Doping graphene with a monovacancy: bonding and magnetism

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Abstract. The possibility of creation of nanostructures on graphene and carbon nanotubes was investigated by placing different atoms at a single vacancy of graphene. Using the SIESTA software package and a high-throughput computing approach, we have consistently identified the binding energy and magnetic properties of 49 elements of the periodic table. The results show that all atomic species are stable at room temperature; some elements exhibit interesting magnetic behavior. E.g. Ni is not magnetic, whereas Al, Ga and P have magnetic moment. It is widely accepted that the rarity of metal-doped graphenes could be explained by the tendency of metal atoms to form clusters instead of doping. We analyzed corresponding binding energies and proved the opposite statement.

1. Introduction

Carbon nanotubes (CNTs) and graphene are unique materials for nanotechnology. The unique properties of these materials can be used in numerous applications, from advanced composite materials to artificial muscles and quantum computers [1, 2].

There is an evidence of the ability of the transition metals to dope graphene-like systems (graphene, onion-like carbon); this process can take place during growth or saturation of existing vacancies, like e. g. in carbon nanostructures synthesized using Ni containing catalyst [3]. The presence of substantial amounts of Ni impurities was revealed in the purified carbon nanostructures produced with a Ni - containing catalyst [4]. In particular, doped graphene and CNT systems were investigated by DFT calculations as promising materials for gas sensors [5-7], hydrogen storage devices [8], electrodes of supercapacitors [9, 10]. Unfortunately, the spectrum of the used dopants is narrow [11]. This study deals with a wide range of atoms (49 atoms).

Computer modeling of properties of CNTs using density functional theory (DFT) method requires very large computer resources. Thus, we investigate doping of graphene sheet as a prototype for the CNT. We can expect qualitative agreement between doping of graphene and CNT [12].

There are two types of graphene doping: electrical and chemical [13]. In this study, we investigate the chemical doping of graphene, where doping occurs via chemical routes, namely substitutional doping with heteroatoms.

Thus, in this paper, we investigated the possibilities of chemical doping and magnetic moments for almost 50 atomic species to find a stable for synthesis, nano structure formation and practical applications.

2. Method

We used the spin-polarized density-functional theory (DFT) as implemented in the localized basis-set SIESTA method [14, 15]. The generalized gradient approximation of Perdew, Burke, and Ernzernhof (PBE) was adopted for the exchange correlation potential [16]. The double zeta plus polarization (DZP) basis set was used in the calculations along with the 300 Ryd mesh cut-off for the grid. Brillouin zone sampling was made by a Monkhorst–Pack mesh $24 \times 24 \times 4$ k-points.

A single layer 3×3 supercell with a vacuum width of 12 Å above was constructed. Dopant atoms were placed at the center of the single vacancy. These structures were entered into the SIESTA code. They were allowed to fully relax according to the atomic positions and cell parameters with an accuracy of 0.04 eV/Å for forces and 1.0 GPa for stresses. All atoms were allowed to relax for all calculations.

We calculated the binding energy from the formula:

$$E_b = E_{tot} - (E_{vac} + E_{atom})$$

where E_b is the binding energy of the atom adsorbed on a single vacancy in a graphene sheet. E_{tot} is the energy of the doped graphene, E_{vac} is the energy of the reconstructed naked vacancy and E_{atom} is the total energy as an isolated atom. E_b is a complex quantity including redistribution of the electron density arising from the adsorption of the isolated atom on the single vacancy of the graphene sheet, as well as the relaxation of the stresses being induced by this adsorption.

