functionalized bilayers.

Figure 8. Fluorescent micrograph of a single-sided plasma-functionalized bilayer after covalent attachment with an amino- and FAM-modified single strand DNA and hybridization with its complementary strand. The inset shows a corresponding bright field image. The scale bars equal 20 μm.
simplicity of the functionalization procedure and the relatively high mobilities of the material provide two advantages over conventional graphene oxide.

3. Conclusion
In conclusion, we have studied the interaction between the top and bottom layer of a chemically functionalized bilayer by mild oxygen plasma. We aim to challenge the usual assumption of layer-by-layer chemical functionalization by plasma exposure. We have shown that plasma treatment is a simple method to tune the coupling between the layers: single-side treatment of bilayer led to the formation of a stable structure with relatively high charge mobility, which could be related to decoupling between the top and bottom layer. In contrast, exposure of both sides of the bilayer leads to a highly disordered structure similar to graphene oxide. This opens the possibility to use plasma treatment not only for etching and patterning of graphene, but also to make heterostructures (through single-sided modification of bilayer) for sensors and transistors and new graphene-derivatives materials (through double-sided modification).

4. Experimental Section
Graphene was produced by mechanical exfoliation of graphite (National de Graphite) onto 300 nm grown silicon oxide on doped silicon substrate (Active Business Company GmbH). Graphene sheets were identified by optical microscopy and the number of layers was confirmed using Raman spectroscopy. The graphene transistors were fabricated using conventional electron beam lithography followed by metal sputtering (1 nm Ti and 50 nm Pd). The source and drain electrodes were separated by 4 μm in order to avoid Raman measurements on the contacts (the laser spot size is ~500 nm). The silicon substrate was used as back gate. Before the measurements, the samples were annealed at 300 °C under vacuum for 4 hours in order to remove residue of PMMA left on graphene after the lithography process.

The graphene samples were modified in oxygen plasma at 100 mTorr, 5 W and with different duration. The experiments were carried out in a Plasmalab 80Plus from Oxford Instruments (capacitively coupled RF at 13.56 MHz). Each oxygen plasma treatment was immediately followed by Raman and electrical characterization. Raman spectra were measured using a 100x objective at 514 nm on a WITec spectrometer. The laser power was adjusted to 1 mW. All peaks were fitted using Lorentzian lines except for the D' band where a Fano line shape was used. Electrical measurements were performed in air at room temperature with an Agilent 4155C semiconductor parametric analyzer. XPS measurements were performed on a Thermo Scientific K-alpha. The spot size and pass energy were set to 30 μm and 50 eV respectively. A monochromated Al Kx line hν = 1486.6 eV was used as the photon source, and photoelectrons were collected at an angle of 90° relative to the sample surface normal. Topography and current AFM images in Figure 3 were obtained with Atomic Force Microscope Nanoscope Dimension V (Bruken) in contact mode with conductive Pt/Ir coated cantilevers PPP-CONTPt (Nanosensors). This technique provides information on local conductivity, and can be used to distinguish the patches of sp² carbon (typically insulating) within perfect graphene matrix.[22,30] Current was measured at fixed bias of 5 mV applied to the tip via Keithley 2400 SourceMeter. Images were obtained in ambient conditions with scan rate 0.2 Hz and applied force of about 5 nN. Topography AFM images in the supporting information were obtained using a Dimension Icon (Bruker) AFM in tapping mode with Tap300AI-G cantilevers (BudgetSensors). Annealing of the oxidized bilayer was performed at 200 °C in high vacuum (10⁻⁶ mbar) for 2 h.

All DNA samples were purchased from Integrated DNA Technologies. The covalent attachment was performed by exposing the sample to a solution of 2.5 μm of the amino- and FAM-modified for 2 h. The fluorescent DNA was then hybridized by adding the sample in a PBS buffer solution (BupH, Thermo Scientific, pH 7.2) containing 3 μm of the complementary DNA. The sample was left in solution overnight and then carefully washed with PBS. The same procedure was repeated twice. Fluorescence images of the fluorescently labeled DNA on graphene were taken on an upright Eclipse 80i fluorescence microscope (Nikon) equipped with an Intensilight (Nikon) and a CoolSNAP HQ2 camera (Photometrics). After putting a cover slip onto the sample still wet with PBS, images were obtained with a 50x objective and 15 s exposure time. Images were contrast enhanced for reproduction only, all intensity measurements and comparisons for control experiments were done on raw and unaltered data from original images.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Supporting Information

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Single- and Double-Sided Chemical Functionalization of Bilayer Graphene

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Supporting Information


**Figure S1.** Full width at half maximum for the D, G and 2D peaks of mono and bilayer graphene versus oxygen-plasma exposure time.

As pointed out in the paper, a broadening of all Raman peaks is observed for the monolayer graphene upon plasma exposure. Such broadening is due to disorder induced in the graphene lattice. In the case of bilayer graphene, the widths of the Raman peaks are increasing much slowly.
2. Additional AFM measurements

Figure S2. (a)-(i) Surface morphology of bilayer and monolayer graphene at different oxygen plasma exposure (power = 5W). Image size is 5x5 µm² for (a-h). Image (i) corresponds to the 1x1 µm² white square in image (g). The arrow indicates the location of a monolayer.

The evolution of the surface topography of the bilayer and monolayer graphene as a function of plasma duration is shown in figure S2(a)-(h). As can be seen in the images, very little changes occur on the bilayer. In contrast, structural variations are observed in the
monolayer (indicated by the white arrow) during the treatment. Figure S2(i) shows a close up of mono- and bi-layer after 100s of oxygen plasma. While the monolayer is etched away, the bilayer graphene surface does not visually change compared to the pristine one, i.e. no holes formation, etching or evident increase in the surface roughness is observed. This result thus confirms the higher resistance of the bilayer to the plasma treatment observed by Raman and transport measurements.

A more careful study of the evolution of the RMS roughness and the thickness is presented in Figure S3(a) and (b). Upon increasing plasma exposure, changes of \( \sim 0.1 \text{ nm} \) in the RMS roughness of the bilayer are observed. These small variations could be attributed to chemical contrast induced by the oxygen plasma. It has to be noted that difference in intrinsic ripple sizes between mono and bilayer would not show up here due to the resolution of the AFM images (pixel size is 10 nm while lateral size of intrinsic ripples should be in the order of 15 nm\(^1\)) and small area of the monolayer leading to underestimation of its roughness. The thickness of the bilayer shown in figure S3b is progressively increasing with treatment duration from 1 nm to 1.6 nm and then stabilizes after 60s. This increase of thickness is consistent with the introduction of oxygen functionalities.\(^2,3\)

![Figure S3. RMS roughness and thickness of mono- and bilayer graphene after increasing oxygen plasma exposure.](image-url)
3. Annealing experiment.

Figure S4. Raman spectra of oxidized bilayer graphene (5W 100s) before and after annealing at 200°C in high vacuum.

No significant changes are observed in the Raman spectra of oxidized bilayer before and after annealing which confirms stable attachment of the oxygen groups at the graphene surface.
4. Additional transport data for two other bilayer graphene transistors.

Figure S5. Resistance of two different bilayer graphene devices as a function of the back gate voltage for increasing oxygen-plasma exposure time.

All bilayer devices studied in this work show similar evolution in the electrical behavior with oxygen-plasma exposure time:

1) first, the device resistance increases slightly with a large shift of the Dirac point to positive gate voltage;

2) Then, the resistance increases showing only hole conduction;

3) Decrease in the resistance accompanied by a downshift of the Dirac point (to 30-50V)

4) The resistance further diminish while the Dirac point is shifting up again (> 80V).
5. Additional hole mobilities calculated for four devices.

Figure S6. Hole mobilities of bilayer graphene devices with increasing oxygen-plasma exposure time.

The mobilities were calculated using the equation shown in the paper. The device 1 is the one discussed in the main text. We observe similar behavior for the 4 devices, i.e. a quick decrease of the hole mobility upon increasing exposure followed by a slight increase and stabilization after 40-60s.
6. Immobilization and hybridization of fluorescently labeled DNA.

