First principles calculations and kinetic process simulations of nitrogen and boron doped graphene

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The precise control of the doping characteristics of graphene-based systems is a key parameter for successful integration in devices and applications. Doping can tune graphene's carrier density, which is important for the optimization of graphene-based flexible and transparent electrodes. Moreover, if doping is confined in one out of the two equivalent graphene sublattices, considerable band gaps can open that could serve for switching devices on and off.

In the first part of this study, we initially use the density functional theory (DFT) to explore the conditions of sublattice symmetry breaking in nitrogen-doped and boron-doped graphene [1]. We show that although two-dimensional graphene structures are not suitable for dopant substitution with a sublattice preference, the nucleation of graphene grains [Fig. 1(a)] and their growth through the propagation of unpassivated zigzag edges could give rise to a highly unbalanced doping [Fig. 1(b)]. The effect is based on exothermic substitutions where nitrogen adatoms occupy unpassivated zigzag edge sites. This aspect is not observed for boron [Fig. 1(c)], where random substitutions for both sublattices should emerge as a result of adsorption in defected sites, rather than as spontaneous substitutions on edges. Based on our DFT results, we calibrate an event-driven Kinetic Monte Carlo model that simulates the growth kinetics of nitrogen-doped graphene and investigates the N incorporation mechanism in real process conditions. We demonstrate that N atoms, in general, preferentially choose one of the two sub-lattices correlated to the propagating zig-zag edge of the growing quasi-hexagonal graphene grain. However, due to the non-ideal edge configuration, this asymmetry does not lead to the fully sub-lattice occupancy in the triangle-like sub-domains of the grains [Fig. 2(a)]. Moreover the degree of symmetry breaking strongly depends on the growing conditions [Fig. 2(b)].

In the second part of this study, we investigate the influence of N- and B-doping on the electronic structure of the two-dimensional system by calculating effective band structures obtained from large supercells with Bloch states that are unfolded to the first Brillouin zone of graphene. For the case of N-doped graphene [1], we argue that the loss of inversion symmetry enhances the creation of a band gap when assisted by dopant agglomeration [Fig. 1(d)]. We moreover note that at higher concentrations of graphitic nitrogen the conduction band gets strongly affected. This aspect could be fundamental for the use of N-doped graphene in innovative devices, like valley-filters and valley valves. For the case of B-doped graphene we note that boron significantly perturbs the intrinsic graphene bands at the valence band of the system, while a minor influence of the boron dopants can also be visible in the conduction band [2]. A crucial issue that emerges for similar impurity concentrations is that the perturbation induced by nitrogen is lower that that of boron.

Our results can be relevant for the design of a series of electronic components, like electrodes, valley-filters, or channel materials for transistors, based on doped graphene structures.

References

[1] I. Deretzis and A. La Magna, Phys. Rev. B 89, 115408 (2014)
[2] I. Deretzis, G. Calogero, G. G. N. Angilella and A. La Magna, EPL 107, 27006 (2014)

