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Computer Simulation of Radiation Defects in Graphene and Relative Structures

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1. Introduction

Graphene is a single layer of carbon atoms arranged in a chicken-wire-like hexagonal lattice and in spite of its recent availability for experimental investigations (Novoselov et al., 2004) it is an object of great interest for many researchers (Elias et al., 2009; Sofo et al., 2007; Luo et al., 2009; Teweldebrhan and Balandin, 2009; Ilyin et al., 2009) because of amazingly wide field of its potential applicability: electronics, sensors, materials science, biology etc. In particular, graphene and few layer graphene fragments as well as carbon nanotubes can be used in production of composites, based on metal, ceramic, polymer matrices, filled with graphene's or few layer graphene fragments as elements of reinforcement. Obviously, the main goal of using graphene or nanotubes in making composites is using their extremely high mechanical characteristics in combination with low weight. It should be noticed, that many difficulties concerning graphene's applications originate from its surface chemical inertness. In other words, the sp^2 electron structure of ideal graphene often results in very low binding energy between graphene's surface and atoms of many elements. It is one of the obstacles for modifying and applications of graphene in production of electronic devices, when controllable electronic properties are needed. Besides, it results in poor interfacial bonding of the graphene fragments with matrices in composite materials and with sliding between few layer graphene sheets under stressed state. The noticeable success in this direction has been recently achieved in the work (Elias et al., 2009), in which the hydrogenation of graphene was performed by using an ion-plasma technique. It should be noticed, that composite of graphene and hydrogen, associated with graphene's surface was theoretically predicted few years ago in the paper (Sofo et al., 2007) and named as graphane. Unfortunately, this success up to now can be surely referred only to graphene-hydrogen composition. But today's technologies especially in the field of materials science need much more wide area of possible compositions and special materials. It was reasonable to suppose, that radiation defects may essentially improve binding ability of graphene with atoms of other elements due to production of additional chemical bonds (Ilyin, 2010; Ilyin & Beall, 2010). It is especially important for application of graphene species in R&D of composites. Moreover defects in such structures may improve mechanical properties by linking reinforcing carbon nanoelements to each other and by increasing the strength and stiffness of the composite (Ilyin et al.,2010). Unfortunately, it is not yet well understood which kinds of stable radiation defects and their complexes can exist in graphene and its derivatives. Obviously, it is not easy to create definite types of radiation defects and

perform direct studies of them in nanoobjects in direct laboratory experiments. In this situation computer simulation of radiation defects in graphene- and relative nanostructures becomes of great importance (Ilyin et al., 2011). In this paper we have submitted some results of computer simulation and calculations of some possible kinds of stable radiation defects in graphene, and more complex configurations, involving atoms of light metals: Be and Al, which are linking with radiation defects. In other words, we consider possible effect of radiation defects on production and modification of graphene – metal composites and calculate energetic and structural properties for some mostly possible configurations. Computer simulation and calculations were performed by the use well known molecular dynamics, extended Hückel technique and density functional theory.

2. Simulation and calculations

The first model which we consider in this chapter is a simple configuration, which consists of a graphene sheet and a carbon atom adsorbed with it. We imply, that in this case no chemical bond between graphene and C atom exists. This kind of interaction refers to well known van der Waals forces. These interactions are weak and insignificant in our common life, but their role increases dramatically among the nano-scaled objects. One of the important features of them - the additivity i.e. every particle of the system makes its contribution into the total interaction energy. Therefore, they can be relatively large for nanosystems, involving 10^2 – 10^3 atoms or molecules. But van der Waals interactions are not accounted by the use widespread computer techniques like molecular orbital linear combination of atomic orbitals by self consistent field (MO LCAO SCF) or density functional theory (DFT). Therefore, in this problem the method of molecular dynamics (MD), which is recognized as the effective tool for similar systems, was chosen. A graphene sheet for MD simulation of single- and diatomic defects on the undamaged structure was built of 78 atoms. Van der Waals interaction between adsorbed atoms and graphene was described by well known Lennard-Johns potential in the usual form.

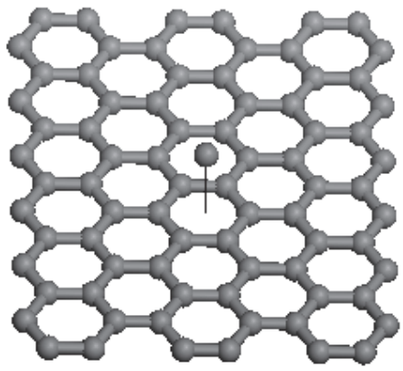


Fig. 1. Configuration of a single adsorbed atom on a graphene structure

Presented in Figure 1 is one of investigated defect configurations which is actually a single carbon atom, adsorbed on the surface of the undamaged graphene sheet. The maximum value of the binding energy for the single adsorbed atom E = – 0.18 eV at a distance Z = 0.25 nm from the graphene plane. One important characteristic is also the energy of carbon atom

in the center point of graphene's hexagon (Z = 0). This position was found to be very unstable with the positive energy equals to E_0 =11.4 eV. It means also, that the graphene sheet is impermeable for displaced carbon atoms with energies lower than E_0.