3. Results

We calculated the binding energy and magnetic moment of 49 atoms shown in figure 1 and figure 2 respectively.
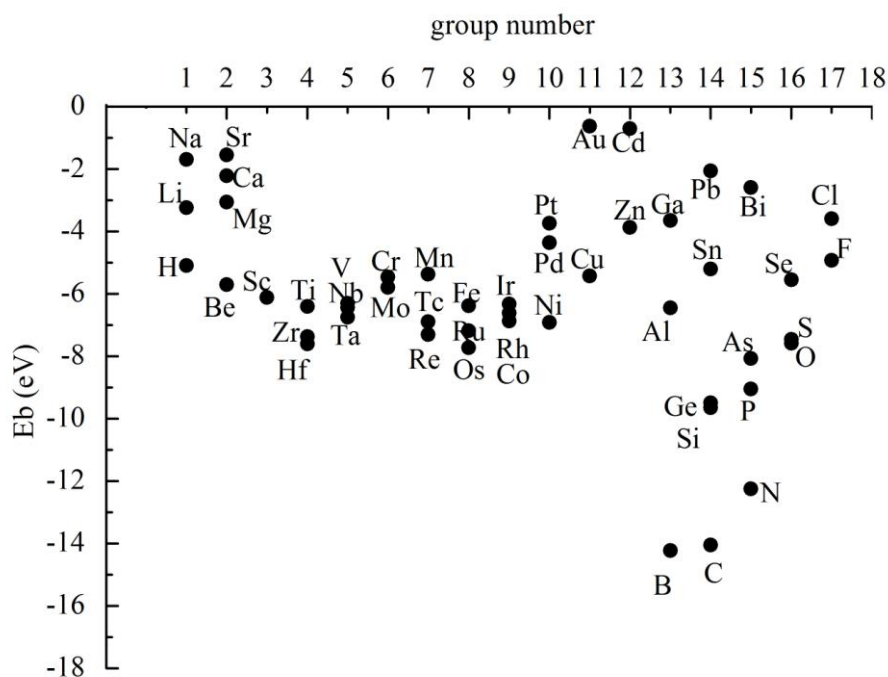

Figure 1. Binding energies Eb of the graphene sheet with atoms adsorbed on single vacancies. The x-axis shows the number of the group in the periodic table.

We found that the types of the atom-single vacancy complexes can be divided into two types: stable and not stable at room temperature. The type of unstable complexes has the binding energy less than 0.4eV. The 0.4eV is roughly the maximum threshold for migration of atoms at room temperature [12]. Thus, all atoms are stable at the room temperature. Moreover, according to first-principles calculation reported by K.Nakada et. al. [17] they can migrate further along the surface of graphene even at the room temperature. The binding energy of a C atom to a graphene sheet with a single vacancy is about -14 eV and C also can migrate along the surface of graphene [17]. As for the stability at high temperatures, the additional simple estimations are required. The additional calculations may be required to check the stability of these species toward oxidation by oxygen of the air.
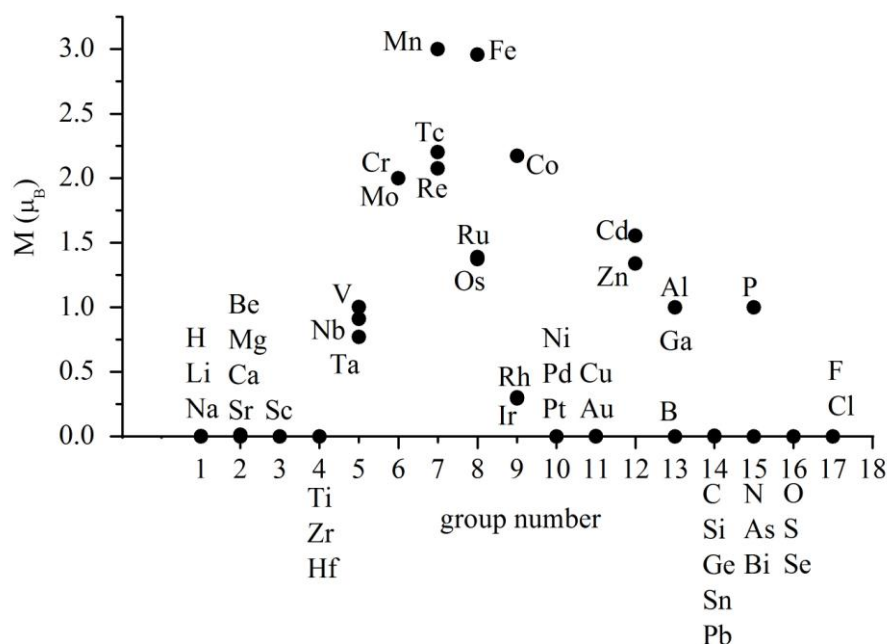

Figure 2. Magnetic moments M of the graphene sheet with atoms adsorbed on single vacancies. The x-axis shows the number of the group in the periodic table.

