Scanning photocurrent microscopy of carbon nanostructures

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Abstract

In this thesis, the electronic structures of low-dimensional carbon allotropes have been studied. In particular, the spatially-resolved photocurrent responses of devices comprising carbon nanostructures were investigated through scanning photocurrent microscopy (SPCM). Experiments were first performed on individual semiconducting single-walled carbon nanotubes, which were simultaneously used to explore the scope of this technique. The effects of the drain-source and gate voltages on the photocurrent response of the nanotubes were systematically studied, and the resulting images revealed that the photoresponses reflect the distribution of the electrostatic potential within the tubes, thus demonstrating the potential of SPCM as a tool for the determination of the electronic band structure profile of such nanodevices. In addition, it was verified that the gate dependent evolution of the nanotube bands agree remarkably well with the widely accepted Schottky barrier transistor model for nanotube-based field-effect transistor devices. Moreover, evidence for the *p*-type doping of the nanotubes under ambient conditions was obtained. The photoresponse signal could also be employed for the estimation of the Schottky barrier height at the metal contacts.

SPCM measurements on carbon nanotube networks revealed a highly localized photoconductive response at a few of the constituting crossed nanotube junctions, thus evidencing that the electrostatic potential drops in a rather inhomogeneous manner within the networks. In order to shine light on the origin of this localization and its implication for the electrical transport in these technologically important devices, individual crossed junction devices were extensively investigated. Zero drain-source bias photocurrent images enabled the direct observation of Schottky barriers and isotype p-p heterojunctions at metallic-semiconducting and semiconductingsemiconducting nanotube crossings, respectively. Furthermore, electrostatic potential profiles obtained from gate dependent SPCM images showed that the metal contacts dominate the dark- and photo-current response in the ON states, while the inter-tube crossings play a more important role in the OFF state. This conclusion provides valuable insights into the electrical response of the corresponding crossed junction devices.

Finally, SPCM was successfully applied to evaluate the impact of the electrical contacts and the sheet edges on the properties of graphene devices. In analogy to the case of carbon nanotubes, strong photocurrent responses were detected around the contacts, thus evidencing the presence of metal-induced doping of the graphene flake. By analyzing the intensity of the photoresponses as a function of gate voltage, the Fermi level shift induced by the graphene doping could be estimated. Moreover, gate dependent photocurrent images revealed that the n- to p-type transition does not occur homogeneously within the graphene flake, surrounded by p-type conducting edges, was observed in the vicinity of the Dirac point. The invasive nature of the metal contacts on graphene was further revealed by SPCM experiments on multi-terminal devices.

Keywords: carbon nanotubes, carbon nanotube networks, graphene, photoconductivity, scanning photocurrent microscopy, field-effect transistor

Résumé

Cette thèse est consacrée à l'étude de la structure électronique d'objets de faible dimensionnalité à base de carbone. En particulier, l'utilisation d'un microscope confocal permet d'obtenir la distribution spatiale du photo-courant induit dans ses objets. Cette technique microscopie de photo-courant à balayage laser (MPCBL) - a tout d'abord été validée sur des nanotubes de carbone mono paroi semiconducteur. L'influence du potentiel source-drain et de celui de la grille sur le photo-courant induit a été étudie de façon systématique. Il en a été déduit que la réponse du nanotube est directement relié au potentiel électrostatique de celui-ci et qu'il est donc en conséquence possible d'utiliser cette technique afin de déterminer la structure de bande de ces nano-objets. De plus, l'évolution de la structure de bande du nanotube lors des changements du potentiel de la grille est en accord avec le model Schottky de fonctionnement d'un transistor à effet de champ et il est possible d'estime la hauteur de la barrière de Schottky. Il a été également démontré que le nanotube est dopé positivement en conditions ambiantes.

Les mesures de photo-courant prises sur des réseaux de nanotubes on mit à jour le fait que la réponse de ceux ci provident principalement de certaines intersections entre nanotubes ce qui suggère que le potentiel électrostatique ne décroit pas de façon homogène dans le réseau. Afin de comprendre ces phénomènes de localisations et les conséquences de ceux-ci dans les applications, la réponse se produisant à l'intersection entre deux nanotubes a été étudié de façon approfondie. A tension source-drain nulle, les images de photo-courant ont permis l'observation de barrière de Schottky lorsqu'un nanotube métallique croise un semiconducteur et d'hétéro jonction de type p-p lorsqu'il s'agit de deux tubes semiconducteur. De plus, l'acquisition du potentiel électrostatique du système lorsque la tension de grille est variée à permis de mettre en évidence le fait que les contacts métallique domine la réponse en condition de courant d'obscurité ainsi que lorsque les nanotubes se trouvent en état conducteur (ON state) alors que les intersections inter-tubes joue un rôle important lorsque les tubes sont en état isolant (OFF state). Ce fait est important pour éclairer le comportement de dispositifs comportant des intersections de nanotubes.

Finalement, la technique MPCBL a été utilise pour évaluer l'effet que les contacts métallique ont sur les propriétés de transport des feuillets de graphene ainsi que l'effet des bords des feuillets eux-mêmes. De façon similaire au cas des nanotubes de carbone, une forte photo réponse ont été détectée en périphérie des contacts mettant ainsi en évidence l'effet dopant de ceux-ci sur le graphene. En étudiant la variation de cette réponse en fonction de la tension de grille il est possible d'estimer le déplacement du niveau de fermi induit par ce dopage. De plus, l'acquisition d'images de photo-courant permettent de montrer que les transitions de l'état n vers p(ou inversement) ne se propagent pas de façon homogène dans le feuillet. En effet, le centre du feuillet est de type n alors que les bords sont de type p à proximité du point de Dirac. L'effet dopant des contacts métalliques a également été étudié par des expériences conduites avec plusieurs contacts par feuillet au lieu de deux.

Mot-clefs: nanotubes de carbone, réseaux de nanotubes, graphene, photoconductivité, microscopie de photo-courant à balayage laser, transistor effet champ

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Chapter 1

General concepts

Carbon is an unique chemical element, due to its ability to form an extremely rich variety of compounds. Moreover, the fact that it constitutes the basis of organic chemistry, and hence of life itself, clearly demonstrates its importance. However, interest in carbon is not only restricted to organic compounds, but also extends to the characteristics and properties of its solid allotropes. Although natural carbonaceous materials have been known to mankind since prehistorical times, it was only in the nineteenth century that the structural difference between diamond and graphite was clarified [1].

In recent years, the discovery of graphitic materials of different dimensionalities constituted a major breakthrough in carbon research. Interestingly, the journey from three to lower dimensions was quite abrupt, starting with the emergence of the zero-dimensional fullerenes. The most prominent fullerene, C_{60} , was first reported by Kroto *et al.* [2] in 1985. In the following years, the fullerene family expanded considerably with reports on other closed polyhedra of varying size, leading the community to speculate the existence of graphitic cylinders as an ultimate limit for the size of fullerenes. In the early nineties, Sumio Iijima reported on the observation of such one-dimensional carbon nanotubes (CNTs), both in the multi- and single-walled forms [3, 4]. Last but not least, the much sought graphene, the two-dimensional form of graphite, was finally reported in 2004 by Novoselov *et al.* [5]. Despite being the latest addition to the family of graphitic materials, graphene can be seen, from a structural point of view, as the "mother" of all other dimensionalities, as schematically illustrated in Figure 1.1.



Figure 1.1: Graphitic materials of different dimensionality. Two-dimensional graphene can be considered as the "mother" of all other dimensionalities, *i.e.* fullerenes (0-dimension), carbon nanotubes (1-dimension) and graphite (3-dimensions). From ref. [6].

1.1 Low-dimensional carbon structures

1.1.1 Graphene

Studies on the electronic structure of graphene date as early as the first half of the twentieth century [7], when they were largely motivated by research on the properties of graphite. As shown in Figure 1.2, graphene represents a monolayer of carbon atoms arranged in a two-dimensional hexagonal lattice. The dotted rhombus represents the corresponding unit cell, which contains two distinct carbon atoms, and with $\vec{a_1} = (\frac{\sqrt{3}}{2}a, \frac{1}{2}a)$ and $\vec{a_2} = (\frac{\sqrt{3}}{2}a, -\frac{1}{2}a)$ as the unit vectors, where a = 0.246 nm is the lattice constant. Tightbinding calculations can be employed to determine the energy dispersions of graphene's π (valence) and π^* (conduction) bands, which are most relevant for its physical properties. This yields the following eigenvalues:

$$E_{g2D}^{\pm}(\mathbf{k}) = \frac{\epsilon_{2p} \pm \gamma_0 w(\mathbf{k})}{1 \mp sw(\mathbf{k})},\tag{1.1}$$

where **k** corresponds to the two-dimensional wavevector, ϵ_{2p} is the orbital energy of the 2p level, γ_0 is the transfer energy, s is the overlap integral, and E_{g2D}^- and E_{g2D}^+ denote the dispersions for the bonding (π) and anti-bonding (π^*) bands, respectively. Furthermore, the function $w(\mathbf{k})$ is given by:



Figure 1.2: Schematic representation of the hexagonal graphene lattice, which is formed by two sublattices of inequivalent carbon atoms A and B. The dotted rhombus corresponds to the unit cell, whereas $\vec{a_1}$ and $\vec{a_2}$ are the unit vectors.

$$w(\mathbf{k}) = \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}.$$
 (1.2)

In Figure 1.3, the energy dispersion of graphene is plotted from equation (1.1) with $\epsilon_{2p} = 0$, $\gamma_0 = 3.013$ eV and s = 0.129, parameters obtained by fitting the tight-binding dispersion to *ab-initio* calculations of graphene [8]. The first Brillouin zone of graphene's reciprocal lattice is indicated by the white lines in the contour plots of the π and π^* energy bands in Figure 1.3b, where the high symmetry points K, Γ and M are also shown.

The major features of the electronic structure of graphene are the degeneracy of the π and π^* bands at the K points of the reciprocal lattice, at which position the Fermi level is located, and the fact that the energy dispersion around these points is linear, as apparent from the energy dispersion shown in Figure 1.3c. Due to this linearity, low-energy quasiparticles are better described by the Dirac equation, and should mimic the behavior of relativistic particles. Accordingly, their energy dispersion is given by $E_{graphene} = \hbar v_F \sqrt{k_x^2 + k_y^2}$, which is analogous to that of photons, $E_{ph} = \hbar ck$, but with the velocity of light c replaced by the Fermi velocity v_F .



Figure 1.3: (a) Tight-binding two-dimensional energy dispersion plot of graphene. The upper (π^*) and lower (π) bands are degenerate at the K points in reciprocal space. It can be seen that the bands are approximately linear in the vicinity of the Fermi level (E = 0). (b) Contour plots of the energy dispersion of the π^* and π bands. The white lines indicate the limits of the first Brillouin zone. (c) Line profile of the energy dispersion along the K $\rightarrow \Gamma \rightarrow M \rightarrow K$ direction.

1.1.2 Carbon Nanotubes

Carbon nanotubes are quasi-one dimensional graphitic structures that exist either in the form of a single cylindrical shell or as concentric arrangements thereof. They are respectively known as single- and multi-walled carbon nanotubes (SWNTs and MWNTs). A SWNT can be thought of as being formed by rolling up a graphene sheet in the shape of a cylinder, as depicted in Figure 1.1. The many geometrical ways in which a graphene layer can be wrapped into a SWNT result in an intriguing structural property of nanotubes, known as helicity or chirality.

By considering the underlying hexagonal graphene lattice, the unit cell of a SWNT is defined by two vectors, namely the chiral $(\vec{C_h})$ and the translational (\vec{T}) vectors, as illustrated in Figure 1.4. The chiral vector $\vec{C_h} = n\vec{a_1}$ $+ m\vec{a_2} \equiv (n, m)$, which is parallel to the circumferential axis of the CNT, is able to completely define the structure of a nanotube. CNTs can be further described in terms of the chiral angle θ , *i.e.* the angle between the vectors $\vec{C_h}$ and $\vec{a_1}$, which assumes values between 0° and 30°. Interestingly, SWNTs with $\theta = 0^\circ$ and $\theta = 30^\circ$, known as of zigzag (m = 0) and armchair (n = m)type, respectively, are the only nanotubes that possess mirror symmetry. All other SWNTs exist as pairs of enantiomers.



Figure 1.4: Unit cell of a (3,3) armchair carbon nanotube (shaded rectangle), with $\vec{T} = (1,-1)$ and $\theta = 30^{\circ}$.

Due to the close structural relation between carbon nanotubes and graphene, the energy dispersion of the former can be readily obtained from that of the latter by applying the zone-folding scheme. In this approximation, periodic boundary conditions are imposed on the SWNT circumferential axis, thus leading to the quantization of the wavevector associated with $\vec{C_h}$ (*i.e.*, $\vec{K_1}$). Since the wavevector associated with the translational axis (*i.e.*, $\vec{K_2}$) remains continuous (in case of an infinite SWNT), the nanotube energy bands consist of a set of N/2 one-dimensional energy dispersions (N being the number of carbon atoms in the unit cell), which are cross-sections in the 2D dispersion of graphene. If one of the lines that represent the allowed wavevectors crosses the K point of the graphene reciprocal lattice, a finite density-of-states is observed at the Fermi level, rendering the nanotube metallic (Figure 1.5a). By contrast, a finite energy band gap between the valence and conduction bands emerges in case the lines do not intersect the K points, as illustrated in Figure 1.5b.

The dispersion relations of SWNTs can be analytically calculated within the zone folding scheme framework, by applying appropriate periodic boundary conditions. It is noteworthy that due to symmetry reasons, this calculation becomes much more complicated for chiral nanotubes. On the other hand, for the much simpler case of the (n, n) armchair nanotubes, the following energy eigenvalues are obtained:

$$E_q(k) = \pm \gamma_0 (1 \pm 4\cos\frac{q\pi}{n}\cos\frac{ka}{2} + 4\cos^2\frac{ka}{2})^{\frac{1}{2}}, \qquad (1.3)$$
$$(-\pi < ka < \pi), \ (q = 1, ..., 2n)$$



Figure 1.5: Energy dispersion of (a) metallic and (b) semiconducting carbon nanotubes (left panels) obtained by applying the zone folding scheme. The green lines represent the allowed wave vectors. The crossing of these lines at the K points of the reciprocal lattice renders the nanotubes metallic. The density of states of the metallic (15,0) and the semiconducting (14,4) nanotubes are shown in the right panels. The double-arrows labeled as $E_{ll}^{s,m}$ indicate the interband optical transition energies, between the van Hove singularities.