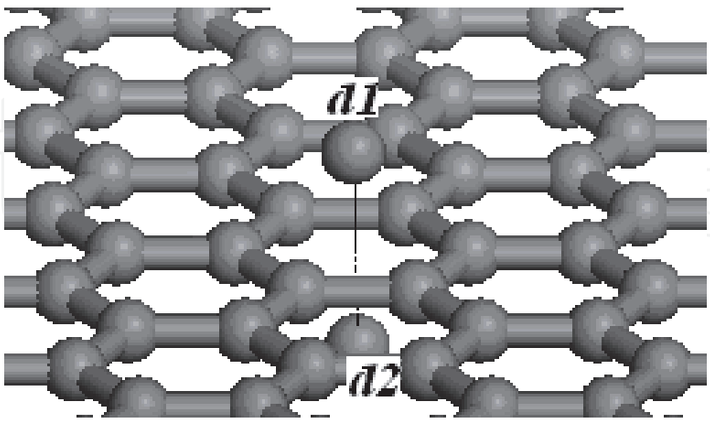


Fig. 2. Configuration of a dumbbell defect on a graphene (N=78) structure

Figure 2 presents a configuration of a more complicated, two-atom defect which is like a dumbbell with a symmetrical configuration of the atoms d1 and d2 normal to the graphene sheet. Calculations of this defect were performed by MD, using the LJ potential.

To begin, in all cases the minimum energy lateral position of the atoms adsorbed, had been found out at the normal axis of symmetry of hexagon (Z-axis). Further we performed calculations with movement of atoms along the Z-axis. Results of calculations of the binding energies for these defects as a function of a distance Z over the center of hexagon are presented in Figure 3. It can be seen, that there is an interval between approximately 2 and 3 angstroms that exhibits a trough with a negative energies, which is evidence of the existence of stable binding states. Low values of bonding energies testify of the vdW nature of the interaction.

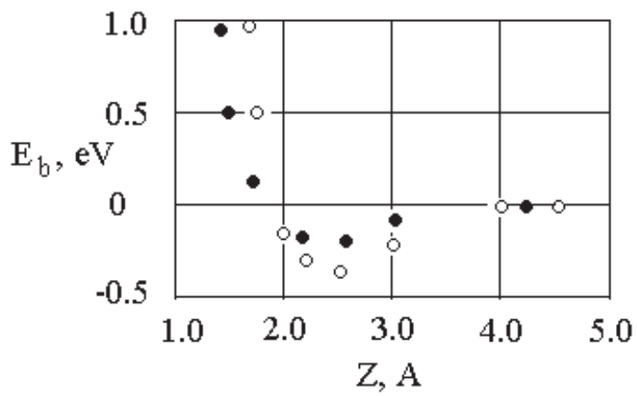
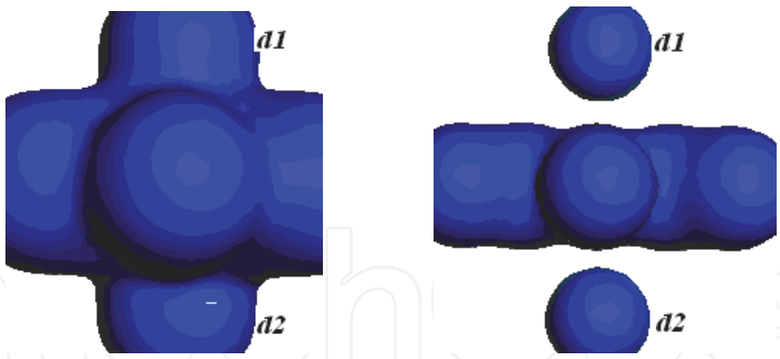


Fig. 3. The binding energy for the single atom and the dumbbell defect as a function of a distance Z over the center of hexagon. The black marks – the single atom configuration (see Figure 1), the light marks – the dumbbell configuration (see Figure 2)



a) b)

Fig. 4. The electron charge distribution for the dumbbell presented in Fig.2. Density of electron charge equals: a) 0.02 el / Å^3 , b) 0.5 el / Å^3 .

