The electronic, thermal, and mechanical properties of graphene are exceptionally sensitive to lattice imperfections, surface functionalization and doping. Therefore, atomic scale structural and electronic investigations in this material are critically important for understanding these properties. Graphene samples produced by CVD method were doped with nitrogen by plasma exposure. We have exploited the complementarities of aberration-corrected TEM, Scanning Tunnelling Microscopy (STM) and micro-Raman spectroscopy to investigate the link between the structural and the electronic properties of N-doped graphene. Our experimental protocol allows applying these characterization techniques on the same samples in order to reduce the gap between micro and atomic scales investigation.

STM and HRTEM were used to characterize the nitrogen-induced single-point defects in graphene and the charge redistribution due to chemical bonding. As previously reported [1], the charge redistribution due to the insertion of nitrogen atoms in graphene that is easily detected by STM, allows the detection of such a low-contrast defect by HRTEM (Fig. 1). Our study highlights two important structural information about N-doped graphene and doping process. At first, Cu-supported graphene during the plasma exposure are more likely to be N-doped than suspended graphene. Secondly, the high variability of the C/N ratio on the same graphene sample reveals that nitrogen doping is not spatially homogeneous. This latter result pushed us to combine HRTEM and micro-Raman investigations on same micron-large areas of the samples, in order to provide a deeper understanding of the Raman spectrum as a function of the structure (holes, number of layers) and the Nitrogen doping rate of graphene (Fig. 2).


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Fig. 1: HRTEM image of single layer graphene before nitrogen doping (a). Atomic scale analysis of nitrogen insertion in graphene: the charge redistribution due to chemical bonding is observed by aberration-corrected TEM (b) and STM (simulation of the structure and charge distribution in insert) (c).

Fig. 2: Raman spectra of the G-band optical phonon in two different spots of a Nitrogen-doped suspended graphene sample: the shift of the phonon peak energy ($\omega_G$) and its broadening show a significant variation of the chemical potential due to different Nitrogen doping.