Ordering in boron and nitrogen functionalized graphene layers

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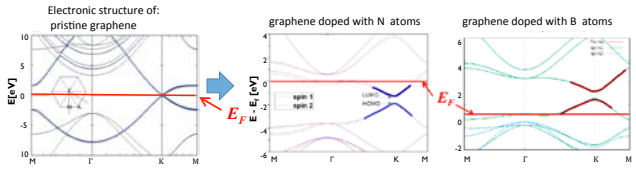
Motivation

- Functionization (doping) of graphene layer with nitride and boron



- For design of devices, functionization is technologically important problem.
- Up to now achieved concentrations of N and B are equal to 10% and 3% respectively.

M. Woińska, K. Z. Milowska, and J. A. Majewski, *Phys. Stat. Sol. (c)* **10**, 1167 (2013); *AIP Conference Proceedings* **1566**, 143 (2013)
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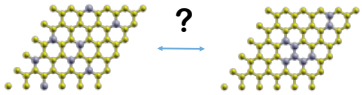
This work issue

- Clustering or random distribution of dopants – which is energetically favorable?



- Is it possible to describe the energies of doped graphene layers with simple Valence Force Field model?

Methods

- Density Functional Theory within GGA approximation
  Siesta package
  Troullier-Martins pseudopotentials, Wu-Cohen exchange-correlation potential
  5x5 graphene supercell
  convergence parametres of SIESTA:

DM.Energy.Tolerance	0.00001 eV
MD.MaxForceTol	0.01 eV/Ang

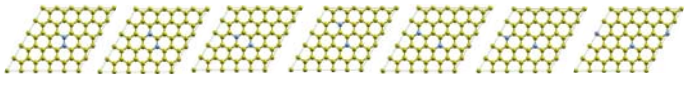
- Keating model for functionalized graphene:

$$\Delta E = \beta\downarrow 1 t\ r\downarrow 0\uparrow -2 \sum$$

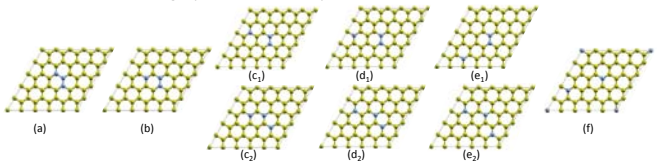
Investigated systems

We calculated energy of different systems with B or N atoms constrained to graphene hexagonal lattice:

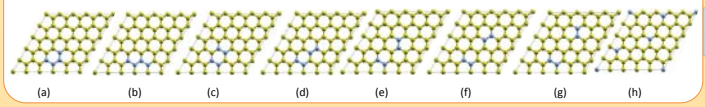
- 2 atoms substituting C per 50 atoms in supercell:



- 3 atoms substituting C per 50 atoms in supercell:

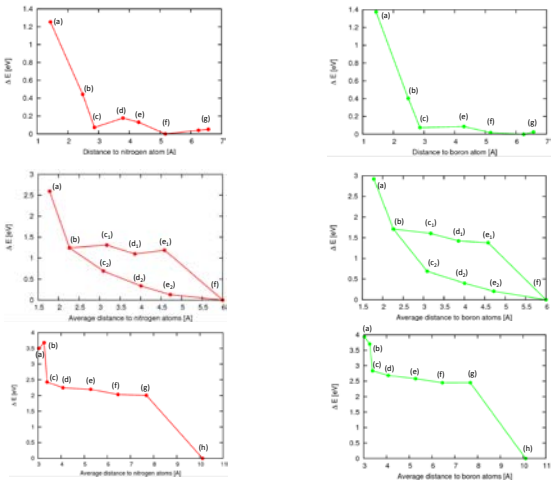


- 4 atoms substituting C per 50 atoms in supercell:

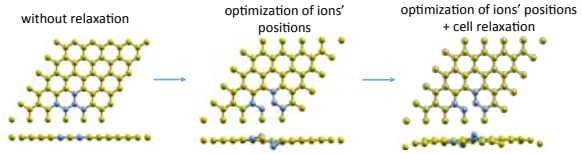


Results: dependence of energy on distances between doping atoms

Nitrogen **Boron**



Results: role of relaxation of doped systems



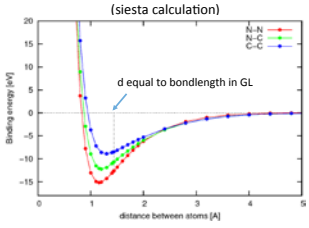
SYSTEM (5x5 supercell)	energy difference after ions' positions relaxation [eV]	energy difference to system with the biggest distances between dopants [eV]
1 N atom	0,03611	0,000000
2 N atoms - 1st nbrs	0,22489	1,213191
2 N atoms - 2nd nbrs	0,21511	0,403146
3 N aroms - clustered	0,4043	2,593905
5 N atoms - clustered	2,48728	4,943967

Results: relation to molecular binding energies

- Tendency to random distribution of dopants is related to binding energies of N_2, NC and C_2 molecules.

molecule	equilibrium distance [A]	binding energy [eV]	energy of molecule constrained to GL bondlength [eV]
C-C	1,2991	8,891836	0,402665
C-N	1,2072	12,232140	1,521825
N-N	1,156	15,172914	2,495522

Binding energy of N_2, NC and C_2 molecules as a function of distance between atoms (siesta calculation)



Conclusions

- Presence of neighbouring nitrogen or boron atoms is not energetically favorable
- However the most significant is direct neighbouring of N or B atoms, the role of second neighbours is not negligible – problems with application of the Keating model
- Geometry optimization reduces partially the differences in energy, but still clustering of dopants is not favoured. Moreover clustered N atoms tend to disturb the flat, hexagonal geometry of graphene layer, which is visible during geometry optimization.

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