Figure 4 illustrates the results of calculations of electron charge distribution for the dumbbell presented in Figure 2, performed by MO LCAO method. These calculations were performed in order to check our assumption about vdW interaction between atoms adsorbed and graphene. One can see some overlapping of electron charge only by very low level of electron density (Figure 4,a). And, obviously, there are no signs of overlapping of electron charge at high level of electron density, which could be responsible for some kind of bonding between graphene and atoms adsorbed. One can see well distinguished electron charge clouds, obviously closed on graphene and d1 and d2 atoms with a gap between them. At the same time graphene's structure is linked with dense electron clouds, which provided strong bonding. It proves that weak bonding interaction for the defects presented above is controlled by vdW forces. It is unlikely, that such defects can be useful for essential modifying of mechanical properties of composite materials.

2.1 Vacancies in graphene

Irradiation of graphene-based electronic devices by fast electrons or ions will be always accompanied by creation of atom vacancies. Therefore, it is very important to know about changes in electronic properties of graphene fragments which should be expected under irradiation and about how they depend on defect concentration. For such estimation we have used large enough graphene's fragment (N=208).

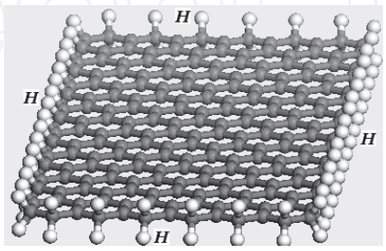


Fig. 5. Graphene for calculations with edge-bonds shut by H-atoms

In order to avoid end-effects by calculations, free end-bonds of carbon atoms were shut with hydrogen atoms. Afterwards, in order to take into account the possible effect of a larger size of a real graphene sheet, which can restrict the atoms neighboring to the vacancy, all edge atoms of graphene were fixed at their initial positions. After that we simulated and

calculated one-, two- and three –vacancy configurations with using in all cases a procedure of energy minimization.

It was revealed, that in all cases, after energy optimization the vacancy zone increased so that all the three two-coordinated atoms, neighboring the vacancy, were shifted nearly symmetrically: all three distances between surrounding atoms 1-2 , 2-3, 3-1 (figure 6) become as large as 2.76 Å instead of 2.46 Å in the initial state.

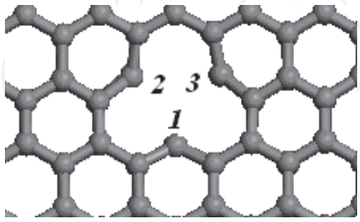


Fig. 6. Vacancy zone in graphene after the optimization procedure

Figure 7 presents a configuration of a graphene with 3 single vacancies displayed by the electron charge distribution.

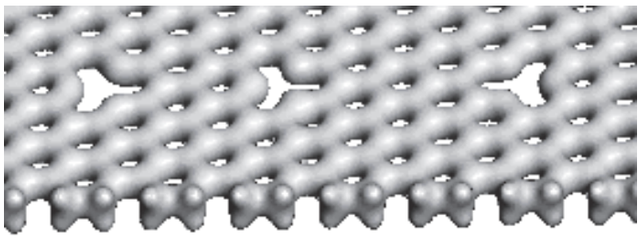


Fig. 7. Graphene with 3 single separated vacancies in the structure

Calculations of HOMO and LUMO were also performed in all cases. Figure 8 presents dependence of Eg = HOMO – LUMO for graphene -208 with different numbers of vacancies. There were one-, two-, and three vacancies in aligned configuration.

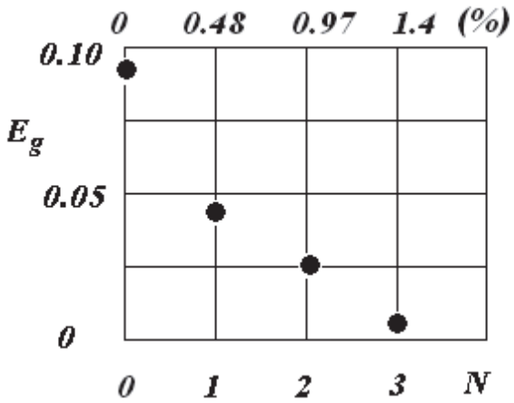


Fig. 8. The value of Eg = HOMO – LUMO as a function of concentration of vacancies in a graphene-208 fragment.

Obviously, data for E_g presented in Figure 8 illustrate the effect of limited size of graphene fragment (so called size-effect), because the infinite graphene (the initial state with N =0) is intrinsically semi-metal with Eg =0. But these and similar effects should be taken into account when physicists and technologists will design devices based on real graphene fragments of limited sizes.

2.2 Radiation defects with strong bonding

As the next step we simulated and calculated energetic and structural characteristics of 3D defect configuration presented in Figure 9. This type of radiation defect, which involves two carbon atoms arranged symmetrically over a vacancy can be named "dumbbell", like to configuration presented in Figure 2.