Figure 1.6: (a) Calculated energy dispersion of a (3, 3) armchair SWNT, where two pairs of subbands are non-degenerate (black lines), while the remaining subbands are doubly-degenerate (green and blue lines). (b) Plot of the corresponding density of states.

where k is the one-dimensional wavevector, and the overlap integral s is taken to be zero. The energy dispersion of the (n, n) SWNT comprises 2npairs of valence and conduction subbands, out of which 2 are non-denegerate and (n-1) are doubly degenerate, as shown in Figure 1.6a for a (3, 3) nanotube. The corresponding density of states (DOS) plot is shown in Figure 1.6b, where a finite constant value is observed around the Fermi level, evidencing the metallic character of the nanotube. Moreover, as also shown in Figure 1.5, pronounced peaks, which are characteristic of the quasi-one dimensionality of the CNTs, are observed on the DOS plots. These peaks correspond to van Hove singularities, which appear around the onset of each subband, and largely determine the electrical and optical properties of carbon nanotubes. The energy spacing between pairs of van Hove singularities, located symmetrically with respect to the Fermi level, is denoted as $E_{II}^{s,m}$ where s and m signify respectively semiconducting or metallic character, and *l* refers to the number of the peak, starting from the Fermi level. For instance, E_{11}^s corresponds to the energy difference between the first set of singularities around the Fermi level of a semiconducting nanotube. The $E_{ll}^{s,m}$ values are related to the optical absorption resonances of a nanotube.

1.2 Electrical Properties

Since the early stages of nanotechnology research, particular interest has been focused on the electrical properties of nanostructures, not only due to the possibility of investigating the effects of quantum confinement on the electrical transport through such materials, but also toward potential electronic applications. Carbon nanotubes have been studied from this perspective for over a decade [9], whereas graphene has only more recently entered the spotlight [6]. This section briefly discusses the main electrical properties of these 1D and 2D carbon nanostructures.

1.2.1 Graphene

As discussed above, the π and π^* bands of graphene are degenerate at the K points of its reciprocal lattice, where the Fermi level is located. Therefore, graphene behaves as a zero band-gap semiconductor, whose valence band is completely filled and conduction band empty (at T = 0 K). The position of the Fermi energy can be shifted with respect to the charge neutrality (Dirac) point by an applied electric field. Such electrostatic doping of graphene can be observed by measuring the sheet resistance as a function of the gate voltage (V_{qs}) , as shown in Figure 1.7. A peak is observed in the resistance curve,



Figure 1.7: Resistance plot of a graphene device as a function of the gate voltage. The peak in resistance is observed at the charge neutrality point, also known as the Dirac point, where the charge carrier density n tends to zero. Electrostatic hole (electron) doping occurs at negative (positive) gate voltages.

corresponding to the situation where the Fermi level is aligned with the Dirac point. The charge carrier density, on the other hand, can be continuously increased by the applied gate voltage, thus leading to a decrease in sheet resistance.

The gate-induced surface charge density in a parallel plate capacitor is given by the relation $n = \alpha V_{qs} = \epsilon_0 \epsilon V_{qs}/te$, where ϵ_0 and ϵ are the permittivities of vacuum and the gate dielectric (usually SiO_2), respectively, e is the electron charge and t is the thickness of the gate oxide. By considering devices prepared on silicon substrates with a 300 nm-thick SiO₂ layer, α corresponds to approximately 7.2×10^{10} cm⁻² V⁻¹. This value agrees remarkably well with those experimentally obtained through electrical measurements in graphene devices, thus indicating that all of the induced charge carriers in graphene are mobile [10]. Interestingly, the conductivity does not disappear at the limit of vanishing charge carrier density. Instead, a conductivity minimum of $\approx 4e^2/h$ is observed, which was suggested to correspond to a conductivity quantum [10]. Although several models based on the Dirac fermion character of graphene quasiparticles point toward the existence of such a minimum quantum conductivity, the values obtained experimentally (*i.e.*, $4e^2/h$) overestimate those predicted theoretically by a factor of π [6]. Recently, Adam et al. [11] proposed a model that is able to explain the relatively large observed minimum conductivities, by analyzing graphene devices from the perspective of semiconductor physics. This model is based on the assumption that charged impurities present on the substrate induce charges within the graphene flake, thus leading to the formation of puddles of electrons or holes. Therefore, in the low carrier density regime (*i.e.* around the Dirac point), electrical transport in graphene devices is governed by the formation of percolating paths of such electron-hole puddles. Experimental support for this model was provided by a scanning single electron transistor study, wherein the observation of electron- and hole-rich regions was reported [12]. Moreover, recent experiments have shown that the minimum conductivity in suspended graphene devices approaches the theoretically predicted value of $4e^2/\pi h$ [13], thus further highlighting the drastic effect of charged impurities.

From the point of view of electronic applications, the high mobility of the quasiparticles is perhaps the most interesting feature of graphene. Early studies on graphene devices reported temperature independent mobilities on the order of 10^4 cm² V⁻¹ s⁻¹, which are retained even at large carrier densities [5, 10, 14]. Furthermore, mobilities improved by approximately one order of magnitude were measured in suspended graphene samples [13]. The reported mobilities exceed by far those of silicon devices [15], and point toward the presence of ballistic transport on length scales below $\approx 0.3 \ \mu m$ at room temperature.

1.2.2 Carbon nanotubes

The electrical resistance of a material is significantly affected by the different scattering mechanisms in which its charge carriers are involved. While the interaction between charge carriers and static potentials, such as structural defects and impurities, is elastic, phonon scattering mechanisms are inelastic [16]. The electrical properties of CNTs are dominated by inelastic scattering, since their quasi-one dimensional character renders elastic scattering mechanisms unfavorable [9]. For example, elastic scattering by small angles is not allowed in a one dimensional material, since carriers exhibit either forward or backward motion. On the other hand, charge carriers in CNTs are able to inelastically interact with low-energy acoustic phonons, or alternatively, with optical phonons. Theoretical calculations have shown that the electron-acoustic phonon coupling in CNTs is relatively weak [17], which leads to long mean free paths of the order of one micrometer for low applied bias. Under these conditions, short SWNTs can exhibit ballistic electrical transport, whereas nanotubes with lengths of a few micrometers display diffusive transport albeit with high carrier mobilities ($\approx 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [18]. However, as the energy of the carriers increases and reaches that required to excite optical ($\sim 180 \text{ meV}$) phonons, inelastic scattering becomes effective



Figure 1.8: Schematic view of (a) a MOSFET and (b) a CNFET. In the case of MOSFETs, the source (S) and drain (D) contacts are composed of heavily doped silicon, which renders them Ohmic.

and the mean free path decreases to approximately 10-20 nm. Such scattering has been observed in metallic CNTs, where a current saturation of approximately 25 μ A is observed as a result of the impact excitation of optical phonons by carriers accelerated at high bias [19]. Nevertheless, metallic tubes sustain remarkably high current densities (~ 10⁹ A/cm²), which make them interesting for application as interconnects in integrated circuits.

1.2.3 Carbon nanotube field-effect transistors

In contrast to metallic carbon nanotubes, the electrical transport through semiconducting CNTs is highly sensitive to external electric fields, and can be switched between a conducting (ON) and an insulating (OFF) state. Such switchability constitutes the basic requirement for field-effect transistor (FET) applications.

The most commonly used FET is the metal-oxide-semiconductor fieldeffect transistor (MOSFET), which is composed of a semiconducting body with source and drain contacts, and whose conductivity is modulated by an applied gate voltage (Figure 1.8) [15]. Although carbon nanotube field-effect transistors (CNFETs) are conceptually very similar to MOSFETs, several distinguished features are related to the use of carbon nanotubes as the semiconducting channel [20]. For example, the gate coupling efficiency is expected to be significantly improved, due to the reduced physical dimensions of the CNTs. In addition, the absence of dangling bonds on the walls of CNTs prevents scattering by surface states, a common source of degradation of MOSFETs. However, as discussed previously, the major advantage of CNTs relates to their low scattering probability, which gives rise to carrier mobilities



Figure 1.9: Schematic illustration of the operation mechanism of a *p*-doped MOS-FET. (a) Band alignment along the M-O-S (gate-gate oxide-semiconductor) axis at $V_{gs} = 0$ V. (b) By applying a positive gate voltage, the band bending increases, such that when the bottom of the semiconductor conduction band (CB) lies below the Fermi level (E_F), a 2D electron gas is induced at the gate oxide interface (*inversion*). (c) By contrast, negative gate voltages induce a hole gas at the O-S interface (*accumulation*).

orders of magnitude higher than those found in standard semiconductors such as silicon.

In spite of the conceptual similarities, the operating mechanism of CN-FETs is fundamentally different from that of MOSFETs. This difference mainly originates from the fact that in MOSFETs, Ohmic contacts can be readily obtained by doping, whereas Schottky barriers are typically present at the electrical contacts of CNTs. Due to their Ohmic nature, transport barriers are absent at the electrical contacts of MOSFETs, and hence the device conductivity is governed by the charge carrier density within the semiconductor channel. More specifically, the carrier density is very low in the OFF state, being given by the (weak) bulk doping concentration, and as a result, high device resistivities are observed. Application of a gate voltage then electrostatically accumulates carriers, resulting in semiconducting channel composed of a high mobility two-dimensional gas at the interface with the gate oxide, *i.e.* the MOSFET is switched ON. This regime is known as *accumulation* or *inversion*, depending on whether the involved carriers are of the same or opposite type, than those in the bulk (Figure 1.9).

Typically, CNT devices contain metals like Au, Pd, Ti and Al for the source and drain electrodes. The difference in the work-functions of the metal and of CNT ($\Phi_{CNT} \sim 4.7 \text{ eV} \pm 0.2 \text{ eV}$) leads to charge transfer across the interface, which results in an energy barrier (Schottky barrier) that limits charge carrier injection from the contacts. The alignment of the Fermi levels of the metal and the CNT, and consequently the Schottky barrier



Figure 1.10: A CNFET operating as Schottky barrier transistor. In the ON states of the device, the Schottky barriers become sufficiently thin to allow efficient charge carrier injection by tunneling. On the other hand, carrier injection is strongly suppressed in the OFF state.

height, depends on their respective work functions (Φ) and the nanotube band gap. Reduced barrier heights for hole injection are observed by using high work-function metals, such as Au or Pd ($\Phi_{Au,Pd} \sim 5.1 \text{ eV}$), for the electrodes [21]. At the same time, the Schottky barrier for electrons is maximal, and hence the corresponding device behaves as an unipolar *p*-type FET. Martel *et al.* [22] were able to fabricate CNFETs with TiC contacts, where the CNT Fermi level is located close to mid-gap, thus resulting in an ambipolar electrical characteristic. More recently, unipolar *n*-type CNFETs were realized prepared by using Sc ($\Phi_{Sc} \sim 3.3 \text{ eV}$) contacts [23].

On this basis, the operation mechanism of CNFETs can be understood by considering how the electronic bands of the tube are altered by the gate voltage. These changes affect directly the charge carrier injection processes, which ultimately limit the conductance in nanotube devices. Heinze et al. [24] reported theoretical calculations showing that the electrostatic potential distribution in nanotube transistors depends strongly on the applied drainsource and gate voltages. It was further predicted that the width of the Schottky barrier can be considerably reduced upon changing the gate voltage, which favors carrier injection by thermal-assisted tunneling. Such a model is supported by the experimental determination of the Schottky barrier height of ambipolar TiC-contacted CNFETs through the analysis of their electrical response in the framework of thermionic emission theory [22]. The gained values were much smaller than those expected (~ 15 meV instead of $\sim 300 \text{ meV}$), providing strong evidence that carrier injection is dominated by tunneling, rather than by thermal emission. The ON and OFF states of a nanotube transistor can be schematically represented by the band diagrams shown in Figure 1.10.

As a consequence of the increased knowledge on the mechanisms of CN-

FET operation, the performance of such devices could be strongly improved in the past decade. State-of-the-art nanotube transistors can even outperform modern silicon MOSFETs. In fact, it has been shown that CNFETs display subthreshold swings as low as 60 mV/decade, while maintaining I_{ON}/I_{OFF} ratios in the range of 10⁵-10⁷ [20].

1.3 Carbon nanotube optoelectronics

The majority of the technologically relevant semiconductors, including silicon, have an indirect band gap. This implies that, in order to conserve momentum, optical transitions at the band edge must involve large changes in the electron wavevector, *e.g.*, by indirect phonon-mediated processes. In contrast, direct band gap materials, such as semiconducting carbon nanotubes, display significantly increased optical transition rates. Accordingly, semiconducting CNTs are particularly attractive for application in optoelectronic devices. Moreover, CNTs show potential for implementing an all-carbon electronic and optoelectronic technology.

1.3.1 Optical absorption and photoluminescence

The optical absorption of bulk direct band gap semiconductors involves interband transitions. Also, carbon nanotubes have been, for a long time, analyzed from this simple perspective. As shown previously, the density of states of SWNTs exhibits a series of peaks, known as van Hove singularities. In the single-particle picture, optical resonances are given by transitions between pairs of such singularities, *i.e.*, the so-called $E_{ll}^{s,m}$ transitions. The compilation of the $E_{ll}^{s,m}$ energies, determined by tight-binding calculations for different tube chiralities, is known as the Kataura plot (Figure 1.11), which was initially used as a roadmap for optical studies on nanotubes. Early experimental studies [25] performed on CNT thin films revealed three pronounced absorption peaks in the infrared-visible range, which were respectively ascribed to the E_{11}^s , E_{22}^s and E_{11}^m transitions. The relatively broad width of the observed peaks was attributed to the nanotube diameter distribution.

Photoluminescence studies on SWNTs were initially hampered by bundling of the nanotubes, which leads to quenching of light emission by the metallic tubes. Thus, development of techniques to disperse nanotubes and avoid their bundling constituted a major breakthrough for studying CNT fluorescence. In this manner, O'Connell *et al.* [26] claimed that light emission of CNTs is given by interband photoluminescence, as suggested by the close correspondence between the measured absorption and fluorescence spectra.



Figure 1.11: The Kataura plot. The tight-binding energy spacing between pairs of van Hove singularities, *i.e.* $E_{ll}^{m,s}$, is plotted as a function of nanotube diameter. Each data point corresponds to a different CNT chirality, whereas m and s denote metallic or semiconducting behavior, respectively.

Bachilo *et al.* [27] subsequently used detailed light emission data, acquired as a function of both emission and excitation wavelength, for assigning the chirality of nanotubes.

Although the single-particle interband picture is able to explain many of the features observed in optical studies of nanotubes, a more complete understanding can only be obtained by taking many-body interactions into account. According to theoretical studies, the electron confinement in quasione dimensional CNTs leads to strong electron-hole interactions, and consequently to the formation of excitons with high binding energy (ranging from approximately 0.2 to 0.5 eV) [28–30]. Spataru *et al.* [29] calculated optical spectra of CNTs, which demonstrate that both absorption and emission are dominated by excitons rather than interband transitions. The experimental demonstration that optical resonances in CNTs are indeed excitonic was reported by Wang *et al.* [31], who found, by means of two-photon excitation measurements, exciton binding energies of ~ 0.4 eV for 0.8 nm diameter SWNTs.



Figure 1.12: Schematic illustration of the mechanisms of (a) ambipolar and (b) unipolar electroluminescence. In the first case, light emission results from the recombination of excitons formed from electrons and holes that are injected simultaneously in the nanotube. In the case of unipolar operation, excitons are generated by high energy carriers through impact-excitation.

