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Bridge-like radiation defects in few-layer graphene

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ABSTRACT

This paper presents computer simulations and quantum mechanical calculations of the electronic energetic and structural characteristics of stable bridge-like radiation defects in few-layer graphene and some experimental results of study such irradiated by scanning electron microscope (30 and 15 keV) electron beams. Results of examination of few-layer graphene specimens in the pre-irradiated and post-irradiated states by optical, electron microscopy, X-ray energy dispersive spectroscopy and Raman spectroscopy are given. A possible physical mechanism of under threshold energy structural defects production is proposed.

1. Introduction

It is known very well that graphene and few-layer graphene structures are considered as exclusively promising elements for electronic nanodevices, supersensitive sensors, hydrogen carriers for hydrogen energetic and even as elements of reinforcement in production of composite materials [1–4]. It is very likely, that in some practical usage few-layer graphene – based devices can be subjected to irradiation by electrons or ions flows (for example, in space applications) which will result in changes of their properties. Moreover, in some cases irradiation can be used as a technological tool of modification of properties of these carbon nanostructures. Therefore study of possible radiation effects in these structures becomes a subject of great importance. It should be noticed that many difficulties concerning graphene's usage originate from its rather closed electronic structure. It leads to low binding energy between graphene's surface and atoms of many potentially favorable matrix materials and to sliding between layers of few-layer graphene elements as well as CNTs. Our recent theoretical investigations have allowed to predict, that so called "bridge-like" radiation defects in carbon nanostructures like few-layer graphene and relative materials can essentially improve binding ability of graphene's surface with atoms of many substances of interest, in particular, with metallic materials due to production of additional fast covalent bonds [5,6]. Moreover, these defects can be effective tools for improving electrical and thermal properties of few-layer graphene and relative carbon nanostructures [7–9]. It has also been stated that bridge-like defects can link together elements of nanostructures (sheets of a few-layer graphene and tubes in MWCNTs) making them much stiffer. However, physical mechanism of production and stable configurations of radiation defects and their complexes which can exist in few-layer graphene is not yet well understood. Recently signs of radiation damages were observed even after conventional SEM investigations with electron energies equal to and less than 30 keV [10,11]. It should be noticed that some data corresponding to radiation effects in monolayer graphene were recently reported [12–15], however, there is very little volume of information corresponding the experimental investigations of radiation effects in few-layer graphene [16]. No doubt, this aspect of the problem must be investigated with all attention. In the paper few-layer graphene specimens were produced by mechanical exfoliation of HOPG and placed on silicon oxide and copper substrates for multiple examinations and irradiation by electron beams in SEM. We also used X-ray energy dispersive spectroscopy in order to prove Raman data from few-layer graphene. In order to get better understanding of physical nature of radiation effects in graphene and graphene-like structures we performed computer simulation and quantum mechanical calculations of energetic and structural characteristics of possible types of stable radiation defects in few-layer graphene structures.

2. Simulations and calculations

Computer simulations and calculations presented in this paper were performed by using molecular dynamics technique and density functional theory (DFT) calculations. All final atomic configura-

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tions of defects were obtained with using the procedure of energy optimization. In Fig. 1 one can see a complex defect configuration with two vacancies, faced each other which were produced in both of two-layer graphene sheets and interstitial carbon atom caught between them. This type of radiation defect is called as a bridge-like defect [5,6]. The essential feature of the defect is that the two graphene sheets are linked with fast covalent bond, based on the interstitial atom. Moreover, as one can see, a few neighboring the vacancy atoms are rather noticeable pulling in the gap between graphene sheets and facilitate the rising additional bonds. Fig. 1b presents the distribution of electron charge around the defect and one can see essential overlapping of electron clouds between sheets. DFT calculations show that there is a large contribution of P_z^- electrons of conduction band in this electron charge bridge. This phenomenon can be considered as creation of electric and thermal cross- conductivity between graphene sheets. Configuration presented in Fig. 2 is possible to be created in the case of irradiation by particles with higher energies (200–400 keV). It can be predicted that irradiation with high fluencies can produce noticeable effect of increasing the electric and heat cross-conduction between graphene's sheets. Fig. 3 illustrates a possible type of complex defects graphene – metal, consisting of graphene's vacancy and Cu atoms. Such defects can be produced due to thermal evaporation of the copper substrate under a SEM observation at high beam current density. It should be noticed, that such effects must be taken into account by interpretation of results, because they can cause some changes in Raman spectra.

3. Experimental

Few-layer graphene specimens were produced by mechanical exfoliation of high oriented pyrolitic graphite and placed on silicon dioxide substrates and a copper substrate. All specimens were preliminary characterized by optical microscopy (Leica DM 6000 M) and Raman spectroscopy (NT-MDT NTegra Spectra confocal spectrometer with laser wavelength 473 nm). All irradiations of specimens (30 keV) were performed in SEM Quanta 3D 200i dual system

