Electronic properties and STM images of N and B doped graphene

L. Henrard[1], S.-O. Guillaume[1], B. Zheng[1,2], J.-C. Charlier[3]

1 Department of Physics (PMR), University of Namur (FUNDP), Belgium
Luc.henrard@fundp.ac.be
2 Department of Materials Science and Engineering, University of Wisconsin-Madison, USA
3 Institute of Condensed Matter and Nanoscience (IMCN), Université Catholique de Louvain (UCL), Louvain-la-Neuve, Belgium

Chemical doping of graphene-based materials represents an active research direction to tune their electronic and transport properties in the same way as for conventional doping in semiconductor (Si, ...). Substitution of one (or several) carbon atoms by Boron (B) or Nitrogen (N) atoms give rise to a small structural effect whereas the electronic property is locally modify. Indeed, the substitution by N is expected to show additional donor states and then a n-type doping whereas B substitution lead to p-type doping. This chemical doping also induces changes in the reactivity of carbon nanostructures, thus allowing the development of chemical sensor, energy storage device (Li-battering) or supercapacitor.

Several attempts have been reported in the literature for doping either flat graphene or carbon nanotubes (CNT). The synthesis of chemically modified graphene has been achieved, following two main strategies : the direct growth of modified layers and the post-growth treatment of pristine graphene. These first studies revealed the presence of several atomic configurations for the nitrogen atoms: the substitutional ('graphitic') N, the pyridine-like N, or the pyrrole-like N. STM and STS are key experimental data in order to correlate the production methods and the atomic configuration of modified graphene. They also permit an analysis of the electronic levels in the vicinity of the dopant. Recent simulations [1] and experimental achievements [2,3] have shown that N-substitution can be achieved and analyzed.

Another way to tune the electronic properties of graphene material is to modify the number of layer (or the stacking order) of the system. Indeed Multilayer graphene (MLG) presents electronic and transport properties drastically different than single-layer graphene (SLG). Indeed, the linear electronic dispersion, characteristic of SLG, disappears in case of stacking (except if layers are disoriented) or when the graphene is deposited on a substrate. At last, when an external field is applied, the interaction between layers can be controlled and tailored, opening new possibilities for the engineering of the band gap in few layer graphene.

The combined influence of both interlayer interaction and of chemical doping has not been investigated in details yet in order to interpret experimental data. In the present study, both Nitrogen and Boron substitutional doping in one of the two layers of a bilayer graphene is investigated using a first-principles approach. A detailed study of the STM features for N or B chemical doping on the top layer of bilayer graphene or for buried defect is performed. Our simulations predict that even if local and direct fingerprints of buried chemical modification are very difficult to image, the delocalisation of the doping charges on the neighboring plane of bilayer graphene leads to a clear modification of the symmetry of the STM patterns, dependent on the bias voltage, for both top-doped and buried-doped layers. Doping multilayer graphene with Bernal (AB) stacking displays hexagonal or triangular STM patterns depending of the sign of the bias and can be misinterpreted as disoriented MLG if a careful STM/STS study is not performed [4].

References

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[2] L. Zhao et al., Science, **333** (2011) 999
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Figures