1.3.2 Electroluminescence

As discussed above, charge carrier injection in ambipolar CNFETs can be controlled by modulating the transparency of the Schottky barriers with the aid of the applied drain-source and gate voltages. Under normal operation conditions, unipolar electron or hole currents flow through the device in the n- and p-type ON regimes, respectively. In the OFF state, however, the electrostatic potential drop is not concentrated only at one of the electrical contacts, as in the case of the ON states. Instead, the potential drops symmetrically at both contacts, with too wide barriers for carriers to be injected (Figure 1.10).

Nonetheless, by increasing the drain-source bias sufficiently, the contact barriers can be made transparent for the simultaneous injection of electrons and holes at the opposite ends of a nanotube (Figure 1.12a). Electroluminescence in CNFETs is then observed by the radiative recombination of excitons formed by the injected carriers [32]. This process closely resembles the emission mechanism of p-n junction-based light-emitting diodes (LEDs), however without the need for chemical doping. Freitag *et al.* [33] showed that the electroluminescence spectra of ambipolar nanotube transistors feature a relatively broad peak in the infrared range, whose energy is close to the E_{11}^s excitonic transition observed in fluorescence experiments.

Recently, a more efficient light emission mechanism has been observed in

CNFETs operating in unipolar conditions [34,35]. In this case, electroluminescence is observed by the radiative decay of excitons that are generated by impact-excitation, which is promoted by high energy charge carriers (Figure 1.12b). Since this process requires high electric fields, unipolar electroluminescence is observed only at high applied bias, and is usually localized at structural inhomogeneities where local voltage drops occur. Theoretical calculations, which show that impact-excitation processes are very effective in carbon nanotubes, strongly support this mechanism [36].

1.3.3 Photoconductivity

In addition to their electroluminescent properties, semiconducting carbon nanotubes can also be used as photodetector devices that convert light into current [37–39]. Photoconductivity can be described as a process where current is generated by the dissociation of photoexcited electron-hole pairs in a semiconductor. Experimentally, photoconductivity is usually detected by observing changes in the drain current, under applied V_{ds} conditions, upon photoexciting a semiconducting device with a wide-field light source (Figure 1.13).

In analogy to most experiments performed in the early stages of nanotube research, photoconductivity was first studied on CNT thin films, due to difficulties encountered in the fabrication of devices comprising individual nanotubes. One of the pioneering studies of this type was performed by Fujiwara *et al.* [40], who reported the observation of two peaks, located at approximately 0.7 and 1.2 eV, in the photoresponse spectra. These features were ascribed to the E_{11}^s and E_{22}^s transitions, and were considered as strong evidence for the existence of photoconductivity in CNTs.

A few years later, Freitag *et al.* [37] extended photoconductivity studies to the individual nanotube level. In these experiments, polarized light with photon energies in the E_{22}^s range (1.27-1.59 eV, laser power ~ 1 kW/cm²) was used as the photoexcitation source. Upon illumination, the OFF state drain current was observed to increase ~ 100 pA, while the whole I_d -V_{gs} curve experienced a shift in respect to the gate voltage axis. The former observation was attributed to photocurrent generation, which was however not observed in the ON states, since in these regimes the dark current dominates the signal. The shifts in the I_d -V_{gs} plots, on the other hand, were ascribed to photovoltage generation, which arise due to the entrapment of carriers that originate from Si excitation at the Si/SiO₂ interface.

More recent studies have shown that photoconductivity in carbon nanotubes is a more complex process, due to the excitonic nature of the optical transitions. Owing to their considerable binding energies, excitons are rel-



Figure 1.13: (a) Schematics of a photoconductivity experiment, where the entire device is illuminated by a wide-field light source. (b) Upon photoexcitation, an increase in the drain current is detected. The dark current corresponds to the drain current flowing through the device in the absence of light irradiation. The inset illustrates the generation of current by the excitation of an electron-hole pair by a photon.

atively difficult to dissociate, which restricts the photocurrent generation, as has been proven for photoexcitation of the E_{11}^s transition. Nevertheless, E_{11}^s excitons are still able to contribute to photocurrent generation, provided that sufficiently high electric fields are applied, as reported by Mohite *et al.* [41]. In contrast, excitons corresponding to higher optical transitions partially decay into free electrons and holes (yield ~ 10%), and therefore notably contribute to the photocurrent signal [42, 43].

Chapter 2

Experimental methods

2.1 Sample preparation

2.1.1 Carbon Nanotubes

Since the first report of the arc-discharge synthesis of single-walled carbon nanotubes [3, 4], several alternative growth techniques have been proposed, including laser ablation [44] and high pressure carbon monoxide conversion (HiPCO) [45]. The development of these methods was mainly driven toward the production of macroscopic amounts of nanotubes. While the large-scale production of SWNTs is indeed of great technological interest, it does not allow for the fabrication of devices comprising individual nanotubes. Moreover, such methods are not chirality selective, and hence the product consists of a mixture of nanotubes with different properties. In addition, the strong intertube van der Waals interaction leads to agglomeration of the synthesized nanotubes, thus resulting in the formation of CNT bundles.

Various technological applications of nanotubes (*e.g.*, electronic and optoelectronic devices) require them to be first deposited on a surface. Due to nanotube agglomeration, the deposition of commercially available SWNTs usually requires a previous step, in which the tubes are "de-bundled" and dispersed within a liquid medium. This is most commonly accomplished by ultra-sonication, in order to break the CNT bundles in an aqueous surfactant solution. The surfactant molecules form micelles that envelope the individual nanotubes, keeping them separate in CNT suspensions [26]. Heavier residues, such as metal catalyst particles and agglomerates, are then removed by centrifugation. Despite the success of such a procedure in the isolation of single CNTs, detrimental effects, such as shortening and defect introduction onto the tubes, cannot be avoided.

A valuable alternative which circumvents part of these problems is to

grow CNTs directly onto a surface, *e.g.* by chemical vapor deposition (CVD). Although this strategy does not yield tubes of uniform chirality, it considerably minimizes the problem of CNT bundling. Moreover, several studies have witnessed on the high structural quality of CVD-grown SWNTs [46,47]. Therefore, all CNTs investigated in this thesis were synthesized by CVD.

Chemical vapor deposition of CNTs

The CVD process involves the exposure of a catalyst material at elevated temperatures to the flow of a hydrocarbon gas. Under these conditions, dissociation of the hydrocarbon molecules is promoted by the catalyst particles, wherein the resulting carbon is dissolved. Once the saturation limit is reached, precipitation of carbon in the form of nanotubes is favored over other graphitic structures, due to the absence of dangling bonds in the tubes.

Typically, CNFET devices are fabricated on Si/SiO₂ substrates, with the oxide being used as gate dielectric, while the highly doped silicon substrate serves as the back gate electrode. Accordingly, the first step towards the realization of such devices consists of controlling the deposition of catalyst particles on the SiO_2 surface. In this work, iron nanoparticles were employed as catalysts. Figure 2.1 schematically illustrates the procedure used for the catalyst preparation. The delivery of iron onto the surface is carried out by ligand molecules, which prevent particle aggregation and uncontrolled growth of the catalyst particles. Polyamidoamine (PAMAM) dendrimers (Sixth-generation, 15.7 % in water, Dendritech Inc.), hyperbranched macromolecules with a large number of amine terminal groups, were used for this purpose, following a similar procedure as reported by Choi et al. [48]. Fe(III) ions were attached to the amine groups of the dendrimers by mixing 30 μ L of the PAMAM solution with 30 μ L of 0.1 M FeCl₃ and 1 mL of distilled water. The pH of the solution was adjusted to approximately 4 by adding hydrochloric acid, in order to avoid aggregation. Immediately prior to deposition, the stock solution was diluted 100 times with distilled water. The Fe(III)-loaded PAMAM dendrimers were then deposited by placing the Si/SiO_2 substrates in the diluted solution for 10 s.

Subsequently, a heat treatment was performed in a tube furnace to induce the catalyst particle formation and the SWNT growth (Figure 2.1). The samples were first submitted to calcination in air (10 minutes at 700°C), whereupon Fe₂O₃ nanoparticles were formed. Subsequently, the furnace temperature was raised to 900°C, and a gas mixture of H₂ and Ar (100 and 400 sccm, respectively) was flown, to promote the reduction of the iron oxide particles. The CNT growth was started by allowing the gas mixture to flow through a liquid ethanol reservoir. In this way, ethanol molecules were car-



Figure 2.1: Overview of the CVD growth of carbon nanotubes. (a) Loading of Fe(III) ions onto polyamidoamine dendrimers. (b) Scheme of the heat treatment procedure, and (c) corresponding changes observed on the surface. First, Fe_2O_3 particles are formed during calcination. Such particles are reduced into Fe catalysts, by flowing a H₂/Ar mixture. Reaction finally starts when ethanol is introduced in the system.

ried towards the center of the furnace, where they served as carbon feedstock. After 15 minutes, when the reaction was completed, the samples were cooled down to room temperature, while maintaining the Ar flow.

Atomic force microscopy (AFM) measurements revealed that long carbon nanotubes (with lengths exceeding 50 μ m) were successfully grown. The single-walled character of the tubes was confirmed by their measured diameter, as obtained by AFM characterization, and by Raman spectroscopy. A broad distribution of SWNT diameters was observed in the grown samples, ranging from ~ 0.8 nm to 2 nm. Figure 2.2 shows that the nanotubes are not aligned with respect to each other, and loops are commonly observed along individual tubes, indicative of turbulent gas flow close to the substrate. It was further observed that the tube density varies throughout the samples, which is most likely due to an inhomogeneous distribution of catalyst particles.

2.1.2 Graphene

Despite recent advances in the preparation of graphene [49–51], high quality samples are still most commonly obtained by the mechanical exfoliation of graphite. It turns out that the major challenge in the preparation of graphene samples is to find monolayer flakes amongst the various types of graphite



Figure 2.2: Atomic force microscopy images of CVD-grown nanotubes, which illustrate the nanotube density variation on the samples. The scale bars correspond to 2.5 μ m.

debris, which are much more numerous. This deficiency was circumvented by the discovery that single graphene layers are visible by optical microscopy [5]. The optical contrast between graphene and the substrate is given by an interference effect, where the oxide thickness and the light wavelength are important parameters. Silicon substrates with a 300 nm-thick SiO₂ layer are most commonly used, since they allow for pronounced contrast in the visible wavelength range.

In this work, graphene samples were prepared using a similar procedure as described by Novoselov *et al.* [5]. An adhesive tape (wafer processing tape SWT10+, Nitto Denko) was used to repeatedly peel layers from highlyoriented pyrolytic graphite (HOPG) crystals (grade ZYA, Momentive Performance Materials Quartz, Inc.). Afterwards, the exfoliated sheets were transferred by pressing the adhesive onto Si/SiO_2 substrates (with 300 nm thick oxide). Ultra-thin flakes were located on the substrate by optical microscopy.

Raman spectroscopy measurements were subsequently performed in order to confirm the presence of monolayers in the prepared samples. The Raman spectrum of monolayer graphene displays a single, sharp and symmetric G'peak, which is roughly four times more intense than the G peak [52], as shown in Figure 2.3 (measurements taken with $\lambda = 633$ nm). Alternatively, the number of layers on a graphene sample could be roughly estimated by the height of the flake, as obtained via AFM characterization. Figure 2.4 displays an AFM image of a graphene flake with ≈ 1.1 nm height, which is consistent with values reported in the literature for monolayers exposed to ambient conditions [14].



Figure 2.3: Raman spectrum of a graphene sample. The inset shows the symmetric G' band, which is characteristic of monolayer graphene.



Figure 2.4: AFM micrograph of a device comprising a graphene monolayer.



Figure 2.5: Schematic illustration of the fabrication of electrodes by electron beam lithography. (a) Starting point: carbon nanostructures prepared on Si/SiO_2 substrates. (b) A layer of electron-beam resist (PMMA) is deposited by spin-coating onto the substrate. (c) EBL is used to define the electrical contacts at pre-determined positions. (d) The resist is developed, by dissolving the electron-beam exposed regions. (e) Evaporation of the contact metals. (f) The residual resist is removed by lift-off.

2.2 Electrical transport measurements

2.2.1 Electrode fabrication

The final step in the preparation of carbon nanotube/graphene devices consisted in the fabrication of electrical contacts, for which purpose standard electron beam lithography (EBL) was employed. The basic idea behind this method is to prepare suitable masks on the surface of the samples, onto which metal evaporation can be performed. To this end, electron beam-sensitive resist poly-(methyl methacrylate) (PMMA) was used. Being a positive resist, PMMA has its molecular weight reduced upon electron beam irradiation, such that the exposed PMMA regions could be preferentially dissolved in an appropriate solvent (*i.e.*, methyl-iso-butyl-ketone, MIBK), which yields masks with desired geometries. This was followed by the evaporation of the contact metals, which in most cases consisted of 0.3 nm of a Ti adhesion layer and 15 nm of AuPd (60%-40%). The procedure was finalized by removing the residual PMMA by means of a lift-off process in 1-methyl-2-pyrrolidone (55° C for 2 hours). Figure 2.5 schematically summarizes the process of electrode fabrication by EBL.

In order to position the electrical contacts at specific coordinates, marker structures were first prepared on the samples. Subsequently, AFM and optical microscopy were used to locate CNTs and graphene flakes relative to the markers. This enabled the alignment between the electrode layout and the sample, during the e-beam writing. Large contact pads ($\approx 200 \ \mu m \times 200 \ \mu m$) were also fabricated to provide the interface to external electrical probes during electrical measurements. In this work, devices were typically prepared with a spacing of at least 3 μm between the source and drain contacts.

2.2.2 Electrical characterization

The experimental setup used for the electrical transport measurements comprises a voltage source (Keithley 2400) that supplies the drain-source bias (V_{ds}) . A home-built current-to-voltage converter is used to amplify the drain current (I_d) signal, before it is recorded by a multimeter (Keithley 2000). Additionally, a second voltage source (Keithley 2400) is used to supply the gate-source voltage (V_{gs}) , and to measure the leakage current (I_g) that flows through the gate oxide.

The current-voltage (I-V) characteristics of the samples were measured by recording I_d as a function of the applied drain-source voltage. Typically, linear responses were observed at low-bias (≤ 0.2 V). By repeating this procedure at different V_{gs} , resistance vs. gate voltage $(R \times V_{gs})$ plots were obtained. It is important to note that, by using a two-probe configuration, the measured resistance comprises both the intrinsic resistance of the nanostructure and the contact resistance. Measurements taken with a four-probe geometry constitute the appropriate approach to determine the intrinsic resistance of a material. However they are not directly applicable to carbon nanostructure devices, due to the invasiveness of the metal contacts on these materials. Four-probe measurements were performed by passing an electrical current between two outer electrodes, while the potential drop between a pair of inner contacts was detected.

Carbon Nanotubes

Electrical measurements were performed at room temperature to determine whether a contacted nanotube displayed metallic or semiconducting behavior. As discussed in the previous chapter, the electrical response of metallic tubes is practically insensitive to gate voltage modulation, whereas semiconducting CNTs display I_{ON}/I_{OFF} ratios ranging between ~ 10⁴-10⁶.