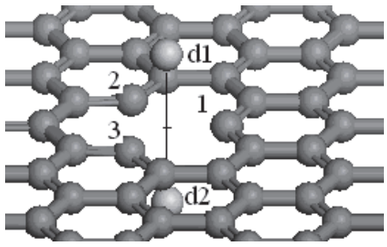


Fig. 9. The complex radiation defect, involving a vacancy and a dumbbell configuration.

But in this case the two carbon atoms (d1,d2) of the dumbbell are chemically bonded with free bonds of atoms, neighboring at the vacancy. One can see from the graph in Figure 10, that there is a strong bonding.

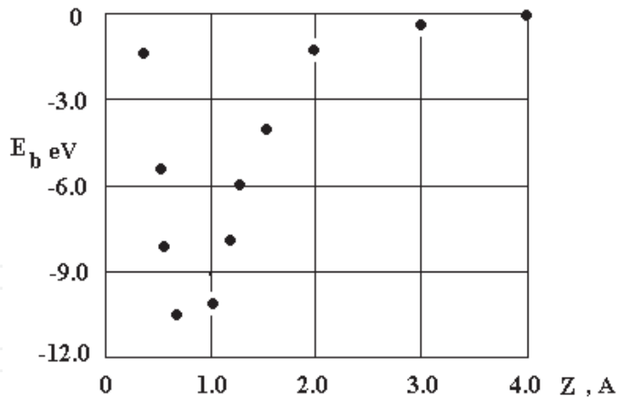


Fig. 10. The binding energy for the dumbbell placed over a vacancy as a function of the distance Z over the graphene sheet

Obviously, the elastic properties of composite materials and their uniformity are of great importance in using composite materials. The E_b - Z curve in Figure 10 can be used for estimation of elastic characteristics of the C-C dumbbell defect along the graphene sheet (under shear stress). One can see, that the maximum slope of the curve is near the point Z = 1.3 Å. The numerical estimation by using $\Delta E/\Delta Z$ at this point with small segments gives the value 0.5 TPa. The maximum binding energy of the dumbbell over the relaxed vacancy was

obtained as large as -10.0 eV and the corresponding distance between the graphene's plate and atoms equals 0.7 A. The electron charge distribution presented in Figures 11 and 12 proves that there is fast chemical bond between dumbbell and graphene sheet.

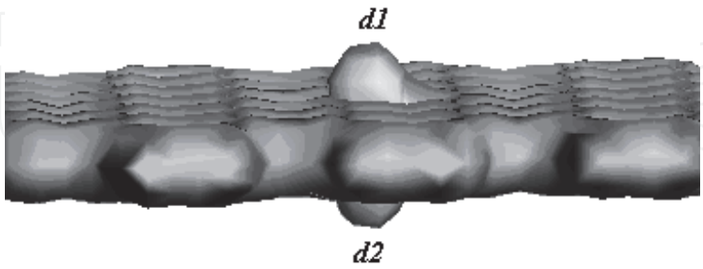


Fig. 11. The electron charge distribution for the graphene-dumbbell configuration at density of the charge equal to 1.0 el/Å^3 .

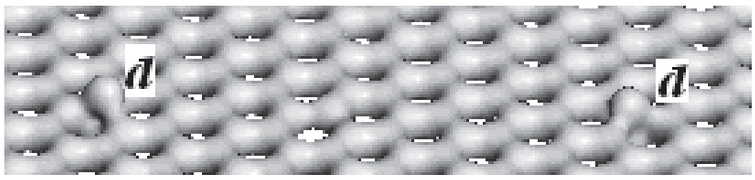


Fig. 12. The electron distribution for a graphene with two separated dumbbells

Calculation of electronic properties of dumbbell configurations presented in Figures 11 and 12 for graphene-208 were also performed. Eg = HOMO – LUMO was as large as 0.05 eV for a case with one- and two dumbbels. Figure 12 displayed no signs of noticed non-uniformity between two dumbbells in the graphene structure. So that, effect of radiation defects like dumbbells can be considered as insignificant by their concentrations about 1%. The large value of the binding energy for the dumbbell defects and the electron charge distribution calculated for these defect configurations obviously demonstrate, that there is significant interaction between the dumbbell and a graphene, as well as between atoms of the dumbbell itself.

The ability of graphene's vacancy to bind atoms of other elements by the chemical way were firstly checked by simulation and calculation of the vacancy - hydrogen complex defect, which was performed in the hydrogenated graphene ("chair"- graphane) structure (Figure 13). Our calculations proved that a vacancy zone can serve as a site with a high concentration of hydrogen. In this case the vacancy zone has non- symmetrical mode of deformation: distances between atoms: C1-C2 = C2-C3 = 2.72 Å, C1-C3 = 2.55 Å

The results of calculations of binding energy of H atoms, bonding at the vacancy are presented in Fig. 14. These data witness, that the value of binding energy depends on the total number of H atoms, placed at the vacancy. One can see, that the binding energy has well defined minimum at N = 3.