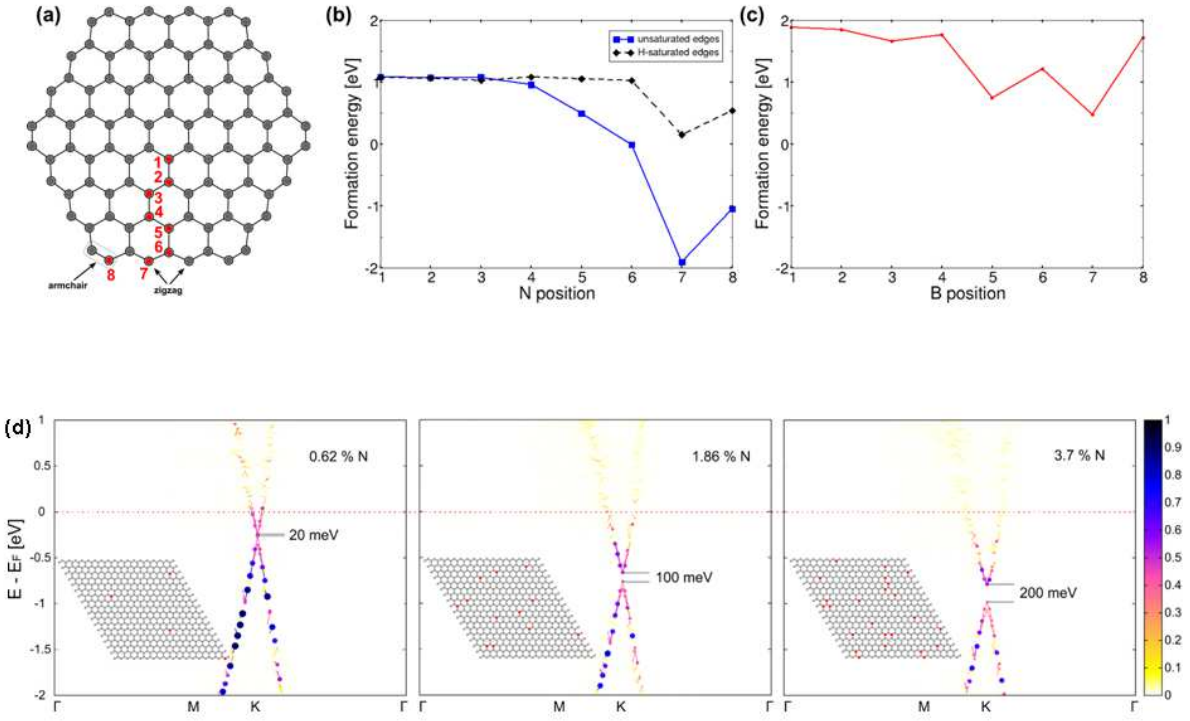

Figure 1: (a) Scheme of the 96-atom hexagonal graphene grain used in the calculations. (b) Relative formation energy for a substitutional N atom at different positions of the graphene grain. (c) Relative formation energy for a B atom at different positions of the graphene grain with unpassivated edges. (d) Effective band structures for 18×18 graphene supercells having a concentration of 0.62%, 1.86%, and 3.7% graphitic N. All N adatoms have been placed at the same graphene sub-lattice.

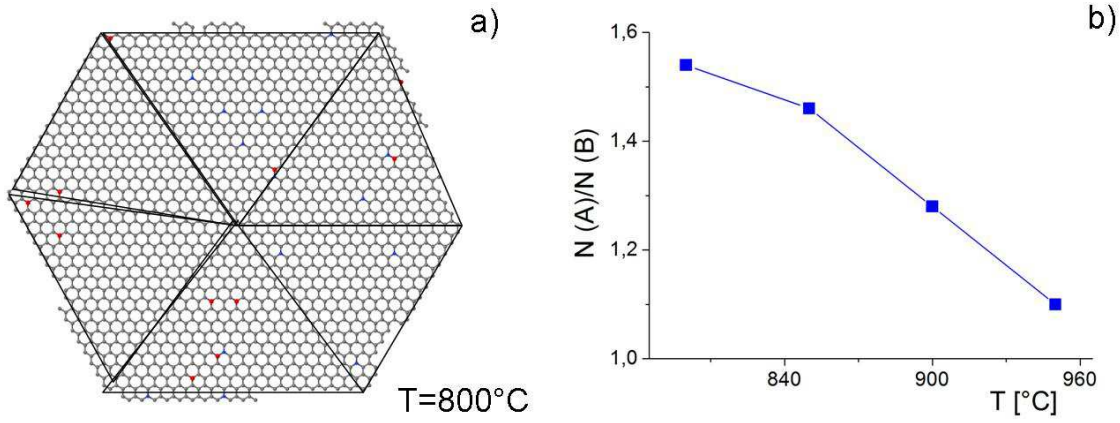

Figure 2: a) Snapshot of N-doped nano-grain of graphene after the early stages of a KLMC simulated growing process on a Cu substrate. The effective atomic flux is $\Phi=10^{18}$at/cm^{2}s. The approximated triangle-like domains are shown. Blue and red colors indicate atoms in different sub-lattices. b) Sub-lattice asymmetry degree as a function of the temperature calculated in large (~μm) domains.