**Figure S7.** Fluorescence microscopy images of (a) and (b) plasma treated graphene flakes and (c) non-treated control sample after incubation with amino- and FAM-modified DNA and complementary strand. Insets show corresponding images in bright field. Scale bars equal 20µm. Areas used for the intensity measurements tabulated in (d) are encircled in green.

To demonstrate the covalent binding of DNA to the graphene flakes, amino-modified fluorescently labeled (FAM) DNA strands were incubated on plasma treated and non-treated control samples as described in the main text. Figure S7 shows the outcome of these experiments for two plasma treated ((a) and (b)) and one non-treated (c) graphene flake. Areas were defined on the flake and nearby on the silicon oxide background (encircled in green) in the raw and unmodified fluorescence images, and the mean fluorescence intensity in these areas was calculated with on-board means of the microscope control software (NIS Elements, Nikon). The mean intensities tabulated in Figure S7 (d) clearly show preferential attachment.
of the DNA strands to the plasma treated graphene flakes (difference in backgroundflake intensity 317 and 656 a.u., respectively, ratio of fluorescence intensity on flake to background 1.9 and 2.4, respectively) compared to an even negative contrast in case of the not plasma treated control samples (-18 a.u., indicating that the pristine graphene sheet might be slightly more repellent in regard to non-specific physisorption of DNA than the silicon oxide background, intensity ratio flake/background is 1.0). The consistent positive contrast on the plasma treated graphene compared to the lower fluorescence intensity and lack of contrast on the negative control sample leads to the conclusion of a covalently attachment of the aminomodified DNA strands to the plasma treated graphene preventing the detachment that takes place in physisorbed DNA strands on the silicon oxide background and the not plasma treated graphene during hybridization and washing.


My contribution

I measured and analyzed the superlattices’ Raman spectra, prepared all the Figures and wrote the manuscript.
Raman Fingerprint of Aligned Graphene-Hexagonal Boron Nitride Superlattices

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Manuscript text

In a crystal a gap is opened at the Brillouin zone boundaries because of the weak periodic potential generated by the nuclei\(^1\). In the case of massless Dirac electrons, it has been shown theoretically and experimentally that a periodic potential leads to the formation of locally gapped regions (mini-gaps) characterized by superlattice Dirac points (SDPs), whose energy is determined by the wavelength of the potential\(^2\)--\(^7\). Van Hove singularities (vHS) in the density of states and anisotropy of the Fermi velocity at the SDPs have been also predicted\(^2\). Therefore, one can modify graphene’s electronic spectrum simply by tuning the periodic potential. One of the simplest ways to apply a periodic potential is to use a superlattice potential, that is a periodic potential induced by another crystal\(^8\).

Hexagonal boron nitride, h-BN, is a perfect candidate to make superlattices: its structure resembles that of graphene with boron and nitrogen atoms placed in a honeycomb lattice, but characterized by a constant lattice \(\sim 1.8\%\) larger than the one of graphene, due to the longer B-N bond compared to the C-C. The superposition of graphene on h-BN in a random rotational orientation leads to the creation of a superlattice with a moiré pattern whose wavelength (\(\lambda\)) depends on the stacking angle (\(\theta\)) between graphene and h-BN\(^6\). The longest moiré wavelength (\(\lambda \sim 14\) nm) is obtained for \(\theta = 0\), i.e. for a perfectly aligned graphene on h-BN. This sets the lowest SDP energy at \(\sim 0.2\) eV, as measured from the Dirac point of graphene, since:

\[ E = 2\pi \hbar v_F / \sqrt{3} \lambda, \]

where \(v_F\) is the Fermi velocity\(^6\). This equation sets the position of the first mini-band, but higher energy mini-bands are also expected\(^2\). Thus, h-BN can be used to strongly reconstruct the Dirac spectrum of graphene\(^2\)--\(^7\) and to produce strong effects in the optical spectroscopy of graphene on h-BN. Therefore, it is vital to study the light interaction with h-BN/graphene superlattices since the ability to generate SDPs at a chosen energy can allow designing novel optical and optoelectronic devices with tunable properties.
In this work we aim at studying the effect of the superlattice potential by Raman spectroscopy. This is a fast and non-destructive technique for investigating the properties of graphene\textsuperscript{9}. In particular, Raman spectroscopy has already proven to be very sensitive to rotational faults in graphene-graphene stacks\textsuperscript{10–19}. The Raman spectrum of twisted bi-layer graphene (tBLG) shows some characteristic features: i) new peaks appear in the spectrum, associated to phonon modes in the interior of the Brillouin zone, activated by an umklapp double resonant Raman process\textsuperscript{13–15,18}. ii) A strong enhancement of the G peak intensity is observed for a twist angle between 10 and 15 degrees, depending on the excitation energy. This is caused by the presence of vHS in the overlapping region of the Dirac cones of the top and bottom layer, which depend on the rotational angle between the two graphene\textsuperscript{16,17,19}. iii) the 2D peak is a single peak since the linear Dirac cones remain in tBLG (potentially with renormalization of the Fermi velocity for slightly misaligned structures)\textsuperscript{20–22}. However, we do expect to see different effects in the Raman spectrum of h-BN/graphene superlattices since the two crystals have different electronic structure and lattice constant.

Raman spectroscopy and transport measurements have been used to study the changes in the Dirac spectrum with the rotational angle. More than 30 graphene on h-BN structures with different degree of alignment have been investigated, following the fabrication process described in Ref\textsuperscript{7}. Note that transport offers a very reliable way to probe SDPs because they appear as a sharp peak in resistivity\textsuperscript{7}. However, the maximum limit achievable in energy with this technique is about 0.35 eV because of dielectric breakdown. Hence these measurements are able to probe SDPs only in perfectly aligned or slightly misaligned structures (θ < 2\(^{\circ}\)).

Figure 1a shows an optical image of a graphene flake produced by micro-mechanical exfoliation and transferred onto a thick flake of h-BN on silicon with random relative orientation. Since graphene partially lies on the silicon substrate, we used this sample to investigate the dependence of the Raman spectrum on the substrate. Figure 1 shows the Raman map of: b) Pos(G); c) FWHM(G); and d) FWHM(2D), measured at an excitation energy of 2.4 eV. This figure shows that there is no appreciable difference in the G peak shape between h-BN and silicon. However, the G peak Raman fit parameters are more uniform when graphene is deposited on h-BN than on silicon. This agrees with recent results\textsuperscript{23}, confirming that doping level and local potential fluctuations are significantly suppressed in graphene on h-BN as compared to silicon\textsuperscript{24}. In the case of the 2D peak, significant differences can be observed: the 2D peak FWHM is larger on silicon (∼ 30 cm\(^{-1}\)) than on h-BN (20 cm\(^{-1}\)). An upshift in the 2D peak position of 9 cm\(^{-1}\) when graphene is deposited on h-BN, as compared to silicon, has also been observed. These observations are in agreement with Ref\textsuperscript{23}, which attributed the peak upshift to the partial removal of the Kohn-anomaly at K, caused by the enhanced screening of the dielectric substrate. Note that exactly the same changes have been observed in twisted bi-layer graphene (tBLG) for rotational angles > 15 degrees (see supporting information and Ref.\textsuperscript{16}).

We then measured h-BN/graphene superlattices in device configuration. From the position of the SDP, measured by electronic transport, we extract the wavelength of the moiré pattern and the rotational angle. Note that electronic transport measurements on these devices show the usual mobility of graphene on h-BN (∼ 20-100 × 10\(^{5}\) cm\(^{2}\) V\(^{-1}\) s\(^{-1}\)) and reduced charge inhomogeneity (see Supporting information). This rules out effects from doping and defects in our Raman spectra.

