

# ABSTRACT

## *GRAPHENE AND CARBON NANOTUBES IN TRANSISTORS, DIODES AND FIELD EMISSION DEVICES*

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Since their discovery, graphene and carbon nanotubes have been playing an important role in nanoscience and nanotechnology thanks to their extraordinary physical and chemical properties.

With silicon-based electronics tending towards its scaling limits, the semiconductor industry is looking for the next switch which can replace the silicon field-effect transistor and graphene can be a possible alternative for silicon. However the development of graphene-based electronics is limited by the quality of contacts between the graphene and metal electrodes; for such reason it becomes of fundamental importance to characterize metal/graphene interfaces at the contacts. Further, due to its important advantage of being naturally compatible with thin film processing, graphene is easy to integrate into existing semiconductor device technologies and the graphene-silicon (Gr/Si) heterojunction is one of the simplest conceivable device in a hybrid graphene-semiconductor technology. For their very high aspect ratio, both graphene and carbon nanotubes are considered extraordinary elements to realize field emission devices.

In this PhD thesis, we study electronic properties and transport mechanisms of graphene and carbon nanotubes through an extensive electrical characterization of field-effect transistors, diodes and field emission devices based on these materials.

We perform electrical characterization of graphene based field effect transistors (GFETs) with Ti, Ni, Nb and Cr contacts, in bottom and side gate configuration, by measuring transfer and output characteristics. We clearly observe the presence of a double-dip feature in the conductance curve for long transistors in bottom gate configuration and we explain it in terms of charge transfer and graphene doping under the metal contacts. The transistor transfer characteristics show a hysteresis that is attributed to charge trapping in silanol group at the gate oxide surface. We study the contact resistance between graphene and the metal electrode with larger values of  $\sim 30 \text{ k}\Omega\mu\text{m}^2$  recorded for Ti-contacts. Importantly, we prove that the contact resistance is modulated by the back-gate voltage. We also analyze the effects of room temperature vacuum degassing and electron bombardment on the electric properties of graphene FETs with Nb contacts. We report asymmetric transfer characteristics with a resistance plateau in the n-branch. We show that weakly chemisorbed Nb acts as p-dopant on graphene and explain the transistor characteristics by Nb/graphene interaction with unpinned Fermi level at the interface. We demonstrate that low energy irradiation is detrimental on the transistor current capability, resulting in an increase of the contact resistance and a reduction of the carrier mobility even at electron doses as low as  $30 \text{ e}^-/\text{nm}^2$ . We show that the irradiated devices recover by returning to their pristine state after few repeated electrical measurements. Moreover, we characterize side-gated all-graphene field effect transistors with gate-to-channel distance of  $100 \text{ nm}$  and channel

width of 500 nm on SiO<sub>2</sub>/Si substrates. We demonstrate that the side-gate is far more efficient than the back gate in modulating the channel conductance. We measure the planar leakage along the SiO<sub>2</sub>/vacuum gate dielectric over a wide voltage range, reporting rapidly growing current above 15 V. We unveil the microscopic mechanisms driving the leakage, as Frenkel-Poole transport through SiO<sub>2</sub> up to the activation of Fowler-Nordheim tunneling in vacuum, which becomes dominant at high voltages. We report a field-emission current density as high as 1  $\mu A/\mu m$  between graphene flakes. These findings are essential for the miniaturization of atomically thin devices.

The research activity about the graphene-silicon (Gr/Si) heterojunction is focused on the study of a new-concept of Gr/Si photodiode made of a single-layer CVD graphene transferred onto a matrix of nanotips patterned on n-type Si wafer. The original layout, where nano-sized graphene/Si heterojunctions alternate to graphene areas exposed to the electric field of the Si substrate, which acts both as diode cathode and transistor gate, results in a two-terminal barristor with single-bias control of the Schottky barrier. The nanotip patterning favors light absorption, and the enhancement of the electric field at the tip apex improves photo-charge separation and enables internal gain by impact ionization. These features render the device a photodetector with responsivity (3 A/W for white LED light at 3 mW/cm<sup>2</sup> intensity) almost an order of magnitude higher than commercial photodiodes. We extensively characterize the voltage and the temperature dependence of the device parameters, and prove that the multi-junction approach does not add extra-inhomogeneity to the Schottky barrier height distribution. This study represents a step forward toward the integration of graphene into existing Si technology for new generation optoelectronic devices.

The research activity related to the carbon nanotubes concerns a deep experimental characterization of the transport and field emission properties of buckypapers. Transport characteristics evidence ohmic behavior in a wide temperature range, non linearity appearing only close to 4.2 K. The temperature dependence of the conductance shows that transport is mostly due to thermal fluctuation induced tunneling, although to explain the whole temperature range from 4.2 K to 430 K a further linear contribution is necessary. The field emission properties are analyzed by means of a nanocontrolled metallic tip as collector electrode to access local information about buckypaper properties from areas as small as 1  $\mu m^2$ . Emitted current up to 10<sup>-5</sup>A and turn-on field of about 140 V/ $\mu m$  are recorded. We demonstrate that our buckypapers are extremely stable emitters with emitted current almost unaffected after half day operating time, and thus they can be considered excellent candidates for the realization of field emission devices.