Figure 2.6 shows $R vs. V_{gs}$ curves of typical metallic and semiconducting nanotube devices prepared in this work. As expected, the resistance of the metallic nanotube exhibited very little gate dependence ($\mathbf{R} = 30-55$ $\mathbf{k}\Omega$), with a conductance value of ~ 0.45 × ($2e^2/h$). Compared to the the-



Figure 2.6: Comparison of the gate dependence of resistance of a metallic (black line) and a semiconducting (green line) carbon nanotube. Measurements were taken with $V_{ds} = \pm 0.1$ V at room temperature.

oretical ballistic conductance of a metallic tube given by $G = 2 \times (2e^2/h)$, the measured value is quite low. This difference stems from the onset of acoustic phonon scattering at room temperature, as previously reported for Pd-contacted metallic nanotubes [53]. The semiconducting CNT, on the other hand, displayed a slightly asymmetric, ambipolar gate dependence, with an ON/OFF ratio of ~ 10⁵. The origin of the asymmetry between the *p*- and *n*-type regimes is still a subject of investigations. Models to explain this effect involves *p*-type chemical doping under ambient conditions [54], or electron traps along the CNT. The *p*-type ON conductance of the semiconducting CNT reached ~ 0.15 × $(2e^2/h)$, which is comparable to the best values reported in the literature [21]. These observations further testify the high quality of the CVD-grown CNTs and of the AuPd electrical contacts.

Under ambient conditions, the gate dependent electrical response of the devices showed a pronounced hysteresis, which has been attributed to water molecules bound to the SiO₂ surface, where they act as charge traps [55]. Due to the hysteresis, the direction of the V_{gs} sweep becomes extremely important in gate dependent measurements, as illustrated in Figure 2.7. Therefore, all data presented as a function of V_{gs} were recorded while sweeping the gate from positive to negative voltages (e.g., 5 V \rightarrow -5 V), after performing a complete gate voltage cycle (e.g., 0 V \rightarrow 5 V \rightarrow -5 V) on the samples.



Figure 2.7: Electrical characterization of a semiconducting CNT in ambient conditions, where a pronounced hysteresis is observed. The measurement starts at $V_{qs} = 0$ V, and follows sequentially the arrows (1), (2) and (3).

2.3 Confocal optical microscopy

In conventional optical microscopes, a wide-field light source is used to illuminate the specimen, and hence the resulting image contains information of both the in-focus and out-of-focus planes. Confocal microscopy emerged as an alternative method, where the out-of-focus reflected light is suppressed, thus leading to an enhancement in the optical resolution.

Figure 2.8 schematically illustrates the principle of a confocal microscope. The specimen is illuminated by a diffraction-limited laser spot, which is focused onto the sample by a high numerical aperture objective lens. The reflected light is recollected by the objective lens, before it is redirected by a beam splitter through a pinhole aperture and to a photodetector, such as a photomultiplier tube (PMT). The detector (*pinhole*) aperture leads to the filtering of out-of-focus information, by obstructing light that does not come from the focal point. Since the signal detected at the PMT corresponds to light reflected from the small volume of the laser spot, complete images are only obtained by scanning the sample with respect to the light spot. This can be achieved by one of two ways, namely (i) by moving the laser spot with scanning mirrors, or (ii) by raster-scanning the sample via a piezoelectric stage.

Recently, confocal laser scanning microscopy (CLSM) has been widely employed for obtaining spatially resolved photo-induced signals [56–58]. This constitutes a major advantage over wide illumination techniques, which yield ensemble-averaged data. For example, Raman spectra of carbon nanotubes



Figure 2.8: Principle of confocal microscopy. A laser beam (red line) is focused by an objective lens into a diffraction-limited spot. The reflected light (blue line) is detected at a photomultiplier tube (PMT), after passing through a pinhole aperture that blocks out-of-focus information.

obtained by wide-field illumination (typical spot size ~ tens of μ m) represent the convoluted response of multiple tubes [59]. On the other hand, a conventional confocal microscope can be readily converted into a confocal Raman microscope by filtering out the original excitation wavelength from the reflected light, before it is detected in a spectrophotometer. This enables not only to detect the Raman response of a single CNT, but also to acquire Raman images by plotting a two dimensional map of the signal intensity, as demonstrated for individual nanotubes by Mews *et al.* [60]. In the present work, CLSM is applied to perform spatially-resolved photocurrent measurements on carbon nanostructure devices. This technique was originally named PhotoElectronic Transport Imaging (PETI) [61], but came to be more popularly known as Scanning PhotoCurrent Microscopy (SPCM).

2.3.1 Scanning photocurrent microscopy

Spatially-resolved photocurrent measurements were performed by irradiating a device with a diffraction-limited laser spot, while measuring the drain current as a function of the (x, y) coordinate (Figure 2.9). A commercial confocal optical microscope (Leica TCS SP2), which contains Helium Neon (HeNe operating at 633 nm and GreNe at 543 nm) and Argon (Ar with 458 nm, 488 nm and 514.5 nm lines) lasers, was employed for photoexcitation. A photodiode was used to detect the reflected light, and the resulting signal was measured by a multimeter (Keithley 2000) after amplification by a currentto-voltage converter. The drain current was detected with a similar setup as for the dark-current measurements (section 2.2.2). Two-dimensional pho-

2.3. CONFOCAL OPTICAL MICROSCOPY

tocurrent maps were obtained by raster-scanning the samples through the laser spot by using a piezoelectric stage. Simultaneously acquired optical reflection images (measured at the photodiode) were useful to assign the photoresponses to actual positions within the devices.

Two different types of SPCM measurements were carried out in this work, namely (i) with zero drain-source bias ($V_{ds} = 0$ V), or (ii) under applied drain-source bias conditions. The latter measurements could only be performed in transport regimes where the dark current is suppressed, such as the OFF state of semiconducting nanotubes. All measurements were carried out under ambient conditions.



Figure 2.9: Scheme of the scanning photocurrent microscopy setup. The sample is raster scanned, by means of a piezoelectric stage, with respect to the laser spot. The reflected light is detected in a confocal configuration by a photodiode, which is fixed above the objective lens, while the drain current is recorded by a multimeter (I). Two voltage sources supply the drain-source voltage (V_{ds}) and the gate voltage (V_{gs}) to the device. S and D stand for the source and drain electrodes, respectively.
Chapter 3

Photoelectrical response of individual semiconducting nanotubes

3.1 Introduction

Significant advances in the understanding of the operation mechanisms of CNFETs have been made since they were first reported in 1998 [9,62]. For instance, theoretical and experimental studies have shown that CNFETs function as Schottky barrier transistors, with the conductance switching being governed by the modulation of the contact resistance with applied gate voltages [24,63]. The Schottky barrier transistor model is now widely accepted, and has enabled optimization of the device's geometry and properties [21,64–67]. However, in spite of this great evolution, several aspects of CNFET operation remain to be studied in closer detail.

Spatially-resolved experimental techniques, such as scanning probe microscopies, have been proven as valuable tools to elucidate processes in nanodevices [68–70]. For example, scanning gate microscopy was used in one of the first observations of the determining role of the electrical contacts on the transport through CNFETs [71]. In this chapter, detailed SPCM measurements, performed on devices comprising individual semiconducting nanotubes, are presented. The motivation for such experiments is two-fold: (i) to investigate in more detail the photoconductivity of CNTs, which has been so far mostly studied using wide-field illumination, and (ii) to gain insights into the electrical transport mechanisms of CNFETs. The obtained results demonstrate that SPCM constitutes a powerful characterization tool, which efficiently enables the determination of the electrostatic potential profile of nanodevices. In addition, evidence of environmental chemical doping of the tubes was gained from the resulting photocurrent images.

3.1.1 Background

In 2004, pioneering work on scanning photocurrent microscopy was carried out by Balasubramanian *et al.* [61], who reported the spatially-resolved photoresponse of semiconducting nanotubes. In that study, photoexcitation was carried out by diffraction-limited laser spots with wavelengths in the visible range ($\lambda = 514.5$ nm or 647 nm). Commercial arc-discharge carbon nanotubes were used in the preparation of the devices, and all signals were recorded in the OFF state under applied bias conditions ($V_{ds} = 0.1$ V). Interestingly, the resulting photocurrent maps evidenced a localized response around one of the two electrodes. This response exhibited an approximately linear dependence of the laser power density, and was maximal for light polarized parallel to the axis of the tube. The authors suggested that the localized photocurrent originates from the built-in electric field associated with the Schottky barrier, which is able to dissociate photo-generated electronhole pairs. The absence of a photoresponse close to the second electrode was attributed to contact asymmetry.

Afterwards, the same technique was applied in the investigation of individual metallic carbon nanotubes [72]. SPCM measurements were taken with with zero drain-source bias ($V_{ds} = 0$ V), in order to maximize the phototo dark-current ratio. Strong photocurrent responses (~ tens of nA) were observed at both electrical contacts, being positive (negative) at the source (drain) electrode. Evidence for the presence of built-in electric fields at the contacts was gained by the observation of a positive (negative) shift of the I - V characteristics, upon fixing the laser spot at the source (drain) contact. Such local electric fields were attributed to the presence of an electrical potential step at the contacts. Furthermore, additional photocurrent signals detected along the tubes were ascribed to potential modulations stemming from local defects.

Subsequent to the SPCM investigations of CNT devices, this technique was also applied to semiconductor nanowires [73, 74]. For example, Gu *et al.* [75] were able to improve the spatial resolution of the photoresponse of CdS nanowires by using a scanning near-field optical microscope (SNOM) as the light source. The photocurrent response of such wires was observed to be qualitatively very similar to that of semiconducting CNTs, *i.e.*, a single photocurrent lobe observed close to one of the electrodes. In another study, SPCM measurements on CdS nanowire devices with Ohmic contacts revealed that, in the absence of built-in electric fields at the contacts, the photoresponse is limited by the intrinsic properties of the charge carriers, such as their lifetime and mobility [74].

All of the above mentioned studies have demonstrated the great potential of SPCM for probing local electric fields, which opens perspectives in the characterization of nanodevices. However, this first requires to fully explore the capabilities of this technique, in particular to perform a systematic study addressing the effects of key parameters such as the drain-source bias and the gate voltage. The results described in this chapter demonstrate that SPCM can indeed be used as a valuable tool to estimate the Schottky barrier height and the electrostatic potential profile within nanotube devices.

3.2 Experimental

3.2.1 Electrical transport

As already mentioned in Chapter 3, the CNFETs used in this study consisted of CVD-grown nanotubes contacted with Ti/AuPd (0.3 nm/15 nm) electrodes. Figure 3.1 displays the transfer characteristic of a typical device, which is ambipolar and slightly asymmetric. The CNFET ehxibited excellent electrical characteristics, with low ON resistances (*i.e.*, ~ 100 k Ω in the *p*-type branch and ~ 50 M Ω in the *n*-type regime), and an ON/OFF ratio of approximately five orders of magnitude. Such performance is comparable to state-of-the-art nanotube transistors [21]. The high quality of these CVDgrown nanotube samples constitutes a significant improvement over previous SPCM studies, which used arc-discharge CNT devices with conductances at least one order of magnitude lower [61].

3.2.2 Zero-bias SPCM measurements

In order to fully evaluate the photocurrent response of CNFETs, the effects of the drain-source bias and the gate voltage were investigated. For the sake of clarity, results obtained with zero drain-source bias are first discussed. All SPCM experiments were performed with $\lambda = 633$ nm (laser power density ~ 100 kW/cm²) excitation.

Photocurrent images were taken in each of the three distinct transport regimes, *i.e.* the p- and n-type ON conducting states and the OFF state. In the p- and n-type ON states (Figure 3.2), enhanced photocurrent responses appear around the metal contacts. By contrast, very weak photoresponses can be observed along the tube in the OFF state. This difference can be understood by considering the changes of the CNFET bands as a result of



Figure 3.1: Ambipolar electrical response of a typical CNFET plotted as a function of the gate voltage. The high resistance OFF state separates p- and n-type conducting regimes. Measurements were performed with $V_{ds} = \pm 0.1$ V.

gate modulation, as depicted schematically in Figure 3.2d-3.2f. Photocurrent is only detected in regions where local electric fields are present, *i.e.*, at the Schottky barriers in the ON state regimes. Moreover, the inversion in the signs of the photocurrents at the contacts, observed upon the p- to nswitching, is consistent with the change in the direction of the respective built-in fields. Similar studies were reported almost concurrent to the work described in this chapter [76, 77].

Although the photoresponses at the metal contacts are qualitatively similar in the *p*- and *n*-type regimes, they exhibit some subtle differences. While in the *p*-type state, the peaks of the photocurrents appear almost exactly at the metal-CNT interface, the peaks in the *n*-type regime are offset by approximately 0.25 μ m towards the center of the device. Such behavior was observed in all of the investigated samples. These findings suggest that the band structure of the CNFET in the *p*-type state is not simply a mirror image of the n-type regime.

In order to understand this dissimilarity, a series of zero-bias measurements were taken while slowly sweeping the gate voltage from the n- to the p-type regime, as shown in Figure 3.3. Autoscaled colormaps have been applied to each of the images in order to maximize the image contrast. When tuning the device from the n-type to the OFF state, the photocurrent lobes shift gradually towards the middle of the channel, become broader and considerably decrease in intensity. These observations indicate that the built-in electric fields at the contacts become weaker and the Schottky barriers become wider, in accordance with theoretical simulations performed on CN-



Figure 3.2: Zero drain-source bias SPCM measurements on a CNFET in the (a) p-type (V_{gs} = -10 V), (b) OFF (V_{gs} = 5 V) and (c) n-type (V_{gs} = 10 V) states. The dotted white lines indicate the positions of drain (D) and source (S) contacts. (d)-(f) Band diagram schemes of the device in the three different transport regimes. The gray and white circles respectively indicate electrons and holes generated by photoexcitation.



Figure 3.3: Sequence of zero drain-source bias photocurrent images depicting the n- to p-type transition. The color scale of each image was normalized such that white (black) corresponds to the maximum (minimum) detected current.

FETs, which show that the Schottky barrier width is determined by the magnitude of the local electric fields at the contacts [24]. On the contrary, when switching the device from the OFF to the *p*-type state, the lobes appear suddenly at the contacts without showing any gradual displacement. Moreover, there is no intermediate state, where the lobes are broader. The sudden appearance of the *p*-type lobes in comparison to the gradual movement and broadening of the *n*-type lobes suggests that, in the *p*-type regime, the width of the Schottky barriers is not significantly affected by the gate voltage modulation.



Figure 3.4: Band diagrams depicting the intrinsic- and doped-CNFET models for the *p*- and *n*-type conducting regimes.