Figure 2a shows the 2D peak measured at 1.96 eV on two superlattices with mismatch angles of 0 and 2\(^{\circ}\) (top and middle spectra). These are compared with
Figure 1: (color on-line) a) Optical micrograph of a graphene flake transferred on a thick BN flake. Raman maps of b) Pos(G), c) FWHM(G) and d) FWHM(2D) measured inside the red window in a).

The 2D peak of a randomly oriented structure (at the bottom). This figure shows that the FWHM(2D) increases moving from large misorientation to a perfectly aligned superlattice.

Figure 2b plots the FWHM(2D), measured at three different excitation energies (1.96, 2.41 and 2.54 eV) for 7 devices against the position of the SDP and the moiré wavelength. We can observe a clear correlation between the SDP energy and FWHM(2D), regardless of the excitation energy used: the FWHM(2D) strongly increases from 21 cm$^{-1}$ to 45 cm$^{-1}$ for decreasing mismatch angle (i.e. for larger moiré pattern) between 0 and 2 degrees.

This is qualitatively similar to the behavior of tBLG: Figure 2c compares the evolution of FWHM(2D) of tBLG$^{16}$ and h-BN/graphene superlattices between 0 and 5 degrees, measured at 1.96 eV. In both cases, there is a sharp increase of the FWHM(2D). Note that at large angles, FWHM(2D) is the same for both superlattices ($\sim$ 21 cm$^{-1}$). Under this condition, there is no overlap between the Dirac cones of tBLG and the two layers are completely decoupled. This means that the top graphene is insensitive to the nature of the bottom layer. Thus, the Raman spectrum is expected to be qualitatively the same for the two superlattices.

At small twist angles, broadening of the FWHM(2D) appears for both superlattices. But in the case of h-BN/graphene superlattices the broadening is very sharp, Figure 2c.

The broadening of the 2D peak is typically attributed to defects$^{25}$, but in this case the presence of defects can be ruled out by transport measurements (see Supplementary Information). Therefore, the sharp increase of FWHM(2D) has a different
misaligned

Figure 2: (color on-line) a) Three representative spectra taken at 633 nm on graphene deposited on BN with a mismatch angle of 0 and 0.6° as compared to a misaligned structure. b) Evolution of FWHM(2D) measured at a laser wavelength of 488, 514 and 633 nm as a function of the position of the second Dirac point. c) Experimental FWHM(2D) measured for graphene superlattices16 and h-BN/graphene hetero-structures: in both cases FWHM(2D) increases at very small angles. A good agreement is found with the calculations obtained with the continuum model26, where the points (open circles) have been downshifted by 10 cm⁻¹ to match the FWHM(2D) in misaligned superlattices (∼ 21 cm⁻¹).

Furthermore, the 2D peak, being triple-resonant27,28, is also very sensitive to the changes in electronic structure. Thus, one may attribute the changes in FWHM(2D) to the presence of the SDPs, including renormalization of the Fermi velocity and vHS. However, we did not observe any appreciable change in the dispersion of the 2D peak (see supporting information), which also rules out strong changes in the Fermi velocity. Since the FWHM(2D) broadening is very sharp only between 0 and 2 degrees, this has to be related to the particular reconstruction of the Dirac cone at small twist angles. This may allow phonons of slightly different wave-vectors to contribute to the Raman scattering process, giving rise to the 2D peak broadening.

It is now interesting to look at the first order Raman spectrum since graphene superlattices have shown the presence of characteristic peaks, associated to the superlattice wave-vector.

Figure 3a plots the G peak measured at 2.14eV nm on 5 different devices with E_{SDP} varying from 0.17 eV (perfectly aligned) to above 0.4 eV (misaligned structure). The G peak of the misaligned device is a single and narrow peak lying at 1584 cm⁻¹ and FWHM(G)=10-13 cm⁻¹, similar to the G peak measured on suspended graphene29. In slightly misaligned devices (< 2 degrees) a small and very sharp peak on the lower energy side of the G peak appears. Note that the position of this peak changes with the rotational angle and it is not dispersive, Figure 3b and c. Because of that, we attribute this peak to the intravalley umklapp activated R’ peak, associated to a LO phonon close to the Γ point14. In order to confirm the origin of this peak, we calculated the rotational wave-vector G characteristic of the
Figure 3: (color on-line) a) G peak of graphene/BN superlattices measured at 514 nm as a function of \( E_{SDP} \) b) and c) multiwavelength analysis of the G peak of the superlattice with \( E_{SDP} = 0.22 \) eV and 0.17eV, respectively. The peak marked with an asterisk is an artifact that was also observed on BN alone.

Figure 4: (color on-line) Plot of the position of R’ as a function of \( \theta \) for tSLG and hBN/graphene superlattice. The difference in the lattice constant dominates only at very small angles (\(< 2\) degrees), that is it affects the phonons with very small wave-vectors. The dots are experimental data obtained from the Raman spectra of aligned and closely aligned h-BN/graphene superlattices. The error bar indicates the uncertainty in the Raman positions, due to the resolution of the instrument (\( \sim 2 \) cm\(^{-1}\)).

h-BN/graphene superlattice by taking the difference between the reciprocal vectors of graphene and h-BN. We found:
\[ |G| = \frac{4\pi \sqrt{2(1 + \delta)(1 - \cos \theta) + \delta^2}}{\sqrt{3(1 + \delta)a_{CC}}} \]  

where \( \delta \) is the constant lattice mismatch (\( \sim 1.8\% \)) and \( a_{CC} \) is the graphene lattice constant. Assuming that the interaction between the two layers does not affect the phonon dispersion of graphene, by using the computed phonon frequencies of Ref\(^{28} \), we can obtain the frequency of the R’ peak as a function of the mismatch angle, Figure 4. The Figure also include the R’ dispersion calculated for tBLG\(^{14} \). One can observe that the lattice mismatch between graphene and h-BN affect the position the R’ peak only in the small twist angle regime (< 2 degrees). The position of the peak observed in Figure 4 agrees well with the calculated R’ peak position in h-BN/graphene superlattices. Note that the R’ peak is not visible in perfectly aligned structures (\( \theta = 0 \)), Figure 3c, since it overlaps with the G peak.

Finally, note that our excitation energies (1.96-2.55 eV) are very far from the typical R’ resonant energy in aligned structures (\( \sim 0.5 eV \), see SI), the R’ peak is therefore observed under non-resonant conditions. A careful analysis of the G peak in slightly misaligned structures also reveals that the G peak is asymmetric. By fitting the G peak with two lorentzians, the asymmetry is attributed to a peak centered at about 1570 cm\(^{-1} \) and FWHM of about 11-13 cm\(^{-1} \). Its position does not change significantly either with mismatch angle or with excitation energy (Figure 4b and 4c). Since the intensity of this peak is rather weak, we used surface enhanced Raman scattering (SERS) by depositing a thin gold film on the superlattice. We obtained an enhancement factor of 10-20 and the Raman spectrum clearly shows a peak at 1575 cm\(^{-1} \).

The position and FWHM of this peak indicate that this is a TO phonon. These type of phonons can become active in superlattices through inter-valley Raman scattering processes\(^{14,18} \). However, those phonons should be visible only at relatively large rotational angles. At small angles and small energies, the phonon wave-vector is too small to allow inter-valley Raman scattering process. It is however possible that the presence of the superlattice potential relaxes the selection rule. This needs to be further investigated.

In conclusion, we have shown that the Raman spectrum of h-BN/graphene superlattices strongly change at very small twist angles. A characteristic broadening of the 2D peak is observed and attributed to the effect of the interlayer hopping. This allows fast identification of aligned h-BN/graphene by Raman spectroscopy, thus enabling further investigation of graphene superlattice-based devices.

**References**


SUPPLEMENTARY INFORMATION

Figure S1 – Optical image of graphene deposited on a thick boron nitride (BN) flake in a device configuration. 1, 2 and 3 denote the location of the 3 graphene mesa on top of the BN substrate.