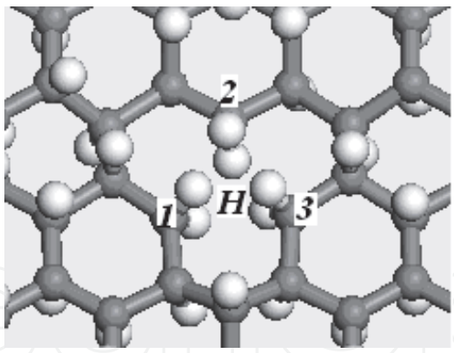


Fig. 13. The atomic structure of vacancy with 6 hydrogen atoms bonding

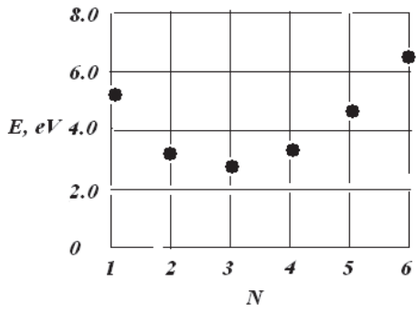


Fig. 14. The dependence of hydrogen – vacancy binding energy on the total number N of hydrogen atoms linking with the vacancy

2.3 Bridge-like radiation defects in graphene

It is known very well that two layer graphene is being one of main components by production of graphene's materials by many technologies. Therefore, it can play a significant role in some applications, using graphene materials. At least, it is reasonable to study properties of two layer graphene, keeping in mind its future applications. In particular, two layer graphene fragments can be used in production of lightweight composite materials with high stiffness and strength. Therefore, calculations were made also for bilayer graphene fragment. The usual AB graphite-like configuration, which is the most common for graphite –like materials, was chosen for calculations (see Figure 15). The Figure 16 illustrates that interaction between undamaged graphene sheets has van der Waals nature, without any signs of electron charge overlapping. The coupled atom pair which were removed by creating the vacancy pair is marked by black. The interstitial C-atom, knocked from the structure was placed between graphene layers. After that relaxation procedure was used to obtain a minimum of the total energy of the defect volume. The edge atoms of graphenes were fixed in order accounting the size effect.

In Figure 16 one can see the typical picture of the electron charge distribution for undamaged bilayer graphene, controlled by van-der-Waals interactions. There is no electron charge overlapping, between different graphene sheets.

In Figure 17 one can see the much more complex defect configuration with vacancies, faced each other, which were produced in both of graphene sheets and interstitial carbon atom (*i*), caught between them. This type of radiation defects can be called as a bridge-like defect. The essential feature of the defect is that the two graphene sheets are linked with fast covalent

bond based on the interstitial atom and as one can see, neighboring atoms 1-2 and 3-4 facilitating the rising two additional bonds, because of pulling in the gap between graphenes. The distribution of the electron charge presented in Figure 18 proves existing of three covalent bonds, originated between graphene layers.

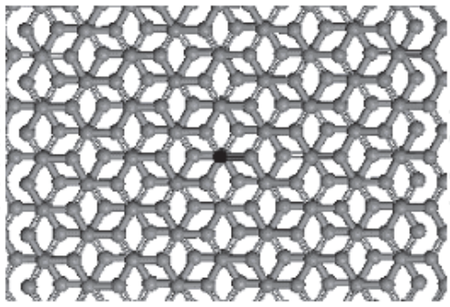


Fig. 15. Graphene AB two layer used for building complex interior defect

Fig. 16. The distribution of the electron charge for undamaged bilayer graphene (the density equals 0.4 el / A^3).

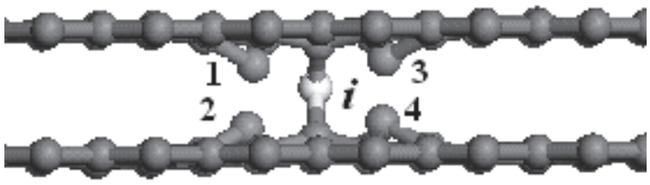


Fig. 17. A complex bridge-like radiation defect bonding together sheets of bilayer graphene after relaxation

The total binding energy for this complex defect configuration was calculated as large as -11.3 eV. We have supposed, that ends of two- or few layer graphene fragments may also serve as sites of bridge-like defects, linking graphene's sheets together. A typical configuration of end-bridge-like bonding of a carbon atom is presented in Figure 19.