In order to interpret this behavior, it is instructive to analyze the band structures of a CNFET in the p- and n-type regimes within the framework of the intrinsic- and doped-CNFET models, which are compared in Figure 3.4. In the former case, the bands are bent over a depletion length W to a similar degree for both the two ON regimes. The Schottky barrier width Wis of the order of magnitude of the gate oxide thickness t. In this model, the presence of oxygen adsorbates changes the metal work-function, resulting in a gate voltage offset in the transport characteristics [22]. On the other hand, in the doped-CNFET model, the nanotubes are chemically *p*-doped upon exposure to ambient conditions [54]. According to Leonard and Tersoff [78], the depletion width varies exponentially with the reciprocal doping fraction f^{-1} :

$$W \sim \frac{d}{2} exp[\frac{2\epsilon\epsilon_0 E_{gap}}{e^2 dN f}],\tag{3.1}$$

where d is the CNT diameter, ϵ is the average dielectric constant of the surrounding medium, ϵ_0 is the vacuum permittivity, E_{gap} is the CNT band gap and N is the number of carbon atoms per unit surface area. Chen and Fuhrer [54] estimated a doping fraction $f \sim 7.6 \ge 10^{-4}$ holes/carbon for their CNFETs under ambient conditions, thus reducing the Schottky barrier width to $W_{doped} \sim 5.5$ nm in the *p*-type regime. In the *n*-type state, the band profile remains similar within W_{doped} , due to the strong chemical doping. However, it displays *n*-type bending in regions away from the contact and charge depletion occurs over an effective barrier width W_{eff} , which is of the order of the gate oxide thickness. Furthermore, sweeping the gate voltage within the *n*-type regime leads to the modulation of W_{eff} , thereby leading to the broadening or thinning of the Schottky barriers, while within the p-type regime the barrier width remains almost unaffected at W_{doped} . Electrical transport studies reported in the literature show that this chemical doping, induced by oxygen and water present in the atmosphere, can be compensated only under quite drastic conditions, such as by applying high voltage ramps in vacuum [54].

Most of the observations in Figures 3.2 and 3.3 can be understood on the basis of the doped-CNFET model. The occurrence of the *p*-type photocurrent lobes at the contacts is in agreement with a Schottky barrier width W_{doped} of the order of a few nm. The shift of ~ 0.25 μ m of the *n*-type photocurrent lobes is consistent with the expected Schottky barrier width W_{eff} that should be of the order of the gate oxide thickness ($t \sim 200$ nm in our devices). This in term again explains the broadening of the *n*-type photocurrent lobes when switching the device to the OFF state, which is absent for *p*-type operation. In addition, the doped-CNFET model explains the asymmetry observed in the transport characteristics of the devices, since charge injection by tunneling is strongly favored in the *p*-type regime.

It is furthermore apparent from the series in Figure 3.3 that the photocurrent image of the device in the OFF state ($V_{gs} = 3.7 \text{ V}$) displays a number of features of very low intensities (in the order of a few tens of pA) along the nanotube. Such features, which are observed in some of the measured samples, appear only in the OFF state, when the fields at the contacts are negligible. They can be attributed to weak local electric fields originating from local disorder, similar to a previous report by Freitag *et al.* [79] who employed confocal Raman microscopy measurements.

Infrared SPCM measurements

Previous wide-field illumination photoconductivity experiments on CNTs have shown that photovoltages are induced at the Si/SiO₂ interface, as a result of the excitation of the back Si substrate [37]. To rule out contributions from such photovoltages, infrared SPCM measurements were performed on the present samples. For this purpose, a continuous wavelength optical parametric oscillator (cw-OPO) laser, with photon energies in the ranges of 0.33 - 0.54 eV and 0.62 - 0.83 eV, was employed. This photon energy is not sufficient to promote the excitation of silicon ($E_{gap}^{Si} \sim 1.1 \text{ eV}$). A typical SPCM image (Figure 3.5), recorded with $V_{gs} = -10 \text{ V}$, $\lambda = 1.6 \mu \text{m}$ ($E_{exc} \sim 0.78 \text{ eV}$) and spot size $\sim 2 \mu \text{m}$, clearly shows photoresponse lobes at the contacts. Moreover, the behavior of the lobes is qualitatively similar to the ones described previously. This observation leads to the conclusion that photovoltages generated at the Si/SiO₂ interface have a negligible contribution to the photocurrents detected in the present SPCM measurements.



Figure 3.5: Zero-bias photocurrent image taken with infrared photoexcitation ($\lambda = 1.6 \ \mu m$). The black dotted lines indicate the position of the electrode edges.

3.2.3 Determination of the Schottky barrier height

In this section, it is demonstrated that SPCM is a valuable tool, in conjunction with electrical transport measurements, for the determination of the Schottky barrier height of CNFET devices. For comparison, the barrier height was also estimated by low temperature transport measurements.

3.2. EXPERIMENTAL

Barrier estimation by thermionic emission theory

The Schottky barrier height in bulk semiconductors is typically estimated by temperature-dependent electrical measurements, using the assumption that charge carrier injection is thermally activated. According to thermionic emission theory, the current flowing over a barrier of height Φ_B is given by [15]:

$$I_d \propto exp(-\frac{\Phi_B}{k_B T})[exp(\frac{qV_{ds}}{k_B T}) - 1)], \qquad (3.2)$$

where k_B is the Boltzmann constant and q is the elementary charge. The current in equation (3.2) is described by an Arrhenius curve when V_{ds} is constant, and hence activation barrier energies ($\Phi_B(V_{ds})$) can be estimated from the slopes of $ln(I_d) \ge 1/T$ plots (Figure 3.6). Due to the Schottky effect, which corresponds to a barrier lowering proportional to the square root of the applied electric field, the true Schottky barrier height (Φ_B^0) is given for zerobias conditions. Therefore, Φ_B^0 is determined by extrapolating the activation barrier energies $\Phi_B(V_{ds})$ to zero drain-source bias, as shown in Figure 3.6c.

A major point to consider is whether equation (3.2) is applicable to CN-FETs, since experimental evidence suggests that charge injection by tunneling may be dominant in such devices [22, 63]. On the other hand tunneling is suppressed when approaching the OFF state, as a consequence of of the broadening of the Schottky barriers. Hence, carrier injection occurs via two mechanisms, namely tunneling and thermionic emission, of which the former dominates the ON states, while the latter is the major component in the OFF state. Accordingly, the most reliable value for Φ_B^0 should be gained via estimation of the activation energy in the OFF state of the device.

For the sample in Figure 3.6, I - V curves were obtained as a function of the gate voltage at various temperatures ranging from 300 K down to 10 K. The activation energy at zero bias extracted from these curves is plotted as a function of gate voltage in Figure 3.6d, together with the device's resistance measured at 90 K. For the *p*- and *n*-type ON states, these energies correspond to 1.7 and 21.3 meV, respectively. Despite their good agreement with other values reported in the literature, they do not reflect the barrier height, because of the reasons mentioned above. As the device is tuned from the ON states to the OFF state, the tunneling component of the charge carrier injection reduces and the thermionic part begins to dominate. As a consequence, the activation barrier energy increases as the device is brought into the OFF state. However, due to the reduced signal-to-noise ratio, it was not possible to access the activation barrier energy in the complete OFF state, but only in its vicinity. From the curve in Figure 3.6d, an activation energy



Figure 3.6: (a) I - V curves of a CNFET measured as a function of temperature with $V_{gs} = 8$ V. (b) Plot of the drain current versus the inverse temperature, taken at $V_{gs} = \pm 10$ V. Two distinct linear regions, which can be attributed to thermal emission of carriers over the contact barrier and to tunneling through the barrier, respectively, are observed. The slope of the linear fits is used to estimate activation barrier energies. (c) Estimation of the "true" activation barrier energy by extrapolating the values obtained at different V_{ds} to zero bias. (d) Activation barrier energies at zero bias (black dots) as a function of the gate voltage. The resistance of the same device, measured at 90 K, is also shown (red line).

of approximately 170 meV can de deduced close to the conductance shutoff region, which represents a Φ_{Bp}^{0} lower limit for the investigated device. Schottky barrier heights of similar values have been previously reported for CNFETs [54].

Barrier estimation by SPCM

The correlation between the photocurrent signals in SPCM and local electric fields can be further utilized to quantitatively extract the Schottky barrier height (Φ_{Bp}) of a device. This approach relies on determining, through SPCM and transport measurements, the voltage difference between the flat-band condition, *i.e.* the condition in which the photocurrent signals at the contacts (I_{ph}) become zero, and the threshold voltage, in which the conductance is shut off (Figure 3.7a). It is apparent from the I_{ph} - V_{gs} curves in Figure 3.7b that the flat-band condition is reached at $V_{gs} = V_{fb} = 6.9$ V.

Furthermore, gate dependent measurements of the drain current at V_{ds} = 0.1 V show that the device conductance is shut off when V_{gs} equals the threshold voltage ($V_{th} = 6$ V for this device). In this situation, the valence band is roughly aligned with the Fermi level at the source contact (Figure 3.7). The energy difference between the flat-band and the shut-off conditions corresponds to Φ_{Bp} . The measured gate voltage difference can be converted into energy values by multiplying the gate efficiency parameter α_p , which can be estimated from the subthreshold slope (S) through the relation S $= (1/\alpha)(k_BT/e)ln(10)$ [80]. For the device in Figure 3.7, the subthreshold slope was found to be approximately 300 mV/decade, which yields an α_p of ~ 0.2 . On this basis, the device's Schottky barrier height for holes is estimated to be approximately 180 meV. Similar values were obtained for other samples. Moreover, this value is in good agreement with the lower limit of the activation energy obtained from the low temperature transport measurements, indicating that SPCM is a simple and reliable method to determine the Schottky barrier height in nanodevices. A similar procedure has been recently applied for estimating the Schottky barrier height of silicon nanowires [73].

3.2.4 Measurements under applied bias and electrostatic potential profiles

After having characterized the devices at zero bias, the effect of finite V_{ds} on the photoresponse of CNT devices has been studied. Figure 3.8 displays a series of SPCM images taken at various drain-source voltages with the device operating in the *n*-type regime ($V_{qs} = 10$ V). At this point, the discussion is



Figure 3.7: Estimation of Schottky barrier height from SPCM data. (a) CNFET band diagrams of two characteristic states, namely the flat-band condition, where no SPCM response is expected, and the conductance shut-off. The energy difference between these conditions corresponds to the Schottky barrier height. (b) Plots of the photoresponses at the electrical contacts (black and green lines), and of the drain current measured at $V_{ds} = 100 \text{ mV}$ (dots), both as a function of the gate voltage.

restricted to the *n*-type regime because of the photo- to dark-current ratio, which is highest under this condition. Nonetheless, a similar discussion would hold equally well for the *p*-type case. The images disclose that an applied voltage enhances one of the photocurrent lobes, depending on the sign of the bias. For sufficiently large bias, a single lobe is observed. By plotting the magnitude of the photoresponse at the contacts as a function of the applied drain-source bias (Figure 3.8b), it becomes evident that photocurrent is only observed for reverse-biased conditions, resembling the behavior of illuminated Schottky diodes [75]. In addition, the photocurrent is observed to saturate at high bias, which can be reasonably explained by the exhaustion of photoexcited charge carriers.

As discussed previously, the spatially-resolved photocurrent responses contain information about the local electric fields present in the devices. According to Ohm's law, the current density (\vec{j}) in a material varies linearly with the applied electric field (\vec{E}) . Since an electric field is given by the gradient of the underlying electrostatic potential, the photocurrent response is directly proportional to the gradient of the potential. Thus, qualitative electrostatic potential profiles of the CNT devices were obtained by integrating the photocurrent signal along the nanotubes.

In Figure 3.9, the resulting profiles are depicted for different bias values, with the source taken as ground and the drain being lifted (lowered) upon application of a negative (positive) potential. It follows from the line profiles



Figure 3.8: (a) Bias dependence of the spatially-resolved photocurrent response of a CNFET ($V_{gs} = 10$ V). (b) Photocurrent intensity at the contacts as a function of V_{ds} .

that the center of the nanotube remains approximately flat, irrespective of the applied bias. Moreover, application of a more negative (positive) bias results in a potential drop predominantly occurring at the source (drain). The changes in the band profiles with increasing bias are consistent with the *n*-type unipolar operation mode of a CNFET, wherein the predominant potential drop at the contacts enhances charge carrier injection to the nanotube (Figure 3.9b). The SPCM-derived profiles thus confirm that charge transport through the CNT is governed by the contacts.



Figure 3.9: (a) Electrostatic potential profiles of a CNFET under applied bias, derived from SPCM data. (b) Schematic illustration of the effect of an applied drain-source bias on the CNFET bands. Charge carrier injection is favored under applied bias condition.

Finally, the effect of gate voltage modulation on the photoresponse of

biased CNFETs was investigated. A series of images, similar to that in Figure 3.2, acquired with $V_{ds} = 0.7$ V are displayed in Figure 3.10. At the starting point of $V_{gs} = 10$ V (*n*-type), a single lobe is observed at the source contact, in close correspondence to the situation depicted in Figure 3.8. By sweeping the gate voltage to lower values, the intensity of this lobe decreases and clear photocurrent signals emerge along the nanotube between the contacts. In the OFF state ($V_{gs} \sim 4.3$ V), the photoresponse is symmetrically distributed along the tube, whereas at $V_{gs} = 3.7$ V, *p*-type operation sets in and a single photocurrent lobe is observed at the drain contact. The set of SPCM images provides a complete picture of the photoconductivity in CNFETs. A major conclusion is that true photoconductivity from an individual CNT is only observable in the OFF state of the device. In the ON states, the local photoresponses observed at the contacts are similar to that obtained from reverse-biased Schottky diodes.



Figure 3.10: Sequence of photocurrent images taken with $V_{ds} = 0.7$ V and different gate voltages, depicting the *n*- to *p*-type transition.

It can be furthermore concluded from the corresponding electrostatic potential profiles in Figure 3.11, that in the p- (n-) type regime, the potential drops are concentrated at the drain (source) contact, as opposed to the OFF state, in which the potential drop is distributed along the entire channel. A closer inspection of the profile at $V_{qs} = 4.3$ V suggests that the potential



Figure 3.11: (a) Potential profiles of a biased CNFET as a function of gate voltage. (b) Band diagrams depicting the operation mechanism of a Schottky barrier transistor. In the p- (n-)type regime, the potential drops predominantly at the drain (source) contact, favoring hole (electron) injection. In the OFF state, symmetric drops on both contacts are observed, in conjunction with a much less pronounced drop along the nanotube. Under this condition, charge carrier injection is suppressed and the CNFETs exhibit low conductance.

drops occurring around the electrical contacts are symmetric and stronger than the one observed in the middle of the tube.

The potential profiles agree very well with the widely accepted Schottky barrier transistor model for the operation mechanism of CNFETs (Figure 3.11b), wherein the Schottky barriers are modulated by the fields induced by the gate voltage and the drain-source bias [24, 63]. The band profiles are also consistent with those expected from results of electroluminescence experiments [81]. This analogy is described in further detail as follows. In the OFF state, the potential drops close to the two contacts are symmetric and hence both electron and hole injection occurs at a similar extent. In this situation, electroluminescence is observed at the center of the device. On the other hand, upon moving away from the OFF state to the p- (n-)type ON state, the potential experiences a larger drop at the drain (source) contact, and hence hole (electron) injection is favored, leading to shifts in the position of electroluminescence emission. Although the drain-source bias used in the present experiments is not ideal for observing electroluminesence (where V_{ds} is required to be twice as high as V_{qs}), the extracted band profiles are able to describe the scenario in a consistent fashion.

