N-doped graphene : Electronic properties and STM

L. Henrard, F. Joucken, S.O. Guillaume, R. Sporken, Ph. Lambin

University of Namur, Namur, Belgium
luc.henrard@fundp.ac.be

Abstract

In this communication, simulations of the electronic properties and of STM-STS results of N-doped graphene are presented and compared with experimental data. Indeed, chemical modification and, in particular nitrogen doping, is one of the major route to tailor the electronic and optical properties of graphene materials. However, the control of the doping atomic configuration is still a challenge and the exact consequences on the physical properties of each configurations is far from being fully understood. Here, we review our recent achievements on this topic with an emphasis on the input of simulations to understand the effect of the long-range interaction between dopant and of the layer stacking on the electronic properties and STM/STS fingerprints.

Post-synthesis N-doping of graphene have been performed by plasma exposure of C-terminated SiC wafer [1]. STM pattern are similar to those obtained by other methods and, for more than 75 % of the doping sites, have been attributed to the substitution of one C atom by an N atom (See Fig 1 for the STM/STS analysis). Other (and more complex) patterns have been images at several sample-tip bias, demonstrated hole doping configurations. Experimental STM reveals that the N-doping pattern depends on the tip-graphene distance and we have performed detailed STM simulations in order to rationalize this observation (For more details, see [1]).

Being a true 2D crystal, graphene has special properties. In particular,a point-like defect may introduce perturbations in the long range. This characteristic questions the validity of using a supercell geometry in an attempt to explore the properties of isolated defect. Fig 2 b and c demonstrate this effect for DFT simulations for a single N substitution in a 9x9 (0.6 %of N) and 10x10 graphene supercell (0.5% of N), as compared to tight-binding approach for an isolated N 'defect' in a infinite graphene layer (Fig 2a). We have also shown that a doping of graphene with a random (not periodic) distribution of dopant has a electronic structure very similar to isolated defect and not to the regularly spaced defect with the same dopant concentration. The dopant concentration has then less importance that the periodicity for low concentration. Of course, as soon as dopant are a few nanometer apart, interaction occurs and the STM pattern become more complicated to analyze (For more details, see [2]).

Chemical doping has also been investigated for bi-layer graphene. Here, we show that a charge transfer occurs between the two layers, even if only one of the two layers is doped. In this case, if the 'pristine' graphene layer is analyzed with STM, no local pattern is found but the symmetry of the graphene pattern (hexagonal or triangular) is modified by the doping level. If the doping occurs on the top layer, the STM pattern is slightly dependent on the doping sub-network site (For more details, see [3]).

References

[1] F. Joucken, Y. Tison, J. Lagoute, J. Dumont, D. Cabosart, B. Zheng, V. Repain, C. Chacon, Y. Girard, A. R. Botello-Mendez, S. Rousset, R. Sporken, J.-C. Charlier, and L. Henrard, Phys. Rev. B, **85** (2012)161408 .
[2] Ph. Lambin, H. Amara, F. Ducastelle, L. Henrard. Phys. Rev. B **86** (2012) 045448
[3] S.O. Guillaume, B. Zheng, J.-C. Charlier, L. Henrard. Phys. Rev. B **85** (2012) 035444