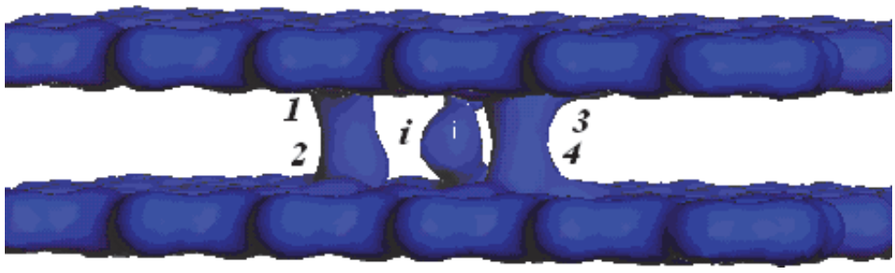


Fig. 18. The distribution of the electron charge (the density equals 1.4 el / A^3)

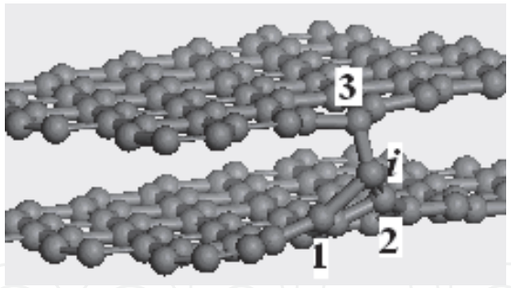
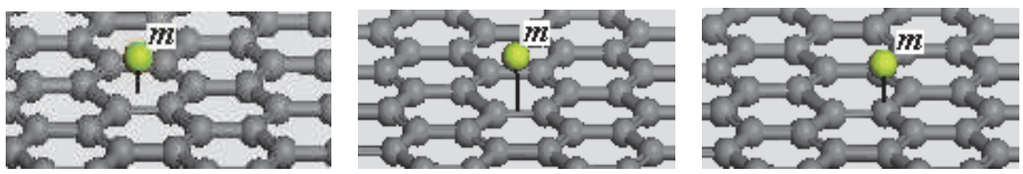


Fig. 19. The bridge-like defect based on an interstitial atom *i* at the edge of bilayer graphene.

2.4 Graphene-metal composition induced by radiation

It is known very well, that graphene and few layer graphene fragments, like to carbon nanotubes can be used as elements of reinforcement in production of composites, based on various matrices. Moreover, many important physical properties of material (particularly, electric and heat conduction, magnetic characteristics and so on) can be modified and improved by using graphene and few layer graphene fragments as filler. As was mentioned above, many difficulties concerning graphene's applications originate from its sp^2 electron structure. In other words, the electron structure of ideal graphene often results in very low binding energy between graphene's surface and atoms of many metals. It is one of the obstacles for modifying and applications of graphene in production of composite materials. In our recent papers we suggested using of radiation modification of composite materials with carbon nanostructures due irradiation by fast electrons or ions. Production of special kind of bridge-like defects may be considered as an effective technological tool of essential modification of physical-mechanical properties of composite materials, filled with carbon nanostructures (Ilyin & Beall, 2010).

Beryllium, aluminum and their alloys are being very important materials for designing new composites, especially for fields where combination of light weight with high strength is needed, for example – transportation systems and air-space technologies. Therefore, in this paper we focused on study of possible production composite materials based on Be and Al matrices, with using graphene fragments as reinforcement elements. We suppose, that radiation defects may essentially improve binding ability of graphene with atoms of light metals due to production of additional chemical bonds. Unfortunately, direct experimental study of such nanosystems with atomic scale defects and operations with them can be hardly performed today even in laboratories with high level equipment. Figure 20 presents some typical possible positions of metallic atoms (Be, Al) arranged on graphene surface in high symmetry sites. Calculations performed for all of these positions gave values of the binding energy of metal atoms on the graphene surface nearly zero.

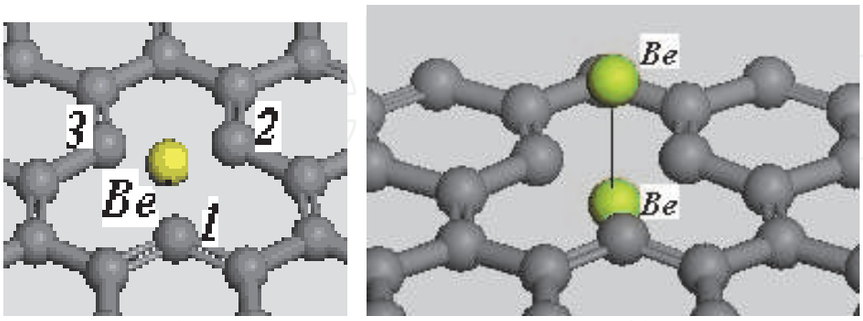


a) b) c)

Fig. 20. Some of calculated symmetrical configurations of metal atoms (Be and Al) on graphene surface with nearly zero binding energies: a) over the center of a hexagon; b) over the center of the C-C bond; c) over a C atom.