Figure S2 – a) Optical image of a tBLG on glass obtained by anodic bonding of graphene [1]; Raman map of: b) FWHM(2D). This parameter is not uniform because anodic bonding is
known to display local changes in the doping level graphene [1]; c) histogram showing that FWHM(2D) of tBLG is on average smaller than FWHM(2D) of single-layer graphene; d) Pos(2D), showing an upshift of the 2D peak position in tBLG, as observed when graphene is deposited on h-BN.

Figure S3 – a) Longitudinal resistivity curve ($R_{xx}$) of a device as shown in Figure S1 as a function of gate voltage. The most intense peak at $V_g$ about -20V corresponds to the principal Dirac point of graphene. On either side and for $V_g = -75$ and +35, two additional peaks appear. They are due to the presence of the additional Dirac points. b) Carrier concentration as a function of gate voltage measured by Hall effect at a magnetic field $B$ of 0.2 T. The carrier concentration is obtained from the Hall resistivity $R_{xy}$ as $n = B/(R_{xy} e)$. The position of the second Dirac point is found by using $E_{2DP} = \sqrt{\frac{\pi n}{e}} \frac{v_F h}{e}$ where $n$ is the carrier concentration at the gate $-75V + 20V = -55V$. A linear approximation of $n(V_g)$ is assumed and obtained at low doping level. Note the changes in sign of the carrier concentration at high gate voltages. This is characteristic of well-isolated secondary Dirac points where the majority charge carrier changes from electrons to holes or vice versa [2]. All measurements were done at 4K.
Figure S4 – SERS spectra measured at 633 nm (3 points measured in aligned device). Note that the G peak intensity is higher than the BN intensity (left). In the right plot we compared SERS on few-layer graphene (FLG) and single-layer graphene (SLG) on silicon with SERS of a h-BN/graphene superlattice. A strong peak at 1574 cm\(^{-1}\) is observed for graphene/BN superlattices.
Figure S5 – 2D peak dispersion in aligned and misaligned devices. The 2D peak dispersion is 96 and 98 cm\(^{-1}\)/eV in misaligned and aligned superlattices, respectively. This would correspond to a change in Fermi velocity of 2%. This rules out a change of Fermi velocity as a possible cause for the broadening of the 2D peak.

References


STRONG LIGHT-MATTER INTERACTIONS IN ATOMICALLY THIN FILMS OF SEMICONDUCTING TRANSITION METAL DICHALCOGENIDES

My contribution

I set up the photo-current apparatus with the assistance of L.B., measured the photore- sponse of the MoS$_2$ and WS$_2$ heterostructures and assisted L.B. in the preparation of the Figures and the preparation of the manuscript.
Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films

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The isolation of various two-dimensional (2D) materials, and the possibility to combine them in vertical stacks, has created a new paradigm in materials science: heterostructures based on 2D crystals. Such a concept has already proven fruitful for a number of electronic applications in the area of ultrathin and flexible devices. Here, we expand the range of such structures to photoactive ones by using semiconducting transition metal dichalcogenides (TMDC)/graphene stacks. Van Hove singularities in the electronic density of states of TMDC guarantee enhanced light-matter interactions, leading to enhanced photon absorption and electron-hole creation (which are collected in transparent graphene electrodes). This allows development of extremely efficient flexible photovoltaic devices with photoprosensitivity above 0.1 A/W (corresponding to an external quantum efficiency of above 30%).

The advent of graphene (1) and the subsequent discovery of its multitude of superior properties (2–5) has led to the identification of many other two-dimensional (2D) crystals (6) through both chemical modification of graphene and exfoliation of other layered compounds. This new area of research and progress in precise transfer of the crystals while maintaining their quality (7, 8) has resulted in the emergence of a new class of materials: heterostructures based on 2D atomic crystals (5, 8, 9). More specifically, there is the possibility to create hybrid materials by stacking combinations of 2D crystals with differing properties. These structures are interesting from both fundamental and application points of view. It has, for instance, been shown that layering sheets of graphene and hexagonal boron nitride (hBN), molybdenum disulfide (MoS2), or tungsten disulfide (WS2) allows operation of tunneling transistors (9, 10) and permitted the observation of phenomena such as Coulomb drag (11) and the fractional quantum Hall effect (12).

Many other crystals have been found to exfoliate to monolayer by both mechanical (6) and chemical methods (13). TMDC is a group of layered materials that has attracted a lot of interest (14). They are structured such that each layer consists of a three atomic planes: a triangular lattice of transition metal atoms sandwiched between two triangular lattices of chalcogen atoms (S, Se, or Te). There is strong covalent bonding between the atoms within each layer and predominantly weak van der Waals bonding between graphene as a good transparent electrode. Using a Gr/TMDC/Gr stack (here, Gr stands for graphene) with appropriately positioned Fermi levels and simply doping the two graphene layers differently (either by electrostatic gating or chemical methods) leads to large photocurrent. The layered nature of our structures and exceptional mechanical strength of graphene and TMDC crystals (25, 26) also allowed us to fabricate flexible devices. Without illumination, such devices act as tunneling transistors (9, 10).

While we concentrate the experimental data on the properties of Gr/WS2/Gr heterostructures, our results are generic for a large class of systems where semiconducting TMDC are the key element. Our devices comprise of three principal elements—top and bottom graphene electrode layers (both micro-mechanically cleaved and CVD-grown graphene were tested) sandwiching a photoactive TMDC layer (Fig. 1). In the fabrication procedure, the flakes were transferred with the ‘dry transfer’ technique (in the case of micro-mechanically cleaved graphene) (7, 8) with thorough annealing (27) at each stage to ensure minimal contamination between the layers (28) and low level doping of the graphene layers. We also chose to use hBN as both a substrate and an encapsulating layer to achieve a higher doping homogeneity (7, 29). Thus, the final structure of a typical device, on top of an oxidized silicon wafer or flexible PET film, was hBN/Gr/WS2/Gr/hBN. In case of nonflexible devices on Si/SiO2,

adjacent layers. Many of these materials—NbSe2, MoS2, WS2, TaS2, to name a few—are structurally similar but have an array of electronic properties ranging from semiconducting (15), to metallic (16), from charge density waves to superconducting (17), depending on their exact composition, electronic density, geometry, and thickness (18).

Besides the traditional applications of TMDC films as solid state lubricants and industrial surface protection (19, 20), films of these materials have long been considered for photovoltaic devices, due to their large optical absorption, which is greater than 10−4 m−1 across the visible range, meaning that 95% of the light can be absorbed by a 300 nm film. A further advantage of WS2 is its chemical stability (21, 22) and band gaps in the visible part of the spectrum (22–24).

Previously, planar WS2 (21) and MoS2 (22) structures were studied for photovoltaic applications. However, efforts to extract photocurrent have been hampered by the need to create a p–n junction to separate the electron-hole (e–h) pairs, created by incoming photons. Here, we show that, with the arrival of vertical 2D-crystal based heterostructures, a beneficial combination of each material’s properties emerges: TMDC as good photovoltaic materials and graphene as good transparent electrode. Using a Gr/TMDC/Gr stack (here, Gr stands for graphene) with appropriately positioned Fermi levels and simply doping the two graphene layers differently (either by electrostatic gating or chemical methods) leads to large photocurrent. The layered nature of our structures and exceptional mechanical strength of graphene and TMDC crystals (25, 26) also allowed us to fabricate flexible devices. Without illumination, such devices act as tunneling transistors (9, 10).

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the doped silicon could be used as a back gate and SiO₂/hBN (typically 300 nm of SiO₂ and 20 nm of hBN) the gate dielectric. A series of such structures was produced where the thickness of the TMDC layer was varied from ~5–50 nm.

The IV characteristics of our samples strongly depended on illumination (Fig. 2A, left axis). Without illumination, the devices displayed strongly nonlinear IV curves (Fig. 2A, right axis). Comparing the two sets of IV curves, there is strong contrast to when they were illuminated: the resistance drops by more than 3 orders of magnitude and the curves are linear around zero bias. At higher bias (~±0.2 V) they began to saturate, as the number of available charge carriers in the photoactive region becomes limited.