There is a slight off-layer position of the dopant atoms, because the doping atom–carbon bond is somewhat longer than a carbon–carbon bond. These data are in agreement with other first-principles calculations [7, 11]. But for the most stable N and B atoms the in-plane position is observed.

Magnetic data are in agreement with the calculation reported by A.Krasheninnikov et. al. [11]. Surprisingly, Zn, Cd, and even Al, Ga and P atoms are magnetic. This phenomena can be explained by the model [11].

Figure 3 shows density of states (DOS) for some doped systems. There exist some enhancement in the absolute value of DOS in the rows B-doped-Ga-doped and pristine-Ge-doped graphene, but for the most of doped graphenes the DOS takes complex form like for the Bi-doped one.

4. Discussion

The character of the doping is expected to be similar between CNT, graphene and also graphite, because there is an experimental evidence that CNT have only slightly lower vacancy formation and diffusivity energy [18]. For graphite, the interaction between the layers in graphite is so small that considering only a single graphene sheet gives only negligible differences [19]. Thus, we can expect

that our calculated results for graphene can be used as a reference to consider the candidate dopant atoms for CNT and graphite.
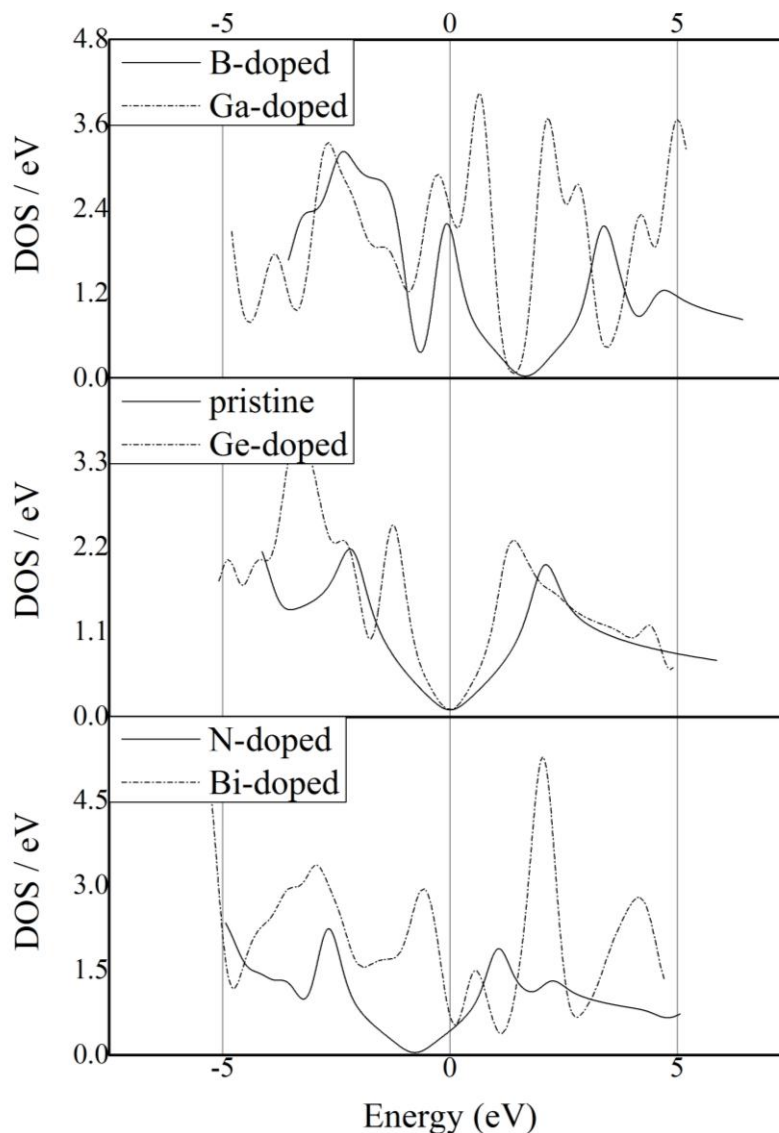

Figure 3. Density of states for some doped graphenes. The Fermi level is at zero energy.