Chapter 4

SPCM measurements on crossed nanotube junctions and networks

4.1 Introduction

The lack of chirality-selective nanotube growth techniques imposes a serious problem for the reproducibility of devices comprising individual CNTs, and consequently for their technological implementation. In the past years, several different strategies have been followed to overcome this limitation, including novel CNT synthesis methods [82, 83], and the development of techniques that enable the separation of specific types of nanotubes [84–86]. However, despite appreciable advances achieved by these approaches, they are still not able to yield sizable quantities of nanotubes of a given chirality.

Alternatively, carbon nanotube networks have emerged as a promising route around such reproducibility problems [87–89]. This is mainly possible due to the fact that the properties of random networks reflect an ensemble average over the properties of the constituting metallic and semiconducting CNTs. While the good performance of CNT networks renders them technologically attractive, the electrical transport mechanisms in such devices are still poorly understood.

The basic components of nanotube networks are crossings between individual tubes, which can be classified as of metal-metal (M-M), metalsemiconductor (M-S) or semiconductor-semiconductor (S-S) type. Thus, a detailed investigation of such crossed junctions is crucial for gaining a deeper understanding of the electrical transport in the networks. So far, spatiallyresolving techniques have yet not been used in the investigation of nanotube crossings, despite their strong capability to unravel the individual contributions of the contacts, nanotubes and junctions to the overall properties of network devices. In this Chapter, SPCM measurements on CNT crossed junctions and networks are described. The resulting photocurrent images give insights into the electrical transport mechanisms of single nanotube crossings, and reveal that a limited amount of crossed junctions determine the response of CNT networks.

4.1.1 Background

Carbon Nanotube Networks

Carbon nanotube network devices are typically prepared by random deposition (or growth) of SWNTs on a substrate, followed by the fabrication of source and drain contacts, separated by a large distance with respect to the average length of the contained tubes. The electrical response of such devices can be readily tuned between metallic and semiconducting, by controlling the density of tubes in the network [89]. This possibility stems from the fact that the probability for the formation of metallic percolating paths increases with increasing CNT density, as expected from standard percolation theory [90].

CNT networks have been considered for various applications, including transparent conducting films, field-effect transistors, and optoelectronic devices [40, 90–92]. Field-effect transistors composed of CVD-grown networks were first reported by Snow et al. [87], who demonstrated that low nanotube densities (~ 1 $\text{CNT}/\mu\text{m}^2$) resulted in *p*-type devices with good electrical characteristics (mobilities ~ 10 cm² V⁻¹ s⁻¹ and ON/OFF ratios ~ 10⁵). Field-effect mobilities as high as $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were obtained by increasing the CNT density, which however at the same time reduced the ON/OFF ratio. A significant advance was achieved by Kang et al. [93], who were able to grow aligned nanotubes along the [2110] direction of quartz substrates. As a result of the CNT ordering, excellent electrical properties were obtained (mobilities ~ 1000 cm² V⁻¹ s⁻¹ and ON/OFF ratios ~ 10⁴), after breaking the metallic nanotubes through high drain-source bias ramps. Furthermore, Bradley et al. [88] fabricated CNT network transistors on transparent polyimide substrates, thus demonstrating the potential of CNTs in flexible electronics. In that study the gating was provided by a metallic electrode, onto which the plastic substrate was placed, and ON/OFF ratios of $\sim 10^4$ and mobilities of $\sim 12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were found. An improvement by one order magnitude in the field-effect mobility of flexible CNT network devices was recently achieved by employing top gate electrodes with a high dielectric constant gate oxide (HfO_2) [94].

4.2. SAMPLE PREPARATION

Carbon Nanotube Crossings

Despite their much higher complexity, nanotube networks have been studied since longer than CNT junctions, due to their much simpler preparation. However, as mentioned previously, a detailed understanding of nanotube crossings is essential for interpreting the behavior of networks.

Electrical transport measurements through individual crossed nanotube junctions were first reported by Fuhrer *et al.* [95], who observed a strong, non-linear electrical response of M-S junctions. This was attributed to the formation of Schottky barriers (height ~ 190-290 meV) at such crossings. By contrast, M-M and S-S junctions were observed to behave Ohmically, which was taken as evidence for a good alignment between the bands of the crossing tubes. Afterwards, diode-like electrical responses have also been reported for S-S crossed junctions [96]. In this type of junction, the current rectification was ascribed to the presence of a semiconducting isotype p-p heterojunction at the crossing site, which results from the difference in the band gap energies of the nanotubes.

All the aforementioned studies suggest the presence of transport barriers at nanotube junctions. Kim et al. [97] focused their work on the quantification of the height of such barriers, in both Y- and crossed-junction devices. To this end, they applied thermionic emission theory in the analysis of low temperature electrical data, under the assumption that the contribution of the electrical contacts can be neglected. Gate dependent measurements revealed two different types of I - V responses in the devices, namely with ambipolar and unipolar characteristics. These responses were respectively ascribed to M-S and S-S inter-tube junctions. In the ambipolar response, the current rectification was observed to switch from forward- to reverse-bias conditions, with an applied gate voltage. This was attributed to the gate modulation of the Schottky barrier at the M-S junction, as a consequence of which either electrons or holes are injected to the semiconducting tube. Barrier heights of approximately 110 meV were estimated for M-S junctions, whereas S-S junction barriers displayed heights in the range of 150-230 meV. The authors further concluded that the electrical transport in their devices is dominated by charge carrier tunneling through the junctions at low temperature, and thermal emission at higher temperatures.

4.2 Sample preparation

Two different types of samples were studied, namely (i) low-density nanotube networks, and (ii) devices comprising either one or two crossed nanotube

junctions. In an attempt to interpret the response of the more complex CNT networks, experiments were extensively performed on the second type of devices.

As already stated in Chapter 3, fluctuations in the nanotube density were commonly observed within the present CVD-grown CNT samples. Isolated nanotube crossings could be frequently observed in regions containing relatively low densities. Crossed junction devices were then prepared by defining electrodes at the ends of the crossing nanotubes, as exemplified by the AFM image in Figure 4.1a. Such configuration allowed each of the CNTs to be first individually characterized, thus enabling the junctions to be assigned as M-M, S-S or M-S. On the other hand, when space constraints prevented such electrode attachment, electrical characterization was achieved by defining additional electrodes after collection of all data. Electrical and SPCM measurements on crossed junction devices were performed in two-terminal configuration while the remaining electrodes were kept at floating potential, enabling the metallic and semiconducting nanotubes to be individually characterized, or the response across the inter-tube junction to be measured.



Figure 4.1: Atomic force microscopy images of typical devices comprising (a) a single crossed nanotube junction, and (b) a low-density random CNT network.

CNT network devices were prepared in a similar procedure as for nanotube crossings, except for using regions of higher nanotube density, and employing an additional plasma etching step to limit the dimensions of the network (Figure 4.2). Electron beam lithography-defined PMMA masks were used to protect networks regions with desired dimensions ($\sim 8 \ \mu m \ge 20 \ \mu m$). The remaining regions of the samples were then etched by oxygen plasma (power ~ 100 W, for 120 s), and electrical contacts were defined by EBL. Figure 4.1b depicts an AFM image of a typical device comprising a lowdensity nanotube network.



Figure 4.2: Scheme of the fabrication of random CNT network devices. (a) AFM images reveal regions with relatively high nanotube densities. (b) A PMMA layer is deposited onto the CNT sample. (c) Electron beam lithography is used to define a PMMA mask over a specific region. (d) Oxygen plasma etching is carried out to remove unwanted CNTs. (e) A second electron beam lithography process is used to define the electrical contacts.

4.3 Carbon nanotube networks

As a starting point for this study, the photoelectrical behavior of low-density random CNT networks was addressed. Figure 4.3a displays an AFM image of a network device that exhibited unipolar *p*-type characteristics with an ON/OFF ratio of ~ 10⁴. SPCM images acquired under zero drain-source bias condition, as exemplified by Figure 4.3b, exhibit a number of photocurrent lobes distributed throughout the network. By comparison with the corresponding AFM image, it can be discerned that in the ON state ($V_{gs} =$ -10 V), the signals are located either at the electrical contacts or at nanotube crossings, whereas in the OFF state ($V_{gs} = 10$ V), the lobes at the contacts disappear, and the photoresponse is given by just a few of the crossed nanotube junctions.

Interestingly, by applying a drain-source bias ($V_{ds} = 1.5$ V), the photocurrent response narrows down to one or at most a few spots within the network, as shown in Figure 4.4. In addition, the relative magnitude of the photoresponses at the CNT crossings is modulated by the applied gate voltage. Unfortunately, a series of photocurrent images over the entire gate voltage dependence could not be obtained for network devices, due to the increased dark-current signal that was detected upon switching the device from the OFF state to the *p*-type ON state. Since the spatially-resolved photocurrent signals reveal the regions of strong local electric fields, these ob-



Figure 4.3: (a) AFM image of a typical low-density network device with randomly oriented nanotubes. The white arrows indicate the position of two nanotube crossings, which are used as reference points within the network. (b) Zero drain-source bias SPCM images of the same device in the *p*-type ON state ($V_{gs} = -10$ V), and OFF state ($V_{gs} = 10$ V). The white lines mark the position of the electrodes.

servations indicate that in network devices, the electrostatic potential drops predominantly at only a few of the nanotube junctions, rather than homogeneously throughout the network. The highly localized photoconductive response within the devices is in contrast to earlier studies, which assumed that the entire network would contribute to the generated photocurrent [40]. In order to shine light onto the origin of the photocurrent localization and its implication for the electrical transport through such networks, model devices comprising single crossed nanotube junctions were investigated.



Figure 4.4: Photocurrent images of the device shown in Figure 4.3, recorded under applied drain-source bias ($V_{ds} = 1.5$ V) at different gate voltages.

4.4 Single crossed junction devices

4.4.1 Electrical transport

Prior to the SPCM characterization, electrical transport measurements were performed on the crossed junction devices. Figure 4.5 reveals that the I - Vcharacteristics of individual metallic and semiconducting nanotubes are not significantly affected by the second crossing tube, as apparent from their linear responses at low-bias. This conclusion is further supported by the current saturation of the nanotubes in the high-bias regime, which can be attributed to excitation of optical phonons [19,98]. The I - V curves measured across the different types of inter-tube crossings are included in the figure for comparison. All types of crossed junctions display a considerable resistance increase, which can be partially attributed to the presence of a tunneling barrier between the two crossing tubes. Moreover, while the low-bias electrical response of the M-M junction device is Ohmic, the M-S and S-S junctions exhibit non-linear responses.



Figure 4.5: I - V characteristics of individual metallic (M) and semiconducting (S) carbon nanotubes, which constitute the crossed junction devices, in the (a) lowbias, and (b) high-bias regimes. The electrical responses of the corresponding M-M, M-S and S-S junctions at low-bias are added for comparison. All measurements were taken with $V_{gs} = -10$ V.

In order to clarify this behavior, detailed gate dependent electrical measurements were performed on the M-S and S-S junctions, the results of which are shown in Figure 4.6. The M-S junction device displays strong current rectification, with a gate voltage-induced modulation of the $I_{forward}/I_{reverse}$ ratio between 5 and ~ 10⁴. The S-S junction device, on the other hand, exhibits a diode-like rectification only in the OFF state, where the $I_{forward}/I_{reverse}$ ratio is ~ 10². Moreover, the reverse current increases considerably when switching the device to the ON state, such that it behaves as a leaky diode.

4.4.2 SPCM measurements

Photocurrent maps acquired at zero drain-source bias from M-M, M-S, and M-S junction devices in the ON state ($V_{gs} = -10$ V) are presented in Figure 4.7, along with the corresponding optical reflection images (left column,



Figure 4.6: Gate dependent I - V characteristics of (a) M-S, and (B) S-S crossed junction devices. The inset highlights the response of S-S junctions observed around the OFF state.

where the dashed lines indicate the position of the nanotubes). In the case of the M-S junction device, the longer nanotube, which is connected to two electrodes, is metallic.

The middle column in Figure 4.7 displays the photocurrent images measured through individual nanotubes within different devices. In all three cases, both the metallic and semiconducting nanotubes show enhanced photoresponses at the metal contacts, similar to previous studies on individual nanotubes (see Chapter 4). Interestingly, no significant photocurrent signals occur at the crossings, in accordance with the above conclusion that the underlying nanotube is only weakly disturbed by the second crossing tube. The images within the right column of Figure 4.7 represent the responses measured across the different junctions. While both M-M and S-S devices display strong photoresponses at the metal contacts, a sizable photocurrent signal at the intertube crossing appears only in the latter device. The negligible photoresponse at the M-M junction evidences the absence of a potential barrier at the crossing, which is in agreement with the Ohmic behavior in the I-V characteristics of the corresponding device. The signal at the intertube crossing within the S-S junction device, on the other hand, reflects the formation of an isotype p-p heterojunction due to the CNT band gap difference [96, 97]. This conclusion is corroborated by the observation of stronger photoresponses at the junction for larger diameter differences between the crossing nanotubes (Figure 4.8).

In the case of the M-S device, the fact that the photoresponse at the intertube crossing, which originates from the local Schottky barrier, is of lower



Figure 4.7: Photocurrent maps acquired at zero drain-source bias of M-M, M-S and S-S crossed junction devices taken with the semiconducting CNTs in the *p*-type ON state ($V_{gs} = -10$ V). The respective optical reflection images are shown in the left column, where the dashed black lines mark the position of the tubes. The longer nanotube in the M-S junction device, which is connected to two electrodes, is metallic. The photocurrent maps of the individual metallic and semiconducting CNTs are shown in the middle column. The right column displays the photocurrent responses measured across the nanotube junctions.



Figure 4.8: Plot of the normalized photocurrent intensity at S-S junctions, as a function of the difference between the inverse diameters of the crossing tubes (estimated by AFM characterization). The inverse diameter difference is proportional to the difference in the band gap energies of the crossing CNTs.

intensity than the signal detected at the drain contact, where the semiconducting CNT is connected, is consistent with the lower work function difference between prototypical metallic and semiconducting CNTs ($\Phi_{CNTs} \sim 4.7 \pm 0.2 \text{ eV}$) [99], as compared to the interface between semiconducting tubes and AuPd ($\Phi_{AuPd} \sim 5.1 \text{ eV}$). Moreover, the stronger signal at the drain contact indicates that the local electric field at the contact to the semiconducting CNT is much stronger than that at the contact to the metallic tube. In conclusion, the M-S device behaves as an asymmetrically contacted semiconducting CNT with a dominant built-in electric field close to the AuPd electrode.

The electrostatic potential profiles of the M-S and S-S crossed junction devices, which were derived from the photocurrent distribution, agree remarkably well with generally accepted models for asymmetric CNFETs or semiconductor heterojunction devices (Figure 4.9). In addition, the profile of the M-S device underscores the relatively stronger potential step at the contact to the semiconducting CNT.