The photocurrent generated in our devices was mapped by scanning photocurrent microscopy, where a laser spot was scanned over the sample, and the resultant photocurrent displayed as a function of laser spot position. Photocurrent is generated only in the region where all three principal layers overlap (Fig. 1C). The origin of the photocurrent can be explained by examining the collective band diagram. In the idealized case the structure is symmetric (Fig. 2B) and the electrons/holes generated in TMDC (by absorption of a photon with sufficient energy) have no preferred diffusion direction and, hence, no net photocurrent is measured. However, in the presence of a built-in electric field (Fig. 2C) across the TMDC (either due to a difference in the initial doping between the graphene sheets or by gating (9)), the e-h pairs are separated and a photocurrent measured.

Immediately after fabrication (which involves the annealing stage) in the undoped state, the devices showed a minimum in the photocurrent, (Fig. 2C) across the TMDC [either due to a difference in the initial doping between the graphene sheets or by gating (9)], the e-h pairs are separated and a photocurrent measured.

We investigated in detail the performance of our prototype photovoltaic devices. An important parameter is the extrinsic quantum efficiency (EQE), defined as the ratio of the number of charge carriers generated to the number of incident photons. This can be expressed in terms of the photocurrent I, incident power per unit area P and excitation wavelength λ by

$$\text{EQE} = \frac{hc}{e} \frac{I}{P \lambda},$$

where h is the Planck constant, c the speed of light in vacuum and e the electron charge. Using the relation for EQE we calculate the efficiency (Fig. 4), where the data were collected for several wavelengths at zero bias and V_fb = −40 V. The extrinsic quantum efficiency did not appear to be dependent on wavelength, as expected from the approximately constant optical absorption, over this range (21). It is likely that the decrease in quantum efficiency with increasing power is due to screening of the built-in electric

$$J_{\text{DOS}}(E) = \frac{1}{4\pi} \sum_{\alpha} \left| d\omega k \Delta E \Delta k \right|$$

where V and C are the valence and conduction bands, respectively. The JDoS is a direct measure of the so-called joint critical points, that is, the van Hove singularities in the Brillouin zone around which a photon of energy, \( \hbar \omega = E_v - E_c \), is very effective in guiding electronic transitions over a relatively large region in momentum space. The large contribution to the transition probability for joint critical points gives rise to the structure observed in the frequency dependence of the optical properties of the TMDC. Thus, the photocurrent, \( I(\omega) \), at some light frequency \( \omega \) is proportional to \( J_{\text{DOS}}(\hbar \omega) \). There is a sharp rise in the photo-absorption in the JDoS of the TMDC in the visible range of all TMDC studied (Fig. 3B). In order to further confirm that our results are not dependent on the thickness of the TMDC, we calculated the DoS and JDoS for bulk (3D) semiconducting TMDCs (27). The peaks in the DoS and the sharp rise of the JDoS is comparable with the values found for a single layer in Fig. 3B, and are consistent with the previous measurements on bulk MoS₂ (32). Hence, the strong light-matter interactions in semiconducting TMDCs is not a unique feature of the bulk material and it can be extended to monolayers.

The effect discussed here has a similar, albeit with a different physical origin, to the strong Raman absorption in 1D semiconducting carbon nanotubes. In that case, the 1D nature of the material leads to 1/\( \sqrt{E} \) singularities in the DoS at the top (bottom) of the valence (conduction) bands, leading also to strong light-matter response (33).

We have also computed the work function, \( \Phi \), for the semiconducting TMDCs studied here. We find that the work functions vary considerably depending on the transition metal used (for monolayer, \( \Phi_{\text{WS₂}} \approx 4.6 \) eV, \( \Phi_{\text{WSe₂}} \approx 4.3 \) eV, \( \Phi_{\text{MoSe₂}} \approx 5.1 \) eV) and their thickness (for bulk, \( \Phi_{\text{WS₂}} \approx 4.2 \) eV, \( \Phi_{\text{WSe₂}} \approx 3.9 \) eV, \( \Phi_{\text{MoSe₂}} \approx 4.5 \) eV). Notice that as the work-function of graphene is not significantly different (\( \Phi_{\text{Gr}} \approx 4.5 \) eV), it has been shown (34) that it has a very minimal effect on the band structure of TMDC, and the Dirac point of graphene stays within the gap, facilitating efficient extraction of both electrons and holes from TMDC.
field by the excited electrons in the conduction band of WS₂.

The already good performance and high EQE of our devices (ensured by the peculiar band structure of TMDC) used can be further improved by optimizing light absorption in the active layer. One possible way—the use of optical resonators (35)—is already partly realized in our devices on SiO₂, where light interference in SiO₂ layer (36, 37) enhances the optical electric field in TMDC (this is one of the reasons of better performance of our devices on SiO₂ in comparison with those on flexible substrates). Another strategy is the utilization of plasmonic nanostructures (38–40) or metamaterials (41). To test the idea, we applied gold nanospheres, Fig. 4C, on top of one of our hBN/Gr/MoS₂/Gr heterostructures, which enhances optical field in the active layer and allowed for 10-fold increase in the photocurrent, Fig. 4, D and E [see (27) for further details and other examples of the use of plasmonic nanostructures].

Atomically thin heterostructures of semiconducting TMDC present strong light-matter interactions that can lead to large photon absorption and photocurrent production. We are able to reach an extrinsic quantum efficiency of 30%, due to the localized character of the electronic wave functions in TMDCs that leads to large peaks in the DoS associated with van Hove singularities. The same devices demonstrate transistor behavior with ON/OFF ratios exceeding those in previously reported devices. The use of various TMDCs, as well as their combinations, would allow one to create new transparent and flexible photonic and optoelectronic structures and devices with unique properties which surpass current technologies.

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Supplementary Materials
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Fig. 1. Device structure and photocurrent mapping. (A) A schematic of the device with the principal layers shown. hBN is not shown. (B) An optical micrograph of one of our devices. The shading of the three constituent layers denotes the regions of the respective materials—top and bottom graphene electrodes shown in red and blue, while WS$_2$ is shown in green. (C) A photograph of one of our flexible devices placed on an electroluminescent mat. (D and E) Photocurrent maps taken before (D) and after (E) doping the top graphene layer with water vapor. A signal is only seen in the area where all three layers overlap. The two graphene layers were connected via 1kΩ resistor, on which the photocurrent was measured. No bias was applied and for both (E) and (D), the maps were taken at gate voltages from –20 V to +20 V. The scale of the maps is given by their width 20 μm.

Fig. 2. Gate dependent IV characteristics. (A) Left axis: IV curves for a device on Si/SiO$_2$ taken under illumination at gate voltages from –20 (red) to +20 V (blue) in 10 V steps, after doping. The laser illumination energy was 2.54 eV and the power 10 μW. The curves are linear at low bias but saturate at higher bias due to limited available charge carriers. Right axis: IV curves for the same device taken in dark at gate voltages from –20 (black) to +20 V (green) in 20 V steps, after doping. (B and C) Schematic band diagram for Gr/WS$_2$/Gr heterostructure with (C) and without (B) a built-in electric field to separate the generated e-h pairs.
Fig. 4. Quantum efficiency. (A) The external quantum efficiency of the devices is the ratio of the number of measured e-h pairs to absorbed incident photons. Due to the small variation in optical absorption across this wavelength range the data for different wavelengths collapse onto a single curve. (B) Photocurrent measured with a 1.95 eV laser as a function of intensity and follows a sublinear dependence. This results in the largest quantum efficiency values at low intensities. Open symbols are for a device on Si/SiO$_2$ substrate, and crossed symbols are for device on a flexible substrate. (C) Schematic representation of hBN/Gr/MoS$_2$/Gr (layers bottom to top) photovoltaic device with gold nanoparticles spattered on top of the top graphene layer for plasmonic enhancement of light absorption. (D and E) Photocurrent maps of one of our hBN/Gr/MoS$_2$/Gr device taken before (D) and after (E) spattering of gold nanoparticles for plasmonic enhancement [illumination parameters: 633 nm, 10 μW; scan size, 14 μm × 14 μm; note the logarithmic scale chosen to represent the 10-fold increase in the photocurrent on (E)].

