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^{*} In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Effect of doping on the electronic properties of graphene

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In the framework of a density functional theory, an ab initio calculation of a band structure of single-layer graphene doped by nitrogen atoms was carried out. It is established that structural and electronic properties of such systems are strongly influenced by a dopant concentration and its location in a crystal lattice of graphene. Effects of doping of the graphene monolayer on its electronic spectrum are studied. These results indicate a possibility to regulate a band gap width by an appropriate choice of the dopant concentration and its location in the crystal lattice of graphene.

PACS: 73.22.-f.

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In honor of Professor Boris Ivanovich Kochelaev

Preface

Each of us had our own teacher in life, whom we wanted to resemble, to be as smart, responsive and demanding. After all, the real teacher is not the one who only transfers knowledge, but the one who forms a personality of his student. It is exactly his image that we carry through all life as the image of the most important teacher in life. For me, the main teacher of life is Boris Ivanovich Kochelaev. Besides the fact that Boris Ivanovich involved me in scientific activities, the most important thing is that thanks to him I met wonderful people, with whom I still maintain friendly relations.

1. Introduction

Graphene has a number of attractive physical and chemical properties, such as high electron mobility, high thermal conductivity, high specific surface area, mechanical strength and flexibility and chemical stability [1–5]. These properties make graphene a promising material for widespread use in flexible electronics, nanoelectronics, as well as in energy conversion and storage devices. All this allows making the electronic devices with much greater functionality than existing ones. However, absence of an energy gap between the valence and conduction bands limits the widespread use of graphene. This leads to the number of problems of its use as the material for creating nanoelectronics, in which semiconductors are used, for example, the p-type or n-type ones are used in transistors.

A promising approach to a controlled change of the electronic properties of graphene is the doping by the nitrogen atoms; in this case, it can be transformed into the *n*-type semiconductor and cause an appearance of the band gap. Introduction of the foreign atoms into the graphene lattice, i.e. substitution of a certain fraction of carbon by the dopant atoms, for example, the nitrogen or boron ones, makes it possible to directly control the electronic structure of graphene [6–11].

This paper focuses on the introduction of nitrogen for the doping of n-type graphene. The nitrogen atom contains one additional electron and by replacing the carbon atom in the graphene lattice the new electronic properties can be provided. As a rule, development of recipes for incorporating nitrogen into a matrix of the carbon-based materials to achieve the desired semiconductor properties is the rapidly developing area in carbon technology.

2. Calculation method

All calculations were performed within the framework of the density functional theory (DFT), using the plane-wave pseudopotential method implemented in Quantum Espresso. A generalized exchange correlation functional of a gradient approximation (XC) in a form of Perdew-Burke-Ernzerhof (PBE) is accepted in structural optimization and calculations of the electronic structure of both pure graphene and various doped graphenes. To take into account interaction between ionic nuclei and valence electrons, the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) model of ultra-soft pseudopotentials is used. The cutoff energy of a basis of atomic orbitals was chosen to be 500 eV. The calculations were carried out for three different supercell sizes 3×3 , 5×5 and 7×7 . As a graphene lattice constant a value was used optimized by the calculation. In addition, to minimize the interactions between two neighboring graphene layers, a vacuum distance of 15 Å is maintained in the calculations. To ensure sufficient accuracy, a set of $13\times13\times1$ k-points in a two-dimensional Brillouin zone of the supercell under study is taken according to the Monchrost-Pack scheme [12]. The structural optimization was carried out using the Broyden-Fletcher-Goldfard-Shanno minimization (BFGS) until residual forces on the atoms fall below 0.003 eV/Å.

3. Results and discussion

Here we study the crystal structure and electronic properties of the monolayer of graphene doped by the nitrogen atoms. It is known that the replacement doping can change the crystal structure, the electronic and optical properties of graphene and such modified graphene structures can be used in various fields of science and technology, such as optoelectronics, tunneling nanoelectronics, sensorics, etc.