The gate dependence of the zero-bias photocurrent response, presented in Figure 4.10, reveals that the magnitude of the photocurrent responses at the metal contacts decreases upon switching the devices from the p-type ON to the OFF state. Such behavior has been previously observed in individual CNTs (see Chapter 4) and reflects the flattening of the nanotube bands at the contacts, as the Fermi level of the CNT is shifted. By contrast, the magnitude



Figure 4.9: Photocurrent (black line) and electrostatic potential (green line) profiles of (a) S-S and (b) M-S junction devices. The estimated profiles agree well with models of isotype p-p heterojunctions (S-S) and asymmetric nanotube transistors (M-S), as illustrated by the respective band diagram schemes.

of the photocurrent signal at the intertube crossing changes to a smaller extent, indicating that the built-in electric field at the nanotube-nanotube interface is only weakly affected by the gate voltage, as expected from the simultaneous shift of the Fermi level of both metallic and semiconducting CNTs. Hence, while the electric fields associated with the barriers at the metal contacts decrease considerably when approaching the OFF state, those located at the intertube crossings remain largely unaffected, as illustrated by the schematic band diagrams in Figure 4.10. From these, it can be concluded that the role of intertube crossings becomes more important in the OFF state, which is in agreement with the behavior observed in network devices (Figure 4.4).

Further insight into the properties of the M-S and S-S inter-tube crossings was gained from gate dependent SPCM measurements under application of a fixed drain-source bias. Such images acquired around the OFF state of the M-S junction device of Figure 4.7 ($V_{ds} = 0.8 \text{ V}$) are presented in Figure 4.11, where it can be seen that the photocurrent generation is restricted to the semiconducting nanotube, independent of the gate voltage. In the *n*-type regime ($V_{gs} = 10 \text{ V}$), the photocurrent is concentrated in the vicinity of the M-S junction, where the metallic tube can be viewed as source contact to the semiconducting tube, since the potential drop along the former is comparatively small, as apparent from its negligible photoresponse. Upon moving



Figure 4.10: Sequence of zero-bias photocurrent maps of the M-S and S-S junction devices shown in Figure 4.7, as a function of the gate voltage. The band profiles illustrate the effect of V_{gs} on the relative magnitude between the electric fields at the contacts and the intertube crossings.



Figure 4.11: Series of photocurrent images of a M-S junction device under applied bias ($V_{ds} = 0.8$ V), as a function of the gate voltage. The thick dashed lines mark the position of the electrical contacts, whereas the thin dashed lines indicate the position of the nanotubes.

towards the *p*-type regime ($V_{gs} = 8$ V), the photocurrent response progressively shifts towards the drain contact. This behavior closely resembles that of individual semiconducting nanotubes, and is in agreement with the theoretically predicted changes in the electrostatic potential profile induced by gate voltage modulation [24]. It further consolidates that M-S junction devices effectively represent semiconducting CNTs with asymmetric Schottky contacts, which accounts for the diode-character of these devices.



Figure 4.12: Gate dependence of the photocurrent response of S-S junctions under applied bias ($V_{ds} = 1.5$ V).

The photoresponse of the S-S junction device $(V_{ds} = 1.5 \text{ V})$ of Figure 4.7 is depicted in Figure 4.12, as it is switched from the n- to the p-type regime. Like for the M-S junction device, the photocurrent is seen to be localized around the source contact in the n-type regime, and upon switching to ptype operation, it is gradually shifted to the drain contact. In the OFF state $(V_{qs} = 9.4 \text{ V})$ the photoresponse occurs almost symmetrically around the S-S junction, whereas it is absent at the electrical contacts. The corresponding electrostatic potential profiles extracted from the photocurrent distribution (Figure 4.13) reveal that in the ON states of the device, the applied bias drops predominantly in vicinity of the contacts, while there is only a slight potential drop at the heterojunction. On this basis, the non-linear electrical response in the ON state of the device can be attributed to the asymmetry of the contacts. In the OFF state, by contrast, the applied potential predominantly drops at the semiconducting heterojunction. Under this condition, the device displays a diode-like behavior, as typically observed for devices comprising heterojunctions [96,97,100]. The overall behavior is schematically illustrated by the band profiles in Figure 4.13(b), which highlight the existence of two

different transport modes controlled by the gate. Specifically, in the contactdominated ON states the contact barriers are thinned, thereby enhancing charge carrier injection by tunneling, in a similar manner as observed for individual semiconducting CNT devices. In comparison, the heterojunctiondominated OFF state is characterized by pronounced current rectification at sufficiently large drain-source bias.



Figure 4.13: (a) Normalized electrostatic potential profiles of a biased S-S junction device at different gate voltages. (b) Schematic illustration of the operating mechanism of the device. In the OFF state, the potential drops predominantly at the nanotube crossing.

4.5 Multiple junctions

In order to explore the next level of complexity, the spatially-resolved photoresponse of devices incorporating two S-S junctions in series was investigated. SPCM images of such a device under applied drain-source bias (V_{ds} = 1.5 V) are collected in Figure 4.14. The observed behavior is qualitatively similar to that of the single S-S junction device shown in Figure 4.12, *i.e.*, in the *n*- (*p*-) ON state the signal appears mainly at the source (drain) contact, whereas in the OFF state, the photoresponse is focused around the two S-S crossings. In addition, in the present device the relative magnitude of the signals detected at the two crossed junctions is altered upon gate voltage modulation. These features are in close correspondence to the response of nanotube networks (Figures 4.3 and 4.4). However, further investigations are



still required in order to identify the mechanism of gate-induced changes in the photocurrent distribution, and the nature of the dominating junctions.

Figure 4.14: SPCM images of a device composed of two S-S nanotube junctions, measured as a function of the gate voltage at $V_{ds} = 1.5$ V. The sequence depicts the transition from the *n*- to the *p*-type regime. The top left panel displays the corresponding optical reflection image, where the dashed lines represent the three semiconducting nanotubes.

Chapter 5

Photoelectronic characterization of graphene devices

5.1 Introduction

Graphene, a zero band-gap semiconductor, displays a unique electronic structure, where the conduction and valence bands meet at the Dirac point. Studies carried out on graphene have been focused on its linear energy dispersion around the Fermi level. In particular, effects associated with the Dirac-like nature of graphene quasiparticles, *e.g*, the half-integer quantum Hall effect and Klein tunneling, have been documented [10,14,101]. However, according to theoretical investigations, some features of electrical transport in graphene are better described by conventional semiconductor physics [11,102].

As already mentioned in Chapter 2, the electrical transport in graphene can be continuously tuned between electron or hole conduction by shifting the Fermi level through an applied gate potential. Graphene devices thus exhibit ambipolar behavior, however, with an unexpectedly high conductivity minimum. This observation could recently be explained by the formation of electron-hole puddles at the Dirac point, which arise from charged impurity centers [11,12]. Despite the increasing knowledge on graphene-based devices, the roles of the contacts and the sheet edges have received only little attention so far. In fact, compared to typical semiconductor devices, wherein the contacts are optimized in order to avoid scattering, much less is known about the properties of metal contacts to graphene [15]. Another important aspect that remains to be explored is the influence of the sheets boundaries, which are expected to significantly influence the charge transport, analogous to the formation of surface-states in the case of bulk semiconductors.

In this chapter, scanning photocurrent microscopy is employed to explore the impact of the electrical contacts and the sheet edges on the charge transport through graphene devices. The resulting photocurrent images reveal the presence of transport barriers at the metal contacts, as well as the presence of potential modulations along the sheets. Moreover, it is found that upon electrostatic gating, the transition from the p- to n-type regime does not occur homogeneously within the sheets. Instead, the formation of p-type conducting edges surrounding a central n-type channel is observed at low carrier densities.

5.1.1 Background

Graphene devices

Owing to its high charge carrier mobility, graphene has been strongly considered for application in electronics [5,6]. Mobilities as high as $\sim 2 \times 10^5$ $\rm cm^2 V^{-1} s^{-1}$ have been reported for suspended graphene devices [13]. Consequently, ballistic transport on the sub-micrometer scale is attainable at room temperature. Recent theoretical work has revealed that metal contacts with different work function than graphene cause local doping of the sheet [103]. Due to the low density of states around the Dirac point of graphene, such charge transfer results in significant shifts in the Fermi level. It has also been predicted that metals that interact more strongly with graphene (Co, Ni and Pd) lead to large perturbations of the graphene bands, and ultimately to the destruction of the Dirac cone. Huard et al. [104], on the other hand, reported on experiments that indirectly evidence the effect of the electrodes on the transport properties of graphene devices. The authors observed an asymmetry in the conductance of electrons and holes, for the same carrier densities. This difference was attributed to the pinning of the charge density below the electrodes, which results in the formation of p-n or p-p junctions, depending on the gating regime of the graphene flake.

Another feature of graphene devices is their relatively poor field-effect conductance switching, with ON/OFF ratios of at most ~ 100, more than two orders of magnitude lower compared to CNFETs [9], being typically observed. One strategy around this limitation consists of imposing a lateral confinement to the graphene flakes, which results in the opening of a band gap [105]. As expected, devices comprising such graphene nanoribbons (GNRs) display good electrical switching, with ON/OFF ratios as high as ~ 10⁶ for ribbons narrower than 10 nm [106]. However, the edges play an important role in GNR devices, leading to charge carrier scattering, and thus greatly reducing the carrier mobility (~ 200 cm² V⁻¹ s-1).

Optical properties

While electrical transport in graphene has been extensively explored, investigations on its optical properties are still limited. Most of the early optical studies on graphene have been focused on the visibility of monolayers by optical microscopy [56, 107], and on Raman spectroscopy measurements [52]. On the other hand, optical experiments offer a great potential for exploring the electronic structure and the excited-state properties of graphene. First steps towards this direction have been undertaken recently. For instance, Wang *et al.* [108] have investigated optical transitions in mono- and bi-layer graphene flakes by means of infrared reflection spectroscopy. The authors have observed a peak in the reflectivity spectra of graphene bilayers, in contrast to the case of monolayers. This finding could be directly attributed to the band gap present in the electronic structure of bilayer graphene. Furthermore, it was observed that the optical transitions in both types of samples are gate dependent, as a consequence of the changes in the band filling induced by shifts in the Fermi level.

Nair *et al.* [109], reported optical absorption studies on suspended graphene sheets, demonstrating that the optical absorption of graphene monolayers can be understood in the framework of Dirac-like fermion quasiparticles. The authors found that the absorbance of a single graphene layer corresponds to ~ $\pi \alpha = 2.3\%$, where $\alpha \equiv e^2/\hbar c \approx 1/137$ is the fine structure constant. In addition, absorbance increments of the same magnitude were observed for each additional graphene layer. Although the photon energy exceeded that corresponding to the linear region of the dispersion curve, the authors presented theoretical calculations demonstrating that the use of relatively high energies (*i.e.*, E > 1 eV) leads to only small corrections to the absorbance.

5.2 Experimental

5.2.1 Sample preparation and electrical transport

Graphene monolayers, prepared by mechanical exfoliation of graphite crystals, were contacted by Ti (0.3 nm)/Au (20 nm) electrodes on Si/SiO₂ substrates. As mentioned in Chapter 3, the single layer character of the graphene sheets was confirmed by their AFM height profile and by Raman spectroscopy. Four-probe electrical measurements were performed on the devices, by measuring the potential drop between two intrusive contacts. By comparing the two- and four-probe resistances (Figure 5.1), it is observed
that the contacts impart a dominant contribution to the device. However, it is noteworthy that, due to the invasiveness of the electrodes, the measured four-probe resistance still overestimates the intrinsic sheet resistance [5, 14].



Figure 5.1: Electrical characterization of a typical graphene device. The two-(black line) and four-probe (red line) sheet resistance at room temperature is plotted as a function of the gate voltage relative to the Dirac point. Due to the invasive nature of the contacts, the four-probe measurement is unable to completely exclude the contact resistance.

5.2.2 SPCM measurements

SPCM measurements were carried out under ambient conditions, using a diffraction-limited laser spot with $\lambda = 514.5$ nm, spot size ~ 0.4 μ m and power density ~ 100 kW/cm². Figure 5.2 displays the zero drain-source bias photocurrent image of a graphene device near the Dirac point ($V_{gs} = 0$ V), along with its corresponding AFM and optical reflection images. Interestingly, several photocurrent responses are observed along the graphene sheet, thus indicating the presence of local built-in electric fields. The existence of such local fields is in accordance with experimentally observed spatial potential fluctuations associated with the formation of electron-hole puddles, as has been shown in a scanning single electron transistor study [12].

In addition to the relatively weak photocurrent signals along the sheet, strong photocurrent responses occur at the two metal contacts. Figure 5.3a displays complete I-V curves taken with the laser spot fixed at the electrical contacts, which evidence the generation of an offset voltage of around 2 mV,



Figure 5.2: (a) Atomic force microscopy image of a graphene monolayer contacted by four gold electrodes. (b) Optical reflection image acquired simultaneously with the photocurrent image. The drain and source electrodes used in the measurements are indicated. (c) Photocurrent image taken at $V_{ds} = V_{gs} = 0$ V. In the false color scale, white (black) corresponds to positive (negative) current.

with only a negligible resistance change of the device. Furthermore, the photocurrent at the contacts exhibits a linear dependence on the incident laser intensities as depicted in Figure 5.3b. These two findings can be attributed to the presence of electrostatic potential steps at the contacts [61, 72]. According to recent theoretical work [103], a difference in the work functions of the metal and graphene leads to charge transfer at the contact interface, and to the formation of pronounced interface dipole layers. Such metal-induced doping has been reproducibly observed in the SPCM images of a wide range of samples.

Another interesting observation in Figure 5.2c is the strong positive (negative) photoresponse at the center of the source (drain) contact, while weaker negative (positive) photocurrent lobes occur at the electrode edges. In order to unravel the origin of this distribution, SPCM images were acquired in different transport regimes by varying the back gate voltage. Figure 5.4 displays such a sequence of zero bias photocurrent images covering the n- to p-type transition. The top-left image, which belongs to the n-type regime, discloses that the photoresponse is dominated by the contacts, involving a positive (negative) photocurrent throughout the entire source- (drain-) graphene interface. The corresponding photocurrent image taken in the p-type regime (bottom right image) is very similar, except for the opposite polarity, comprising positive (negative) photocurrent at the drain (source) contact. The inverted photocurrent polarities in the two regimes demonstrate that the magnitude of the interfacial potential step changes with the gate voltage.



Figure 5.3: Measurements taken on the device shown in Figure 5.2, by fixing the laser spot at the electrodes. (a) I - V characteristics recorded in the dark, and with the laser positioned at the source and drain contacts. The inset displays a photocurrent image, in which the positions where the laser spot was fixed during the measurements, are indicated. (c) Photocurrent detected at the source contact as a function of the laser power.