Fig. 3. Electronic DoS for single layer TMDCs. (A) The DoS for monolayer TMDCs: MoS$_2$, WS$_2$, and WSe$_2$. Strong peaks are present in all three materials which lead to a strong light-matter interaction. (B) The JDoS with the same three TMDC materials.
Supplementary Materials for

Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films


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This PDF file includes:

Materials and Methods
Supplementary Text
Figs. S1 to S9
References
Device preparation

Graphene and thin graphite flakes were produced by micromechanical exfoliation of graphite. We used single crystal WS\textsubscript{2} supplied in powder form by Sigma-Aldrich. Despite an average crystal size of only 2 μm it is possible to find crystals up to 50 μm that could be exfoliated as well.

Recent progress has led to relatively facile fabrication of graphene hybrid devices with a large degree of versatility (7-9). The method allows flakes of layered materials to be transferred to the surfaces of one another with a high degree of accuracy and cleanliness. In this way, stacks of different materials can be created with precise control over the constituents of the new hybrid material.

We have used a so-called ‘dry’ transfer technique (7, 8) to create these structures. This technique involves the mechanical exfoliation of the required flakes onto a dual layer polymer stack. The bottom polymer layer can be selectively dissolved and the resulting membrane inverted and positioned above the target flake—the initial bottom flake was instead cleaved onto a Si/SiO\textsubscript{2} wafer (290 nm oxide). After each transfer the top polymer layer was dissolved and the device annealed thoroughly in a gaseous mixture of H\textsubscript{2}/Ar (10:90) at 250 °C before the subsequent transfer of the next flake. In this way stacks with an arbitrary number of layers can be produced. Once the required flake stack had been fabricated, electrical contact was made via standard photolithographic processing and e-beam evaporation of a Cr adhesion layer (5nm) and Au (50 nm) and placed in a package for measurements. In order to make scanning photocurrent microscopy measurements we utilize a WITec scanning Raman system. The sample was placed onto a piezoelectric stage with laser light incident from above. The laser was focused by a 100x microscope objective with a laser spot size that is diffraction limited (diameter ~500 nm). The laser spot is scanned over the surface and the resultant current flow between the two graphene electrodes is measured simultaneously with the Raman spectra for each point in the scan.

We used chemical vapour deposition (CVD) to fabricate high-quality, large area graphene electrodes. The graphene was grown on 25 μm thick copper (Cu) foil (from Alfa Aesar, item no. 13382). Before graphene deposition, the Cu foils were cleaned with subsequent washes in acetone, DI water and IPA in order to remove both organic and inorganic contamination from the surface. To further improve the CVD graphene quality and increase grain size, the Cu foil was then annealed in a quartz tube for 30 minutes at 1000 °C in a flux of H\textsubscript{2} at 20 sccm and chamber pressure 200 mTorr. Graphene was grown on the Cu surface by adding 40 sccm CH\textsubscript{4} to the gas flow (chamber pressure fixed at 600 mTorr) whilst maintaining a temperature of
1000 °C. The sample was allowed to cool in a H₂ atmosphere and then removed from the chamber at room temperature. The graphene could then be transferred to a silicon wafer by etching of the Cu foil. Details of the transfer procedure are given in ref (42).

**Examples of device operation with molybdenum disulfide (MoS₂)**

The manuscript focuses on the most efficient devices that we measured which were fabricated with WS₂ as the semiconducting region. However, the results apply universally to all the transition metal dichalcogenides. Here we show that a similar behaviour was observed with MoS₂. The devices were fabricated in the same fashion as described above. To summarise, the devices consist of a tri-layer structure comprising a TMDC flake sandwiched between two electrically isolated graphene layers which act as transparent electrodes. The device sits on an oxidised silicon wafer with the doped silicon acting as a gate electrode. The electric field across the semiconducting region can be altered by applying a voltage between the bottom graphene layer and the doped silicon back gate.

**Figure S1 MoS₂ photovoltaic device.**

a The photocurrent of a MoS₂ device as a function of gate voltage for three laser lines: red – 633 nm, green – 514 nm and blue – 488 nm. The device was fabricated on an oxidised silicon wafer (300 nm thick thermally grown oxide – IDB Technologies) with a BN substrate (~30 nm thick) flake. The current flow between the two graphene layers was recorded as a function of the laser spot position as it was raster scanned across the surface. The data points shown are the average values taken from photocurrent maps taken at each gate voltage (shown in panel c). b An optical image of the device where the top (bottom) graphene layer is outlined in green (red) and the MoS₂ flake is outlined by the solid black line. c A photocurrent map taken at V_g = -60 V. The region over which the average photocurrent signal was measured is shown by the dotted outline. This corresponds to the same area shown in b.
The efficiency of our devices fabricated with MoS$_2$ was found to be lower than for WS$_2$. This is unexpected from the calculated DOS which are similar for all the TMDCs but it is speculated that a higher level of impurity atoms such as rhenium present in the MoS$_2$ lattice could be responsible due to creation of impurity states in the band gap which increase the rate of recombination.

![Photocurrent maps recorded over a range of gate voltages from -60 to +60 V. The electric field due to the back gate tunes the sign and magnitude of the photocurrent signal. The region shown in the maps is indicated by the back square shown in the optical image in the bottom right hand panel where the outline of the graphene layers is also indicated by the dashed black lines.](image1)

**Figure S2 Photocurrent maps of a MoS$_2$ device.** Photocurrent maps recorded over a range of gate voltages from -60 to +60 V. The electric field due to the back gate tunes the sign and magnitude of the photocurrent signal. The region shown in the maps is indicated by the back square shown in the optical image in the bottom right hand panel where the outline of the graphene layers is also indicated by the dashed black lines.

**Examples of device operation with GaSe**

![Optical image of a GaSe device with top and bottom graphene contacts as labelled on the image. The outlines of the various component materials are drawn due to the lack of optical contrast. A photocurrent map recorded with a +1 V bias between the graphene electrodes due to the high resistance of the device. The region shown is centred on the active region where the bright area is the overlap top and bottom graphene electrodes with the GaSe crystal. I-V curves taken on the device with and without laser illumination on the active region. The laser was 2.54 eV at an intensity of 90 mW.](image2)

**Figure S3 Photocurrent maps of a GaSe device.**

a. Optical image of a GaSe device with top and bottom graphene contacts as labelled on the image. The outlines of the various component materials are drawn due to the lack of optical contrast.

b. A photocurrent map recorded with a +1 V bias between the graphene electrodes due to the high resistance of the device. The region shown is centred on the active region where the bright area is the overlap top and bottom graphene electrodes with the GaSe crystal.

c. I-V curves taken on the device with and without laser illumination on the active region. The laser was 2.54 eV at an intensity of 90 mW.
Figure S3 shows the optical and corresponding photocurrent map of a GaSe device. The efficiency was found to be lower than for WS$_2$ but qualitatively the same behaviour was observed. As expected the illumination with visible wavelength laser light led to a decrease in the resistivity of the device.

**Power dependent IV curves for WS$_2$**

![IV curves for WS$_2$](image)

**Figure S4 Photoresistivity.** IV characteristics of the device shown in fig 2, under laser illumination of varying intensity. The resistivity of the device changes only when laser light is incident on the region where all three constituent flakes overlap and the slope of the IV curves is dependent on the power. Shown are IV curves taken with a 2.54 eV laser set to a total power of 10, 20 and 30 $\mu$W, all at $V_g = -20$ V. The IV curve without illumination is too small to see on this scale but one can compare with fig. 2 of the main text.

Three IV curves taken at different power’s showing the photo-resistivity dependent on illumination intensity. The saturation current (at higher bias) is proportional to intensity.