We carried out our calculations with the different concentrations of doping nitrogen (16.66%, 11.11%, 6.00%, 4.00%, 3.06% and 2.04%) in graphene, and also took into account the different locations of nitrogen impurities in the crystal lattice at the same concentrations. The nitrogen atom is easily inserted into the crystal structure of graphene; in addition, in the case of the substitution the crystal structure does not deform and vacancies efficiently scattering electrons are not formed, thereby the high mobility of charge carriers is preserved, so necessary in the electronic devices [10, 11].

Next, we looked at the replacement of two carbon atoms by two nitrogen atoms in the 3×3 , 5×5 and 7×7 supercells. From Figs. 1–3 it can be seen that the graphene systems doped by the two nitrogen atoms retain flat geometry of pure graphene. Fig. 1 shows the optimized geometry of the two 3×3 graphene supercells doped by the two nitrogen atoms. The optimized lattice constant decreases from 2.445 Å to 2.425 Å for the supercell doped by the two nitrogen atoms, when the two nitrogen atoms are in the same sublattice. And the optimized lattice constant decreases from 2.447 Å to 2.468 Å for the graphene supercell doped by the two nitrogen atoms, when the two nitrogen atoms are located in the neighboring sublattices. Fig. 2 shows the optimized lattice constant decreases from 2.361 Å to 2.393 Å, when the nitrogen atoms are on the same sublattice and from 2.389 Å to 2.392 Å, when the nitrogen atoms are in the neighboring supercell doped by the neighboring sublattices. Fig. 3 shows the optimized structures of the 7×7 graphene supercell doped by the neighboring atoms are on the same sublattice constant decreases from 2.441 Å to 2.455 Å when the nitrogen atoms are on the neighboring sublattices.

Fig. 4 shows graphs of the band structure and density of states (DOS) of the 3×3 supercell of pure single-layer graphene. Our calculations of the band structure and density of states of pure



Figure 1. Optimized geometry of 3×3 supercell of single-layer graphene doped by nitrogen atoms; (a) – two nitrogen atoms are in same sublattice; (b) – two nitrogen atoms are located in neighboring sublattices; carbon and nitrogen atoms are represented by black and light circles. Distances between atoms are given in Å.



Figure 2. Optimized geometry of 5×5 graphene supercell doped by two nitrogen atoms; (a) – nitrogen atoms are on same sublattice; (b) – nitrogen atoms are located on neighboring sublattices; carbon and nitrogen atoms are represented by black and light circles. Distances between atoms are given in Å.



Figure 3. Optimized geometry of 7×7 graphene supercell doped by two nitrogen atoms; (a) – nitrogen atoms are on same sublattice; (b) – nitrogen atoms are located on neighboring sublattices; atoms carbon and nitrogen are represented by black and light circles. Distances between atoms are given in Å.

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Figure 4. Band structure and density of states of 3×3 supercell of single-layer graphene. Band structure and density of states are represented on same energy scale from $-5 \,\text{eV}$ to $4 \,\text{eV}$.



Figure 5. Band structure of 3×3 supercell of graphene monolayer doped by nitrogen atoms: (a) and (b) show graphene supercell doped by two nitrogen atoms on one sublattice and on neighboring sublattices, respectively; (c), (d), (f) show supercell of graphene doped by three nitrogen atoms on one sublattice, on neighboring and alternate sublattices, respectively.

graphene are in good agreement with the previous studies. Here we research the band structure of partially doped graphene with the different concentrations of the nitrogen atoms and study the change in its electronic properties depending on the concentration and a relative position of the doped atoms in the crystal lattice.

Fig. 5 shows the band structures calculated for the optimized 3×3 supercells of the graphene monolayer doped by the nitrogen atoms. Figs. 5(a,b) show the energy band structures of the 3×3 supercell of single-layer graphene doped by the two nitrogen atoms (the N concentration is 11.1%). In Figs. 5(c-f), the energy band structure is a 3×3 graphene layer of the supercell doped by the three nitrogen atoms (nitrogen concentration is 16.6%). From these figures it is clear

that linear dispersion near the Dirac point is not completely destroyed and the energy gap near the Dirac point opens in all the cases. The doping by nitrogen causes a positive displacement of the Fermi energy at the top of the graphene Brillouin zone, forming the *n*-type doping system. The 3×3 graphene structure doped by the two and three nitrogen atoms exhibits a metallic behavior, since some surface states are present at the Fermi level.