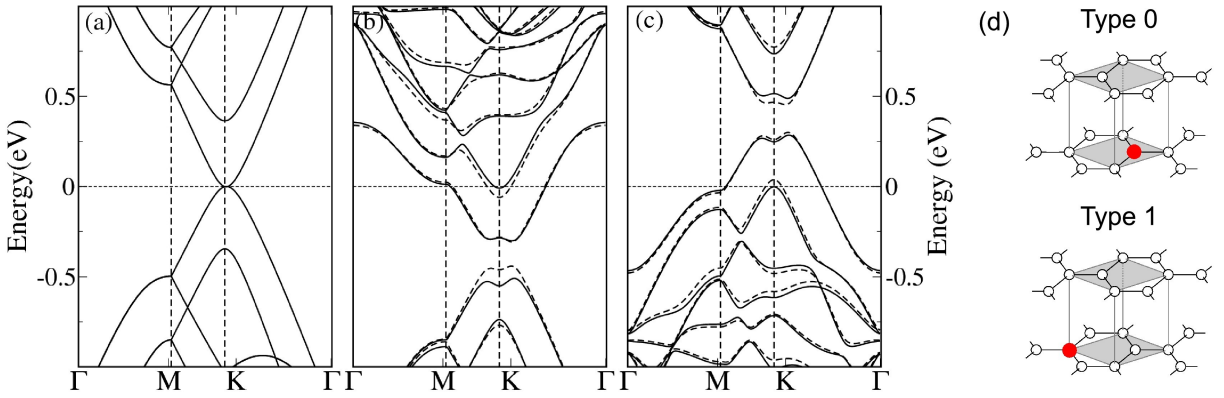

Figure caption : ab-initio Electronic band structures of (a) pristine, (b) N-doped, and (c) B-doped bilayer graphene. Only one of the two layers is doped by substitution of a single carbon atom. Type 0 (solid line) and type 1 (dashed line) doping sites are considered. A 10 x 10 supercell was used to model the three systems, including 399 C atoms and one dopant. (d) Schematic representations of type 0 (top) and type 1 (bottom) doping. Open symbols (resp. solid symbols) represent the carbon atoms (resp. the dopant).

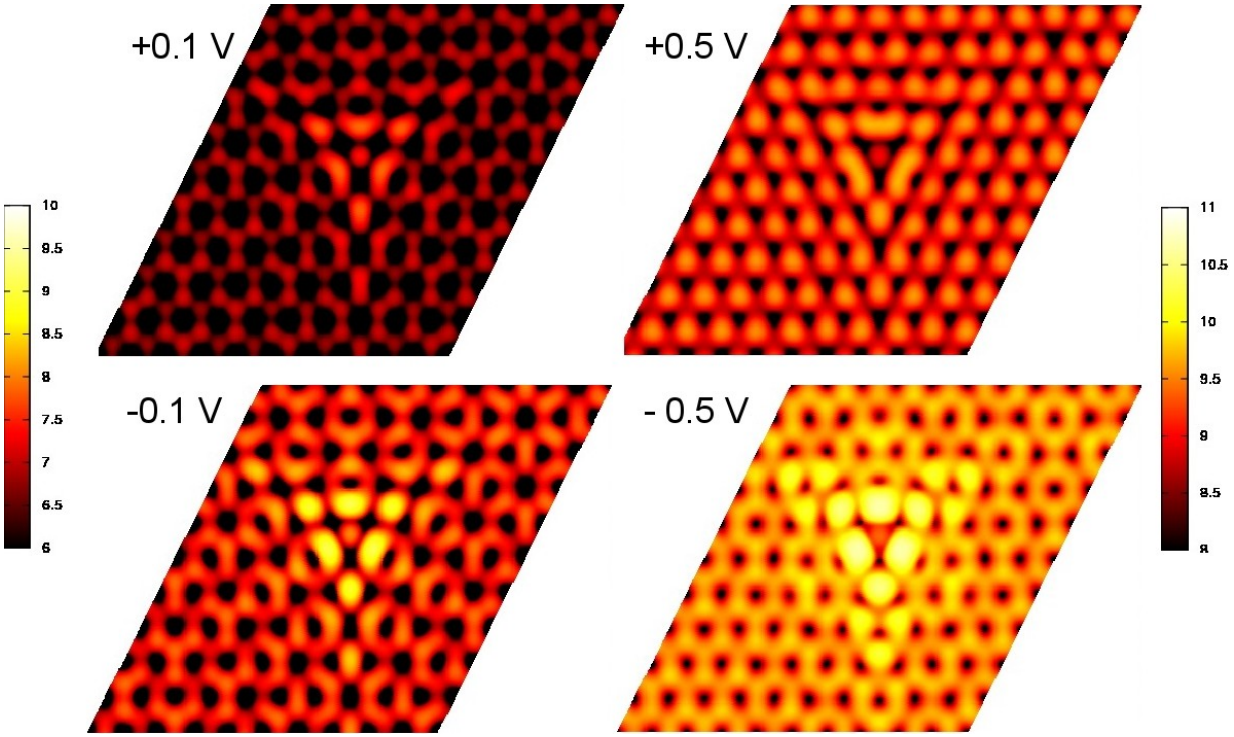

Figure caption : Ab initio STM images of N-doped bilayer graphene for various bias voltage : +0.1 V (top left), +0.5 V (top right), -0.1 V (bottom left), and -0.5 V (bottom right), respectively. The Nitrogen dopant is located at the center of the pattern, on the top layer. }