**Plasmonic enhancement**

The already good performance and high EQE of our devices (ensured by the peculiar band structure of TMDC used) can be further improved by optimizing light absorption in the active layer. However, the simplest strategy of increasing the thickness of TMDC layer might not be the optimum one, since the internal electric field (which dissociate the electron-hole pairs) decreases as the thickness increases, and also other recombination channels might become more effective, thus reducing the photocurrent. Alternative ways to boost the light adsorption are the use of optical resonators (35) or plasmonic enhancement of light absorption (38-40). The further is already partly realized in our devices on SiO$_2$, where light interference in SiO$_2$...
layer (36, 37) enhances the optical electric field in TMDC (this is one of the reasons of better performance of our devices on SiO$_2$ in comparison with those on flexible substrates).

The latter strategy of utilization plasmonic nanostructures (38-40) or metamaterials (41) allows even more freedom. One can use metal nanoparticles to generate evanescent photons in near-field under light illumination. The proximity to TMDC layer leads to adsorption of such near-field photons in the active layer with very high efficiency, due to specific confinement of such photons(43). We tested this idea on several of our MoS$_2$ by spattering thing layer of gold, which, after successive annealing coagulate into droplets of 5-10nm in height. It has been shown previously, that such strategy allows for a significant enhancement of the Raman signal in graphene(44). Here we observed 10-fold increase of the photocurrent signal after introduction of such plasmonic nanostructures, proving that this strategy is a viable route of pushing the EQE of such heterostructures even higher (Fig. S5).

![Figure S5](image)

**Figure S5 Plasmonic enhancement.** (A) Schematic representation of hBN/Gr/MoS$_2$/Gr device with gold nano-dots on top. (B-C) Optical photograph of one of such device before (B) and after (C) deposition of nano-dots. The size of the images is 50µm×50µm. (D) Dependence of photocurrent on gate voltage. Each point is the average photocurrent over the active area of device. (E-F) Maps of photocurrent as the focused laser beam scans across the active area of device with (F) and without (E) golden nano-dots. The size of each map is 14µm×14µm.
DFT calculations

The density functional calculations were performed using the open source code Quantum Espresso (45). We performed full relativistic calculations with spin-orbit. The exchange correlation energy was described by the generalized gradient approximation (GGA), in the scheme proposed by Perdew-Burke-Ernzerhof (46) (PBE) and a semi-empirical dispersion term (47, 48) (DFT-D) was applied.

The Brillouin-zone (BZ) was sampled for integrations according to the scheme proposed by Monkhorst–Pack (49). A grid of 16x16x16 k-points was used for the bulk samples and a grid of 16x16x1 k-points for the single layer samples. An increase in the number of points did not result in a significant total energy change. The energy cut-off was 150 Ry. An increase in the energy cut-off did not result in a significant total energy change.

We used norm conserving, full relativistic pseudopotentials with nonlinear core-correction to describe the ion cores. The W pseudopotential was produced with 6s2 5d4 electrons in the valence band, Mo with 5s1 4d5 electrons, and S and Se with ns2 np4 electrons in the valence band.

Single layer samples were modeled in a slab geometry by including a vacuum region of 45 Bohr in the direction perpendicular to the surface. The lattice parameters were also relaxed, at the same time as the atoms positions. In the calculations, all the atoms were fully relaxed to their equilibrium positions until there were no forces larger than 0.005 eV/Å.

The electronic density of states was calculated by sampling 17576 points in the BZ for the bulk samples and 3888 in the single layers, and broadened with a 0.01 eV Gaussian width. The tetrahedron method (50) was used.

The equation used to calculate JDoS(E) is given in the main text. A Gaussian broadening of 0.04 eV width was applied.

The continuum energy was determined in the three single layer samples by calculating the total electric potential along the normal to the surface, and taking the value when the potential becomes constant. For the bulk samples, the difference in energy between the lowest energy bands of the bulk and single layer was determined. These bands are sufficiently low in energy that are not much affected by the environment, and keep essentially the same shape in bulk and single layer (except for the factor of 2 resulting from the bulk having twice as many atoms in the unit cell). Figure S6 shows the electronic density of states of the deep bands used to calculate the continuum energy; it can be seen that the shape of these bands are very
similar in the bulk and the single layer. The main differences come from the fact that in the single layer the spin orbit interaction barely removes the degeneracy, while in the bulk it does (see figure S7).

Figure S7 shows the band structure of WSe$_2$ both in bulk and single layer. The zero energy is aligned with the vacuum energy. The notation of the symmetry points is the standard, and is depicted in figure S8.

**Figure S6**: The electronic density of states of deep bands used to calculate the continuum energy of bulk samples. The single layer density of states were multiplied by two to show the superposition of the bands more clearly.

**Figure S7**: The band structure of bulk (left) and single layer (right) of WSe$_2$
DFT calculations for bulk TMDC

In order to further confirm that our results are not dependent on the thickness of the TMDC, we calculated the DoS and JDoS for bulk (3D) semiconducting TMDCs. The sharp peaks in the DoS and the sharp rise of the JDoS is comparable with the values found for a single layer in Fig.3B. Hence, the strong light-mater interactions in semiconducting TMDCs is not a unique feature of the bulk material and it can be extended to monolayers.

Figure S9: Electronic DoS for bulk TMDCs.

(A) The DoS for bulk TMDCs: MoS$_2$, WS$_2$ and WSe$_2$. Similar to the single layer case strong peaks are again present. (B) The JDoS with the same three TMDC materials again showing a sharp rise in the visible range.
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Part III

Conclusion and future plans
Main experimental results

In conclusion, this thesis has shown investigation of the electronic, optical and vibrational properties of graphene, its chemical derivatives, and graphene based heterostructures, including h-BN/graphene superlattices.

Raman spectroscopy has been extensively used because this technique allows a fast rich characterization of graphene. It is for instance sensitive to defects, stacking order, doping. This technique is particularly well suited for the investigation of graphene because the Raman scattering processes involve resonant conditions and strong electron-phonon coupling effects, which makes the spectrum extremely sensitive to changes in the electronic structure and doping level.

The work presented here started with the quantification of the strength of the resonance and compared it with other materials. Therefore, Chapter 3 was dedicated to the calculation of the Raman scattering efficiency (also called Raman cross section) of the G and 2D peaks. This requires comparing the intensity of the Raman peaks as compared to the intensity of a well known material, which is used as a reference, exactly under the same conditions (substitutional method). We have shown that silicon cannot be used as reference material because it does not allow one to measure the intrinsic intensity of the Raman peaks: first, the Raman intensities are affected by the doping produced by the charged impurities in the substrate; second the oxide layer on top of the silicon wafer acts as a spacer which modulates the Raman intensities with the excitation energy. Our measurements show that the dependence of the Raman intensities on the excitation energy strongly depends on the thickness of the oxide layer, in agreement with calculations made with the transfer matrix method for layered structures. Calcium fluoride (CaF\(_2\)) has often been used as a reference material because it is a wide band gap insulator with a known scattering efficiency. It further presents the advantage of suppressing the interference effects. Therefore, graphene was directly placed on a CaF\(_2\) substrate so that the Raman spectrum of CaF\(_2\) and graphene could be measured at the same time under exactly the same conditions. The Raman spectra of graphene on CaF\(_2\) are defect-free (no D peak) and display a very low doping level. This means that the analysis of the intrinsic Raman intensities is not flawed by the presence of doping or defects. The Raman scattering efficiency was obtained by comparison with the 322 cm\(^{-1}\) peak area of CaF\(_2\). At 2.41 eV, the Raman efficiency of the G peak is about 200 \(\times 10^{-5}\) m\(^{-1}\) Sr\(^{-1}\), and changes with the excitation energy to the power of 4. The 2D Raman efficiency is at least one order of magnitude higher than that of the G peak, with a different excitation energy dependence. Furthermore, its absolute value strongly depends on light polarization. The high Raman scattering efficiency of the 2D peak and its dependence on the excitation energy further confirm the resonant nature of the Raman process activating this peak.