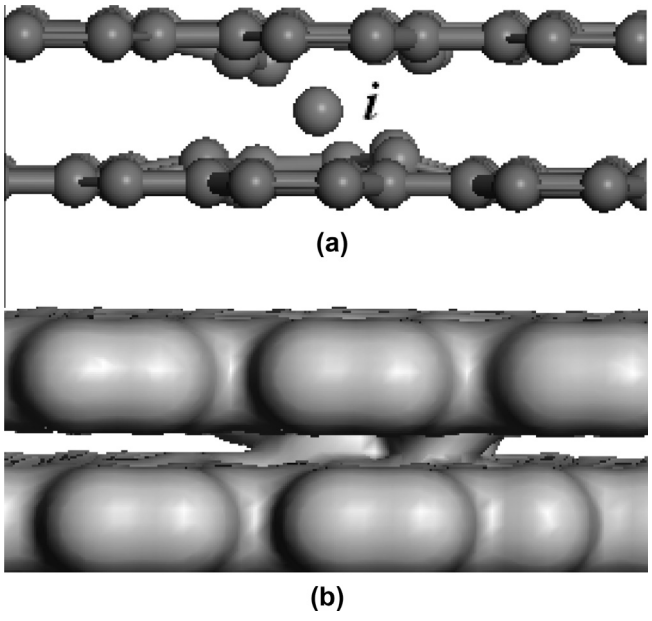

Fig. 1. (a) Atomic structure of complex bridge-like radiation defect bonding together sheets of bilayer graphene after relaxation; (b) the distribution of the electron charge in the zone of bridge-like defect (the density equals 0.3 el/Å^3).

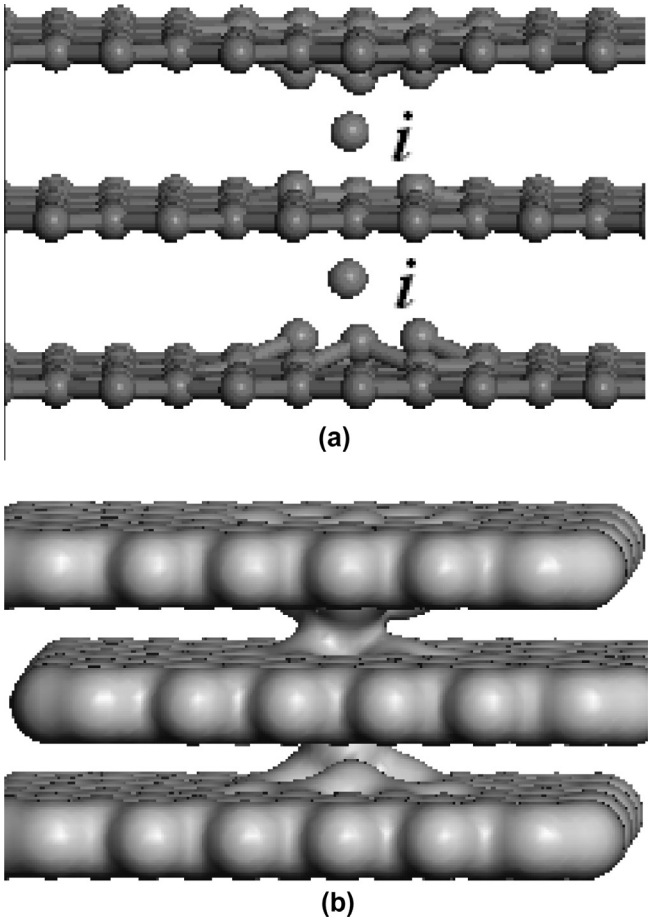

Fig. 2. (a) Atomic structure of complex bridge-like radiation defect bonding together sheets of tri-layer graphene; (b) the distribution of the electron charge in the zone of a complex bridge-like defect (the density equals 0.3 el/Å^3).

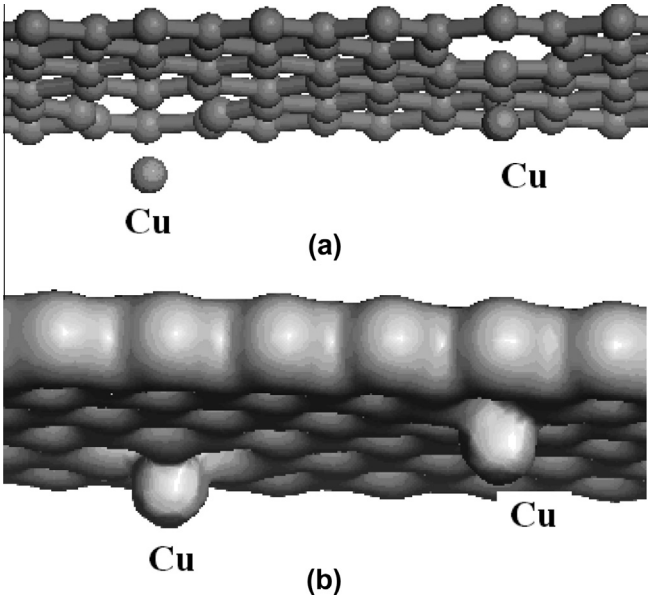

Fig. 3. (a) Atomic structure of possible compound of defect zones of graphene with copper atoms. Distances are: 1–2 = 2.91 Å; 2–3 = 3–1 = 2.96 Å; distance between graphene's plate and Cu atoms is equal to 1.5 Å; (b) the electron charge distribution calculated for this defects at electron charge density 0.2 el/Å^3. The binding energy of Cu atom with a vacancy is equal 1.1 eV.

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