## Fabrication of 2D heterojunction in graphene via low energy N<sub>2</sub><sup>+</sup> irradiation

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Graphene attracts the interest of the scientific community due to its unique physical properties, e.g. high mobility of charge carriers, massless relativistic carriers, linear band dispersion and anomalous quantum hall effect. Such properties make graphene a promising key component for post-silicon electronic devices. In this sense, a great effort is put to tailor the electrical properties of graphene via p-type and n-type doping [1], which is carried out via chemical vapor deposition (CVD), redox reactions and plasma treatment. Recent results show that n-doping can be also achieved by implantation of nitrogen by low-energy ion bombardment [2]. Such technique offers a great advantage as it allows, in principle, to lithographically pattern heterostructures in thin graphene films, fostering the fabrication of atomically thin circuitry. Yet, this property holds solely for high energy beams, although the nano-focusing still poses challenges when low energy ions are considered. Here we report a proof-of-principle experiment demonstrating that low energy ion irradiation through a mask can be used to achieve local control on the doping in graphene. In particular, we tackle the fabrication of a sharp junction between *n*-doped and neutral graphene on Ir(111), exhibiting metallic or semimetal-like density of states. Notably, our method is both versatile and scalable. The miniaturization of graphene heterojunction to the nanometer scale allows the creation of 2D nanocircuits at the ultimate thickness limit, with enormous application potential in the field of modern integrated circuitry [3].

To study the potential of ion implantation with low energy N ions, we grew graphene on Ir(111) substrate via CVD of ethylene at 880 °C. Ir(111) offers the advantages of straightforward preparation and weak graphene-substrate interaction [4]. The growth conditions resulted in the formation of a continuous, predominantly single-layer thickness and non-rotated graphene. After growth, the sample was irradiated at room temperature with low energy (100 eV)  $N_2^+$  ions through a mask (e.g. a 30  $\mu$ m circular aperture or a 1 mm slit), positioned as close as possible to the surface. A sketch of the system is presented in Figure 1a. Subsequently, selected patterns on irradiated film were characterized with the Spectroscopic Photo-Emission and Low Energy Electron Microscope (SPELEEM) at Nanospectroscopy beamline of the Elettra storage ring, Italy [5]. By imaging the N 1s core level emission we could assess the quality of the fabricated junction, e.g. the width of the transition region (boundary) between irradiated and pristine regions (Fig. 1b) as well as the local electronic properties of the film. The lateral extent of the boundary region, determined presumably by the sample-mask distance and distortions of the electric field between gun and target, was found to be less than 3.8 µm. Laterally resolved XPS spectra of N 1s allowed the type of defects induced by doping and their abundance to be quantified. µ-ARPES measurements of the doped and non-doped areas display a local shift of the Dirac energy depending on the irradiation time: for example, 3 min of ion implantation produce a shift of -0.45 eV (Fig. 2). In order to test the thermal stability of the implanted nitrogen, the patterned graphene film was then annealed to 800 °C in UHV,. The SPELEEM capabilities of acquiring selected area XPS spectra proved that the implanted N can survive treatment to rather high temperatures and that the temperature has an effect on the relative abundance of the defect species. Finally, the possibility to preserve the doping pattern in normal atmospheric conditions and the way to

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improve miniaturization of such technique to achieve fabrication of 2D circuitry in the nanometer scale will be discussed.

## References

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Figure 1: a) Sketch of the system used for ion implantation. The preparation chamber was filled with N<sub>2</sub> (partial pressure  $2x10^{-5}$  mbar). The graphene-covered Ir(111) substrate and the metallic mask were placed in front of the ion gun and then irradiated at room temperature. b) LEEM (E<sub>K</sub> = 7 eV) and XPEEM N 1s (E<sub>B</sub> = 400.8 eV) images of the junction area between neutral (left) and n-doped (right) single-layer graphene. The boundary region (white dashed lines) has a width of 3.8 µm. c) momentum distribution curves obtained from µ-ARPES measurements on neutral (left) and n-doped (right) single layer graphene after 3 min of irradiation. The shift of the Dirac cone, highlighted with the blue dashed line, is -0.45±0.07 eV. The red dashed line represents the Fermi energy. hv ~ 40.5 eV