Figures

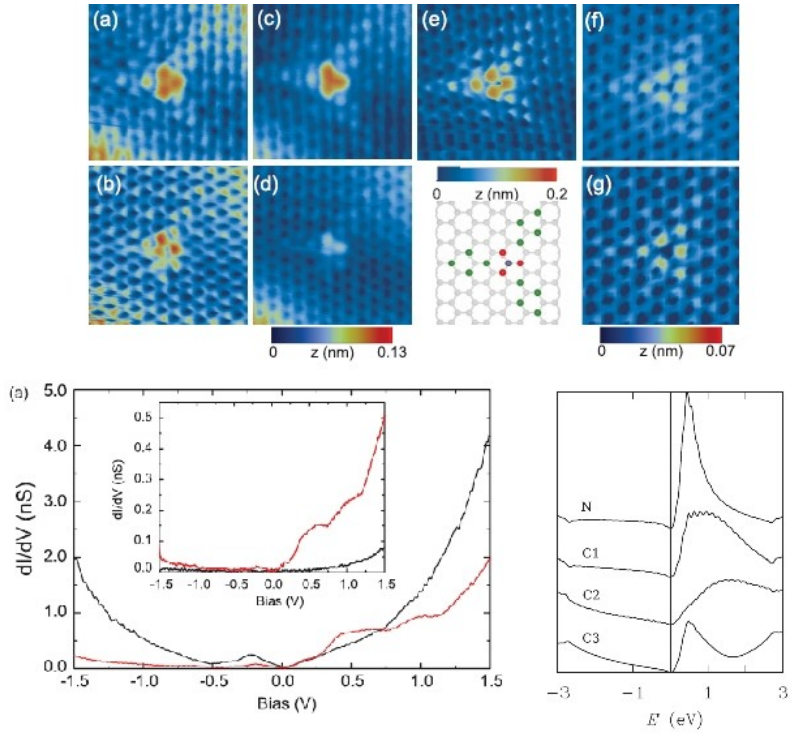

Fig 1 : Top : Topographic images of a substitutional nitrogen atom at (a) V_s = +0.2 V, I = 200 pA, (b) V_s = −0.2 V, I = 100 pA, (c) V_s = +0.5 V, I = 700 pA, (d) V_s = −0.4 V, I = 100 pA, and (e) V_s = +0.35 V, I = 800 pA. (e) Schematic view, (f) and (g) Simulations for N substitution in a 10x10 graphene supercell at (f) V_s = +0.5 V and (g) V_s = −0.5 V. *Bottom left* : Experimental Scanning tunneling spectra between graphene (black curve) and the simple substitution (red curve). Spectra taken with the feedback loop active when moving from one spot to another. Inset: Spectra taken with the feedback loop off when moving from one spot to another. *Bottom right* : Partial DOS of isolated N-doped graphene. From refs[1,2]

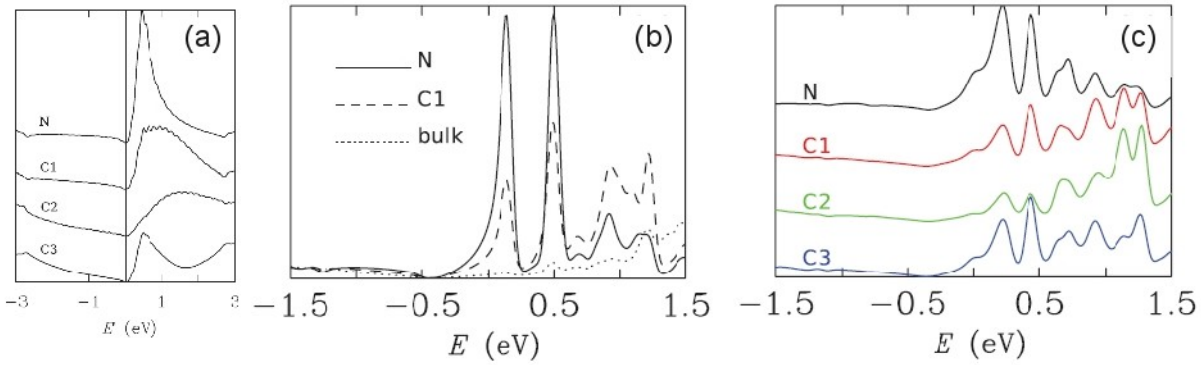

Fig 2. Partial Density of States of substitutional N-doped graphene. (a) Tight-binding calculations for an isolated N atom in a infinite graphene sheet. (b) and (c) DFT calculations of a N atom in a (9x9) and (10x10) supercell. From ref[2]