2.4.1 Be – graphene composition

Figure 22 presents a scheme of estimation elastic characteristics of defect involving Be dumbbell at vacancy by techniques like above for C-C dumbbell. The value of elastic modulus for direction "to right" in the Figure 21 was calculated as large as 0.05 TPa and 0.02 TPa in the perpendicular direction.



a) b)

Fig. 21. Configurations of Be atoms bonded with a vacancy: a) a stable position of the single Be atom in the graphene sheet. The binding energy E_b equals 2.6 eV; b) Configuration of "Be – dumbbell" over a vacancy with binding energy 4.1 eV.

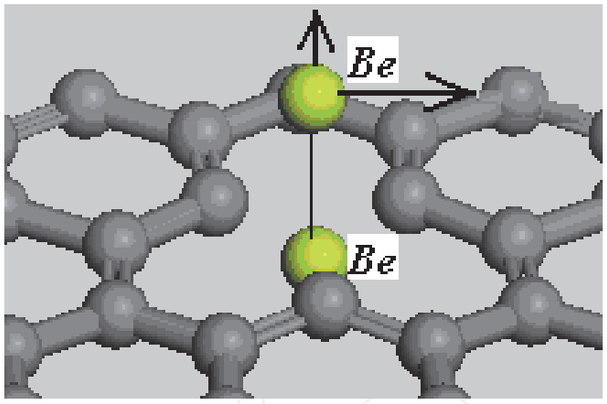
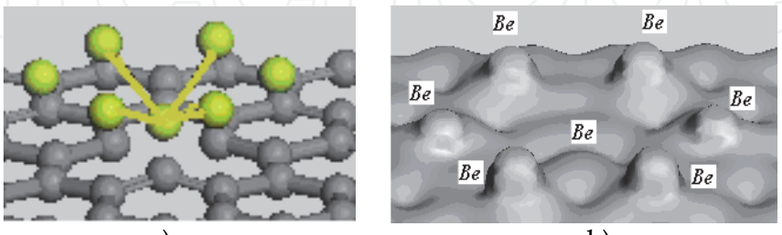


Fig. 22. Scheme of the elastic modulus calculation for the Be dumbbell at vacancy.



a) b)

Fig. 23. a) A configuration of an initially flat Be-cluster over vacancy after optimization. The binding energy of the cluster with graphene was obtained as large as 7.2 eV; b) the electron charge distribution in the area of the metal cluster – vacancy with a density of charge 0.2 el / Å^3.

2.4.2 Al – graphene composition

A stable configuration with a minimum of total energy was provided by Al atom placed in the plate of graphene sheet within the vacancy. One can see in figure 24 that the vacancy zone essentially and symmetrically increased with all three lengths of bonds equal 1.7 Å.
Figure 25 presents configuration of Al – dumbbell placed at the vacancy. The equilibrium distance between Al atoms equals 2.5 Å, the binding energy is as large as 2.9 eV.
Very interesting and important result for technological applications by production of composite materials based on Al or Al –alloys matrix with graphene filler shows computational model in Figure 27. One can see, that Al atoms can be chemically attached to a bridge-like defect in vacancy's zones. One also can see a significant deformation of graphene sheets around the defect zone. The binding energy of the interstitial carbon atom *i* at this configuration was equal to -9.3 eV.

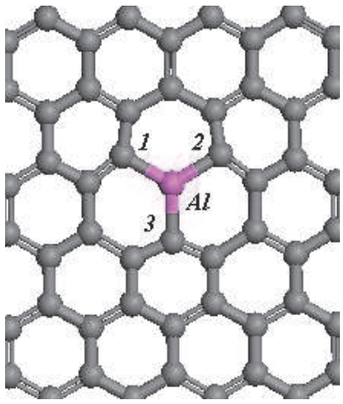


Fig. 24. Configuration of a single Al-atom bonded with a vacancy.

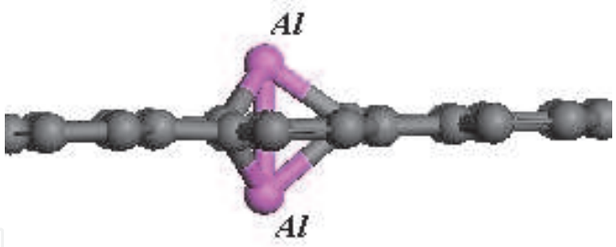


Fig. 25. Configuration of Al – dumbbell bonded with a vacancy.