The Raman intensities of defective graphene were then addressed. The two-dimensional nature of graphene allows the introduction in the crystal of specific type of defects with a controllable concentration which makes the investigation of the sensitivity of the Raman
spectrum on the nature of defects possible. Defective graphene samples were produced by partial hydrogenation, fluorination and oxidation. In this last case, particular attention was paid to the plasma conditions used in order to functionalize graphene instead etching the material. A study of other defective sheets produced by implantation of boron atoms and anodic bonding under non optimal conditions was presented. We show that anodic bonding is a simple alternative method to mechanical exfoliation to fabricate high quality graphene. Moreover, it is completely solvent and tape free, which reduces the number of contamination sources. However, the quality of the crystals strongly depends on the deposition parameters such as voltage and temperature. Atomic force microscopy and Raman mapping show that under non optimal conditions graphene is defective and characterized by holes with average size of 80 nm. Overall, we investigated defective graphene containing three types of defects: \( \text{sp}^3 \) sites, vacancy-like defects, and boron atoms. The systematic analysis of the amorphisation trajectory shows the same behaviour for all types of defects here investigated with a characteristic two-stage evolution. At low defect concentration, stage I is characterized by an increase of \( \frac{I(D)}{I(G)} \) for increasing defect concentration, while the full width at half maximum of the peaks are roughly constant; Stage II, at higher defect concentration, is characterized by a decrease of \( \frac{I(D)}{I(G)} \) for increasing defect concentration and strong broadening of the Raman peaks. Thus, attention must be paid when using \( \frac{I(D)}{I(G)} \) to quantify defects. Overall, we did not observe any strong dependence of \( \frac{I(D)}{I(G)} \) with different defective graphene samples. However a careful analysis of the Raman spectra shows that the D’ peak is strongly sensitive to the type of defects. For vacancy-like defects, \( \frac{I(D)}{I(D')} \) is 7, while it is, 13, 9 and 3 for \( \text{sp}^3 \) sites, substitutional atoms and grain boundaries (in graphite), respectively. A change in \( \frac{I(D)}{I(D') \) is in agreement with tight binding calculations, but our experimental values do not match with the calculated ones. We attribute this discrepancy to the simple model used to simulate defects in the tight binding calculations. In the framework of the local activation model, we attribute the strong dependence of the D’ peak on the nature of defects to the factor \( C_{S,D'} \) which is found to be 2.5 times larger for vacancies than for \( \text{sp}^3 \) sites.

Bilayer appeared to be less reactive than monolayer for a single sided exposure to oxygen plasma. This is attributed to the modification of the top layer while the bottom layer conserves its pristine graphene properties, eventually leading to a decoupling between the two layers. This may explain the relatively good mobility we have measured for modified bilayer. As a result, oxidized bilayer graphene is an ideal candidate as active material in biosensors as it benefits from both an easy to functionalize layer combined to a highly conductive layer for electrical sensing of species grafted on the top layer. Double sided functionalization of a suspended bilayer graphene was demonstrated and opens the way to asymmetric functionalization of graphene and thus increases the arrays of possible modification of the properties of graphene.

A simple way to tune the properties of graphene without modifying its structure by in-
Introducing defects is to use the periodic potential generated by another crystal. Hexagonal boron nitride (h-BN) is a perfect candidate to make superlattices: its structure resembles that of graphene with boron and nitrogen atoms placed in a honeycomb lattice, but characterized by a lattice constant $\sim 1.8\%$ larger than the one of graphene, due to the longer B-N bond compared to the C-C. The creation of a moiré pattern modifies the low energy band structure of graphene by introducing minigaps, whose energy depends on the rotational angle between graphene and h-BN. We show that the Raman spectrum of h-BN/graphene superlattices strongly changes at very small twist angles. A characteristic broadening of the 2D peak is observed and attributed to the reconstruction of the Dirac cone. This allows fast identification of aligned h-BN/graphene by Raman spectroscopy, enabling further studies of these systems.

Finally, the possibility to combine graphene with other two-dimensional crystals is discussed, for example with the good light absorber material WS$_2$ in vertical heterostructures. The high absorption of WS$_2$ is attributed to the presence of van Hove singularities in the density of states of WS$_2$ that enhances the light matter interaction. A graphene/WS$_2$/graphene sandwich acts as a flexible photovoltaic device with an external quantum efficiency as high as $30\%$ and a response on the order of 0.1 A/W. The photoreponse can be further improved by plasmonics, i.e. by depositing gold nanoparticles on top of the heterostructure.

**Future work and perspectives**

This thesis discussed a broad range of modifications of the properties of graphene with means to control and monitor them. For instance, the ability to introduce defects of controllable types and amount in localized areas of the graphene sheet could lead to the creation of complex electronic devices entirely made of graphene. The patterning of defected areas could be achieved by substrate engineering. The chemical reactivity of graphene is indeed influenced by the type of substrate where it is deposited and more work testing different grades of materials should give a better understanding on what features affect the chemical reactivity of graphene.

Moreover, preliminary results and theoretical calculations show that tensile strain also affect the chemical reactivity of graphene to a hydrogen plasma. Strain engineering through a lithographic patterning of the substrate can be a possible route towards localized hydrogenation of graphene. Asymmetric functionalization of graphene or bilayer graphene membranes, for instance hydrogenated on one side and fluorinated on the other side is another unexplored route for the modification of graphene properties.

The advent of graphene-based vertical heterostructure is also particularly promising. As far as superlattices are concerned, the BN/graphene case has already shown promising features. The method presented here to probe by Raman spectroscopy the relative orientation of the lattice straight after transfer of graphene on BN should accelerate the other-
wise tedious fabrication of such structures. However, some of the features characteristic of graphene/graphene superlattices have not yet been observed such as the enhancement of the G peak when the excitation energy matches the van Hove singularities produced by the interaction of the bottom Dirac cones with the top ones. In graphene/BN superlattices, these van Hove singularities appear at energies too low to be probed with visible excitation energies. Therefore, Raman spectroscopy with infrared excitation lines should give a deeper insight on the electronic reconstruction occurring in such structures. Gateing of these superlattices should also be done as some quantum pathways in the Raman scattering mechanism can be blocked. Doping graphene above the superlattice minigap energy is feasible and should result in different superlattice Raman spectra than for the undoped case. It would also be interesting to study the case of other superlattices, such as Graphene/MoS2, MoS2/WS2 and other materials. For these studies, optical characterization methods such as Raman spectroscopy and photoluminescence measurements are particularly adapted.

More work should also be done towards scalability of the graphene/WS2 photovoltaic device. The demonstration of a relatively strong photovoltaic effect in graphene/WS2 was indeed made on a sample with an active regions of only a few microns across. This is limited by the use of high quality flakes obtained by micromechanical exfoliation which only yields small flakes. First of all, the size of such devices must be increased and adapted to film technologies. Methods to produce thin films of high quality TMDCs must be developed alongside the slightly more advanced production of graphene conductive, flexible and transparent films. CVD and liquid phase exfoliation are possible candidates.

Finally to generate a sufficient power for future applications, several routes must be explored, and perhaps combined. The EQE can be further enhanced by both improving light absorption or charge separation. On the one hand, light absorption can be increased for instance by surface texturing for an improved trapping of the light in the photoactive material as is done in commercial Si-based solar cells. In addition, well defined plasmonic structures could enhance the incoming electromagnetic field and concentrate it on the photoactive region. On the other hand charge separation depends on the built-in field that drives the photoexcited charges to the electrodes before they recombine. Thus creating an asymmetry between the two electrodes is necessary and could be achieved by chemical intercalation of one or both of the electrodes with intercalants of opposite doping effects.

However the demonstration of a photovoltaic cell at the micro-scale with a current of switchable polarity could be embedded in more complex self-powered optoelectronic micro-devices.
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