Now we will consider the substitution of the two and three carbon atoms, respectively, by the two and three nitrogen atoms in the 5×5 supercell of single-layer graphene (Fig. 6). Figs. 6(a,b) show the 5×5 supercells doped by the two nitrogen atoms (the nitrogen atom concentration is 4%). Figs. 6(c-f) show the supercells of the 5×5 monolayers of graphene doped by the three N atoms (the nitrogen atom concentration is 6%). The band structure of the 5×5 supercell of single-layer graphene doped by the two nitrogen atoms in the same and neighboring sublattices (which corresponds to the 4% nitrogen concentration) is shown in Figs. 6(a,b), respectively. At the 4% nitrogen atom concentration, the band gap is ~0.17 eV (Fig. 6a), when the nitrogen impurities are in the neighboring sublattices. Both graphene structures exhibited the semiconductor behaviors with the small band gap. Figs. 6(c-f) show the band structures of the 5×5 supercell of monolayer graphene doped by the three nitrogen atoms on the same sublattice, neighboring and alternate sublattices (which corresponds to the 6% nitrogen impurity), respectively. All these graphene structures exhibit the metallic conductivity.

Here we consider the supercell of 7×7 single-layer graphene doped by the nitrogen atoms. Figs. 7(a,b) show the band structures calculated for the graphene systems doped by the two nitrogen atoms (which corresponds to the nitrogen concentration of 2.04%), located on the same sublattice and on the neighboring sublattices, respectively. The band structures calculated for the graphene systems doped by the three nitrogen atoms (which corresponds to the 3.06% nitrogen concentration) on one sublattice and on the neighboring and alternate sublattices, respectively, are shown in Figs. 7(c-f). The linear dispersion law near the Dirac point is



Figure 6. Band structure of 5×5 supercells of single-layer graphene doped by nitrogen atoms; (a), (b) show supercell of graphene doped by two N atoms on one sublattice and on neighboring sublattices, respectively; (c), (d), (f) show supercell of graphene doped by three N atoms on one sublattice, on neighboring and alternate sublattices, respectively.

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Figure 7. Band structure 7×7 supercell of single-layer graphene doped by nitrogen impurities; (a), (b) show supercell of graphene doped by two nitrogen atoms on one sublattice and on neighboring sublattices, respectively; (c), (d), (f) show supercell of graphene doped by three nitrogen atoms on one sublattice, on neighboring and alternate sublattices, respectively

not completely destroyed. At the nitrogen concentrations of 2.06% and 3.06%, the graphene structure has the band gap $\sim 0.11 \text{ eV}$ (Fig. 7b) and $\sim 0.34 \text{ eV}$ (Fig. 7c), when the nitrogen atoms are on the neighboring and same sublattices, respectively. Both of these structures are the semiconductors with the small band gaps. The energy gap near the Dirac point opens in all the cases. The band structures shown in Figs. 7(a,d,f) indicate that all these graphene structures have the metallic conductivity.

4. Summary

We studied the structural and electronic properties of single-layer graphene doped by the nitrogen impurities, depending on the concentration of the dopant and the location of the impurity atom in the crystal lattice. The concentration of the impurity atom varied from 2.04% to 16.16%. It was established that the crystal structure of graphene doped by the nitrogen atom impurities has the same crystal structure as pure graphene. In this case, only bond lengths change, namely the lengths of C-N atom bonds, which are shorter than the lengths of C-C atom bonds, which agrees with the results of [6-8]. The calculation results show that by appropriate selection of the concentration and position of the dopant, the appearance and variation of the forbidden bandwidth of the graphene structure can be achieved. This makes it possible to use the modified carbon nanomaterials in production of a new generation of the electronic devices.

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