This dependence is highlighted in Figure 5.5a, where the photocurrent detected at the center of the source contact is plotted as a function of the gate voltage. The sign of the detected photocurrent is observed to reverse at approximately $V_{gs} = 28$ V, on the right side of the Dirac point (corresponding to minimum conductance). For comparison, devices with contacts comprising a lower work function metal (10 nm of Ti covered by 5 nm of Au) were also studied. Contrary to the gold contact case, the latter devices exhibit the zero-photocurrent crossing on the left side of the Dirac point, as shown in Figure 5.5b. In order to analyze this difference, it is instructive to express the potential step at zero gate voltage in terms of the work functions of the metal (Φ_m) and of graphene (Φ_g) and the Fermi level shift imparted by the metal doping on the graphene flake (ΔE_F), according to the scheme in Figure 5.5c [103]. When the gating-induced shift of the Fermi level is included, the potential step is given by:

$$\Delta V = \Phi_m - \Phi_g - \Delta E_F + sgn(V_{gs} - V_{gs}^{Dirac})\hbar v_F \sqrt{\pi\alpha(V_{gs} - V_{gs}^{Dirac})}, \quad (5.1)$$

where $\alpha = 7.2 \times 10^{10} \text{ cm}^{-2} \text{ V}^{-1}$ and $\hbar v_F = 5.52 \text{ eV} \text{ Å} [10, 110]$. By assuming a work function of $\Phi_{Ti} = 4.3 \text{ eV}$ for titanium, $\Phi_{Au} = 4.7 \text{ eV}$ (accounting for oxygen adsorption from the ambient [111]) for gold, and Φ_g = 4.5 eV for graphene, the potential step magnitude can be plotted as a function of the gate voltage and ΔE_F (Figure 5.5d). Best agreement with

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the measured gate voltage differences between the zero-photocurrent crossing and the Dirac point is obtained with $\Delta E_F = -0.23$ eV and 0.25 eV for the Tiand Au-contacted devices, respectively, as schematized in Figure 5.5d. Consistent with recent theoretical calculations [103], these values confirm that (Ti) Au contacts result in (*n*-) *p*-type doping of graphene, with a carrier density of ~ (5.5 × 10¹² electrons/cm²) 6.5 × 10¹² holes/cm². Furthermore, equation (5.1) yields a value of -50 meV (30 meV) for the potential step at the gold (titanium)/graphene interface at the Dirac point.



Figure 5.4: Spatially resolved photocurrent maps within various transport regimes of a graphene device. The sequence of images display the n- to p-type transition, as the gate voltage is swept from -30 to 30 V. The dotted lines in the top-left image indicate the position of the source and drain contacts.

In addition to the contact regions, a gate-dependent modulation of the photoresponse can be observed also along the graphene flake. Specifically, at higher carrier densities, a weak photocurrent compared to the contact regions occurs within the sheet, which is predominantly positive (negative) with a few weak oscillations in the n- (p-) type regime. By contrast, closer to the Dirac point the relative photocurrent intensity within the sheet increases, and randomly distributed regions of positive and negative photocurrent emerge (Figure 5.2). This characteristic indicates that in those gating regimes, the local electric fields associated with the barriers at the contacts



Figure 5.5: Quantitative determination of the potential steps at the metal/graphene interface. (a) and (b) Gate dependence of the dark current (I_d) and the photocurrent at the source contact, for Au- and Ti-contacted devices, respectively. $V_{ds} = 1 \text{ mV}$ in (a) and $V_{ds} = 2 \text{ mV}$ in (b). (c) Schematic of the metal/graphene interface, where Φ_m and Φ_g are the work-functions of the contact metal and graphene, respectively, ΔV is the potential step, ΔE_F is the Fermi level shift induced by metal doping, and $\Delta E_{F,electr.}$ is the Fermi level shift due to electrostatic doping. The upper and lower panels depict the Dirac point and the condition in which $\Delta V = 0$. (d) Plot of the potential step at the metal/graphene interface as a function of the gate voltage. The green and blue lines correspond to the cases of Au- and Ti-contacted devices, where $\Phi_{Au} = 4.7 \text{ eV}$ and $\Phi_{Ti} = 4.3 \text{ eV}$, and ΔE_F was obtained by fitting equation (5.1) to the experimental data. The black curve corresponds to the gate dependence of the charge carrier density.

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become substantially larger than the potential landscape within the graphene sheet. By contrast, at low carrier densities, potential fluctuations associated with charged impurities gain importance, because the screening promoted by charge carriers in the graphene flake is reduced.

The course of the n- to p-type transition furthermore displays the "nu*cleation*" of photocurrent signals of opposite sign (with respect to the signal detected at the center of the electrodes) at the metal/graphene edge interfaces when the gate voltage is decreased starting from the *n*-type regime (Figure 5.4). The intensity of these edges signals rises as V_{qs} is further decreased, and approaches that at the center of the electrodes when the Dirac point is reached. Hence, it can be concluded that in this gate voltage range, *p*-type transport prevails at the edges of the graphene sheet, while in the central region electron conduction is dominating. Homogeneous p-type conduction across the entire device, as reflected by the coalescing of the edge lobes, requires decreasing V_{gs} past the Dirac point. The fact that the *n*to p-type transition occurs at different V_{qs} for the edges and central region of the sheet, testifies an altered electronic structure at the edges, as expected from the symmetry breaking of the honeycomb lattice. Signatures of pronounced disorder and the existence of local electronic states have been previously detected at graphene edges by spatially-resolved Raman and scanning tunneling spectroscopy [112, 113]. The overall device behavior and the formation of transversal p-n-p profiles close to the Dirac point can be further visualized through electrostatic potential maps (Figure 5.6), obtained using a similar procedure as for CNTs (see Chapter 4). As a first approximation, the potential steps were obtained by integrating the photocurrent response in one dimension, along the axis parallel to the channel. Since the potential fluctuations observed on the graphene flakes may induce current signals that flow in different directions, the potential maps may be thought of as disorder averaged.

5.2.3 Multi-terminal devices

The metal-induced doping of graphene evidenced by the SPCM investigation raises the question as to the impact of electrodes that are kept at floating potential. As demonstrated in Figures 5.7a and 5.7b for the same device in Figure 5.2, photocurrent signals of opposite polarity can be observed around the floating electrode located between the drain and source contacts. This observation is consistent with the introduction of a local potential dip displaying gradients of opposite signs at the two faces of the floating electrode. Upon switching the device from the p- to n-type regime, the sign of the photoresponses is inverted, which can be explained by the carrier density be-



Figure 5.6: Two-dimensional electrostatic potential maps of the graphene device shown in Figure 5.4. (a) Gate dependence of the electrostatic potential distribution, extracted from photocurrent data measured at $V_{ds} = 0$ V. The dashed lines mark the source and drain electrodes. (b) Line profiles of the electrostatic potential taken in the transversal direction and at the center of the channel (position shown in the inset), with the device operating in different transport regimes, *i.e.*, *p*-type, *n*-type and at the Dirac point. At the Dirac point, a *p*-type character is apparent at the edges, leading to a *p*-*n*-*p* transversal profile in the device.

ing pinned below the floating electrode, while within the graphene it can be effectively modulated through the gate voltage. Similar signs of the invasiveness of metal contacts on graphene were observed on multi-terminal devices with floating electrodes at the periphery of the graphene flake, as depicted in Figures 5.7c and 5.7d. In this case, although much stronger photoresponses appear at the drain and source electrodes, pairs of positive/negative photocurrent lobes can be discerned around all floating electrodes.



Figure 5.7: Invasive nature of metal contacts to graphene. Zero bias photocurrent images of the graphene device shown in Figure 5.2, with the middle electrode kept at floating potential (F) at (a) $V_{gs} = -50$ V, and (b) $V_{gs} = 50$ V. The inset schematically illustrates the pinning of the carrier density beneath the floating electrode. (c) Optical reflection image of a graphene multi-terminal device. The source (S), drain (D) and floating (F) electrodes are correspondingly indicated, whereas the non-marked electrode is not connected to the sheet. (d) Photocurrent image of the device shown in (c). The inset displays the photocurrent at the marked region, with a normalized color scale to enhance contrast.

Chapter 6

Conclusions and outlook

In this thesis, scanning photocurrent microscopy was employed in the investigation of devices comprising carbon nanostructures. Individual semiconducting carbon nanotubes constituted ideal samples for the initial experiments, since the accumulated knowledge on these nano-objects enabled the photoresponses to be more accurately interpreted. By performing detailed measurements on individual nanotubes, SPCM was found to be a powerful tool for the characterization of nanodevices. More specifically, it was shown that the spatially-resolved photocurrent signal reflects the distribution of the electrostatic potential within the devices. On this basis, potential profiles obtained in different operating regimes yielded valuable information on the transport mechanism of the nanotube devices. Moreover, the photocurrent response could be further applied to estimate the Schottky barrier heights at the metal contacts.

Having demonstrated the capabilities of SPCM for individual tubes, the technique was expanded to the characterization of more complex systems, namely carbon nanotube crossed junctions and low-density networks. This task was motivated by the technological relevance of CNT networks, and the important role of crossed junctions in such devices. The resulting photocurrent images evidenced the presence of Schottky barriers and semiconducting heterojunctions at M-S and S-S junctions, respectively. Furthermore, the potential profiles revealed two different transport modes for crossed nanotube junctions, where in the ON states, the potential drops are concentrated around the contacts. By contrast, in the OFF state, the potential drops almost exclusively at the inter-tube junction, imparting a diode-like behavior to the devices. A similar behavior was observed in carbon nanotube networks, as reflected by the strong localization of the photoresponse at only a few of the constituting junctions. Thus, it was demonstrated that the photoconductivity response in such devices is not homogeneously distributed through the

network, as assumed by previous studies. Moreover, the finding that a few of the junctions dominate the response of networks provides valuable guidelines for the future optimization of CNT network-based devices.

Finally, scanning photocurrent microscopy proved ideally suited to probe local changes in the electronic structure of graphene sheets introduced by deposited metal contacts and by local symmetry breaking at the edges. The obtained results highlight the relevance of both, the contact interfaces and the edges in the operation of graphene devices. More specifically, the photocurrent response evidenced a metal-induced doping of the graphene sheets. Furthermore, it was found that the p- to n-type transition does not occur homogeneously within the graphene sheet, resulting in the formation of p-n-ptransversal profiles in the vicinity of the Dirac point.

6.1 Outlook

The capability to determine the band structure profile of nanodevices by SPCM could be further exploited by investigating other aspects of carbon nanotube field-effect transistors. For instance, the effect of the environment on the operation of CNFETs is a fundamental question that remains to be studied in more detail, in spite of recent advances that suggest that nanotubes are p-doped under ambient conditions (see Chapter 4 and ref. [54]). In order to further clarify the doping, a more systematic study would be necessary. This could be carried out by mapping the Schottky barriers of CNFETs, by means of SPCM measurements, in a controlled atmosphere. A significant change in the depletion width, and in its gate dependence, would be expected by undoping the devices through application of, *e.g.*, high drain-source bias ramps in vacuum [54].

Intentional chemical doping is another interesting issue to be addressed, due to its capability of converting nanotube devices into *n*-type transistors. Siddons *et al.* [114] reported chemical doping of CNFETs by means of polymer electrolytes with chemical groups of either electron accepting or donating character. SPCM is a perfectly suited technique to probe nanotube devices subjected to such doping, since it allows for the observation of doping-induced changes in the depletion width of the Schottky barriers, without being affected by the polymer coating. The result of a preliminary experiment towards this direction is shown in Figure 6.1. A gradual *n*-type doping is observed in the transfer characteristics of a typical CNFET, after the deposition of poly(ethyleneimine) (PEI) onto the device. Zero-bias photocurrent images, acquired in the ON states of the CNFET before (t = 0) and after (t = 15 min) the PEI deposition, are respectively displayed in Figures 6.1b

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and 6.1c. It is noteworthy that upon chemical doping, the photocurrent lobe at the source contact reverses sign and becomes more elongated, whereas the photoresponse at the drain contact disappears. These observations underscore that the Schottky barriers are indeed significantly affected by chemical doping. Moreover, the sign inversion of the source contact lobe confirms the *n*-type character of the nanotubes, while its elongation indicates an increase in the depletion width of the corresponding Schottky barrier. On the other hand, the absence of a photocurrent response at the drain contact reflects an inhomogeneous doping along the tube, which renders the CNFET asymmetric, as also evidenced by its non-linear I - V characteristics. More experiments are still required for the study of chemical doping in CNFETs, and by applying equation (3.1), it should be even possible to evaluate the doping kinetics, by measuring the depletion width as a function of time.



Figure 6.1: (a) Transfer characteristics of a CNFET before (t = 0) and after PEI deposition. The black and red dots indicate the transport regimes, in which the zero-bias photocurrent images shown in (b) and (c) were respectively recorded.

Another interesting topic for future studies is the spatially-resolved photocurrent response of metallic nanotubes. To date, only one SPCM study has been reported on metallic tubes [72], where issues such as the gate dependence of the photoresponse were not addressed. Preliminary experiments show that photoresponses of metallic tubes are much less affected by gate modulation than those of semiconducting CNTs. Nevertheless, by increasing the gate voltage, the lobes at the electrical contacts become weaker, and signals along the nanotube become more pronounced. Further experiments on such devices are expected to yield valuable information related to their operation.

In addition, SPCM can also be employed as a spectroscopic tool, wherein fundamental issues related to the optical properties of carbon nanotubes could be addressed. This could be achieved by detecting the dependence of the photocurrent response on the excitation energy, which should provide insights into the optical absorption of CNTs. Perebeinos *et al.* [115] theoretically predicted that the optical absorption of nanotubes around the E_{11}^s transition should be significantly affected by electric fields applied parallel to the CNT axis. Such behavior could be investigated by extending SPCM measurements in the infrared range into spectroscopical experiments.

Regarding carbon nanotube networks, the SPCM data described in Chapter 5 were unfortunately not sufficient to fully clarify all the observed phenomena. For example, the reason why only a few of the crossed junctions dominate the response of the networks could not be clarified. In order to do so, further SPCM measurements on devices comprising multiple crossed junctions would be of great value. On the other hand, the existence of Schottky barriers and semiconducting heterojunctions at nanotube crossings opens interesting perspectives for new experiments. For example, the application of crossed nanotube junctions in junction field-effect transistor (JFET) devices could be evaluated. Such device geometries have been demonstrated for bulk semiconductor heterojunctions, where the conductance switching is given by the modulation of the local junction barrier.

Finally, a wide range of possibilities emerge for future SPCM studies on graphene. Analogous to the case of individual nanotubes, spatially-resolved photocurrent measurements are expected to provide valuable information regarding the effects of chemical doping on the transport properties of graphene devices. Moreover, the investigation of sheets comprising multi-layers or structural perturbations is also promising, as evidenced by the response of the multi-terminal device shown in Figure 6.2. The AFM image of the device reveals the presence of a corrugation on the larger monolayer sheet, as well as a smaller bilayer flake connected by two electrodes. Zero-bias photocurrent images taken at $V_{gs} = \pm 20$ V show stronger photoresponses at the contacts to the bilayer flake, which seem to be less affected by gate modulation. The dissimilarities in the photoresponse of mono- and bi-layers can be attributed to differences in their electronic structure, and constitute a direction for further experiments. Furthermore, pronounced photocurrent signals are detected at the interface between the sheet corrugation and the electrodes, in the vicinity of the Dirac point ($V_{gs} = 20$ V), suggesting that local electric fields are induced by strain on graphene.



Figure 6.2: (a) Atomic force microscopy image of a multi-terminal graphene device, which contains contacted bi- and folded-layer regions, as indicated by the white arrows. A line profile of the height is shown in the inset. (b) Optical reflection image of the same device. (c) and (d) Photocurrent images of the multi-terminal device taken with zero drain-source bias, at $V_{gs} = \pm 20$ V.

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