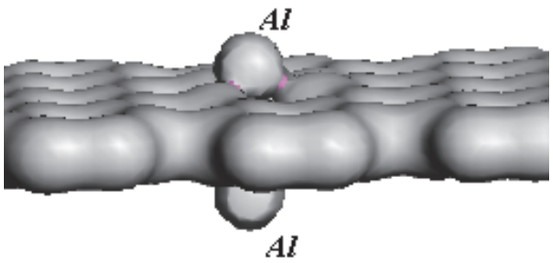


Fig. 26. The distribution of the electron charge (the density equals 1.4 el / A^3) for the Al – dumbbell bonded with a vacancy in graphene

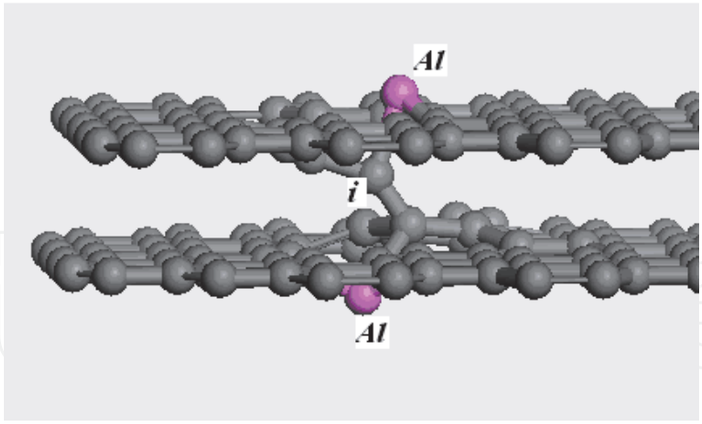


Fig. 27. Complex defect: a bridge-like defect in two- layer graphene with Al atoms attached on both graphene sheets.

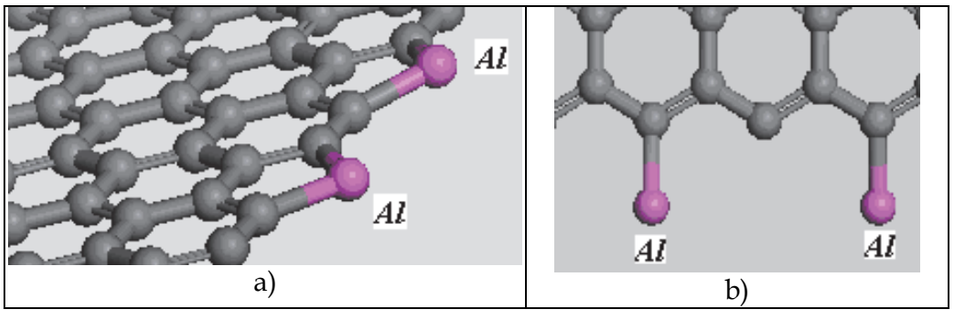


Fig. 28. Edge bonds of graphene fragments with Al atoms caught with binding energy E_b as large as 4.2 eV (a) and 3.5 eV (b).

Figure 28 illustrates one more possible way of creation additional chemical bonds between Al atoms and graphene fragments. Free end bonds can serve as additional sites of linking Al atoms providing better adhesion between metal matrix and graphene filler with binding energy as large as 4.2 eV in the case of "arm-chair" edge and 3.5 eV for "zig-zag" edge.

3.Conclusion

Some stable radiation defect configurations, involving single adsorbed carbon atom, 3D C-dumbbell defect and a vacancy-like defect in graphene sheet, associated with a dumbbell of adsorbed atoms as well as complex interior defects : bridge-like radiation defects, which can originate under fast electron or ions irradiation and attach metal atoms, were simulated. The binding energy, structure characteristics and some electron characteristics of defects have been determined by using molecular dynamics, MO LCAO and DFT. Our calculations show, that electronic properties of graphene fragments are rather stable to radiation damage in the form of vacancies and dumbbells. Results of simulations and calculations also show, that special kind of radiation defects, namely bridge-like radiation defects produced by irradiation with fast electrons or ions can become an effective technological tool by production of composite materials, based on light metal matrices with carbon nanostructures, in particular, graphene's fragments, as reinforcement elements.

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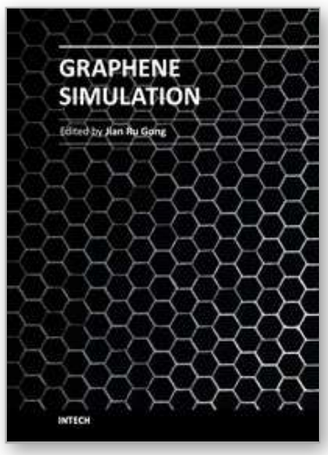

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Graphene, a conceptually new class of materials in condensed-matter physics, has been the interest of many theoretical studies due to the extraordinary thermal, mechanical and electrical properties for a long time. This book is a collection of the recent theoretical work on graphene from many experts, and will help readers to have a thorough and deep understanding in this fast developing field.

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