We found that for all atomic species the binding is strong at room temperature. Moreover, most of the atoms are allowed to migrate along the surface, so that doped nanostructures could be obtained by filling of the existing vacancies. It should be taken into account that in their initial state the empty vacancies are saturated by stable O groups, such as ether (C-O-C), carbonyl (C-O), anhydride (O=C-O-C=O) and other groups [19]. Other synthesis routes could use the doping in plasma process [9], chemical vapor deposition (CVD), thermal annealing of graphene oxide, catalytic growth of carbon nanostructures, ball milling, etc [20]. The range of dopants used experimentally is quite wide (B, N, S, F, Cl, I, Br and Se). According to our calculations (figure 1) the binding energy for these dopants is in

a wide range from -14.25 to -3.59 eV, so from this energetical point of view there are no obstacles in using of other atomic species as dopant.

Such heteroatom-doped graphene could be also used as electrode material for supercapacitors, providing the binding energy is at least 2.5-4.6 eV (the voltage window of stability for current commercial electrolytes) divided by 2. The division by 2 is necessary because the voltage is distributed across the two electrodes. These values of binding energy will not allow the voltage to pull out the dopant atom from the vacancy of the graphene.

The doping of graphene with metal atoms has rarely been confirmed experimentally. X. Wang et. al. [20] suggest that this is probably because the binding energy of these atoms in graphene vacancy is much lower than their cohesive energy. And because of this these atoms tend to form clusters instead of doping. But if we compare some of our calculation results with the one available from the literature (table 1), we can see that this statement is wrong. As a rule, the binding energy of atoms in cluster ($E_{cluster}$) increases with the cluster size. We took the maximum value of $E_{cluster}$ available from the literature and gave the corresponding cluster size. This allowed us to consider the worst-case scenario, and even in this case, (for the most of metal atoms, except for Au) the doping is energetically more favorable than the forming of clusters. We believe that the only prerequisite for the doping is the presence of sufficient amount of single vacancies/divacancies, which should be free from oxygen or other contaminants. Moreover, as already mentioned above, these metal atoms can migrate along the surface of graphene even at the room temperature, so they can reach these vacancies just after the adsorption and fill them. And in evidence of our assumptions the possible existence of such doped structures was proved experimentally by direct observations of Au – vacancy and Pt – vacancy complexes in carbon nanostructures [18].

Table 1. The calculated binding energies of some metal atoms and Si adsorbed on single vacancy of the graphene sheet (E_{dopant}) in comparison with the corresponding binding energies per atom in clusters ($E_{cluster}$). N is the cluster size.

Element	E_{dopant} (eV/atom)	$E_{cluster}$ (eV/atom)	N	Reference
Al	-6.44	-2.95	34	[21]
Si	-9.64	-4.61	16	[22]
Fe	-6.38	-3.67	100	[23]
Co	-6.88	-3.93	200	[24]
Cu	-5.43	-3.35	13	[25]
Mo	-5.79	-5.96	100	[23]
Pt	-3.73	-3.60	15	[26]
Au	-0.63	-3.14	13	[25]
Pb	-2.06	-1.68	160	[27]

5. Conclusion

We calculated the binding energy and magnetic moment for 49 atoms embedded in single vacancies in a graphene sheet as a prototype for the CNT and graphite. The result shows us that for all of atomic species the binding is strong, even at room temperature, and that they exhibit interesting magnetic behavior. In particular, all transition-metal atoms and Al, Ga, P are magnetic, whereas Ni, Sc, Pd, Pt, Cu, Au are not. We compared our calculated binding energies for metal atoms with the ones for metal clusters available in the literature, and concluded that, in contrast to the suggestions of other authors [20], the doping is more energetically favorable than clusterforming,. We discussed the experimental realization of such systems.

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