Advances in Nano Research, *Vol. 4, No. 1 (2016) 45-50*
DOI: http://dx.doi.org/10.12989/anr.2016.4.1.045

Structural damaging in few -layer graphene due to the low energy electron irradiation

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(Received November 30, 2015, Revised March 7, 2016, Accepted March 9, 2016)

Abstract. Data of Raman spectroscopy from graphene and few-layer graphene (FLG) irradiated by SEM electron beam in the range of energies 0.2 -30 keV are presented. The obvious effect of damaging the nano-structures by all used beam energies for specimens placed on insulator substrates (SiO_2) was revealed. At the same time, no signs of structural defects were observed in the cases when FLG have been arranged on metallic substrate. A new physical mechanism of under threshold energy defect production supposing possible formation of intensive electrical charged puddles on insulator substrate surface is suggested.

Keywords: few-layer graphene; radiation effects; electric charged puddles

1. Introduction

Graphene and few-layer graphene (FLG) are considered as promising materials for a wide range of future technologies, relating to the production of new composites Huang *et al.* (2012), reinforcement of different composites Das *et al.* (2009), developing new polymer composite materials Sun (2013). save and capable hydrogen carriers for hydrogen energetic Ilyin *et al.* (2011), electronic devices Chen (2007), electrical sources, in particular, lithium-ion power sources Zhao (2011). It is not difficult of predicting that in some practical applications, FLG-based devices can be modified by structural defects. In recent paper Ilyin *et al.* (2015) it has been shown that introduction into the FLG nanostructures of bridge-like defects can essentially improve physico-mechanical properties of such materials and increase size-stability and life-time of Li-batteries. But it should be noted, that although there is an extensive experience in using irradiation as technological tool for modification of properties of materials, physical nature of radiation effects in graphene and FLG nanostructures is insufficiently understood. In the paper Teweldebrhan and Balandin (2011) was reported that noticeable signs of structural defects production in graphene and FLG even after conventional SEM investigations have appeared and Ilyin *et al.* (2013) reported preliminary results about middle-energy SEM beam effects in FLG nanostructures. No doubt, this aspect of the problem must be investigated with all attention. Moreover, recent theoretical investigations Ilyin *et al.* (2009) of irradiated graphene and bridge-like defects in carbon nanostructures Ilyin *et al.* (2010) have allowed to predict, that some types of structural

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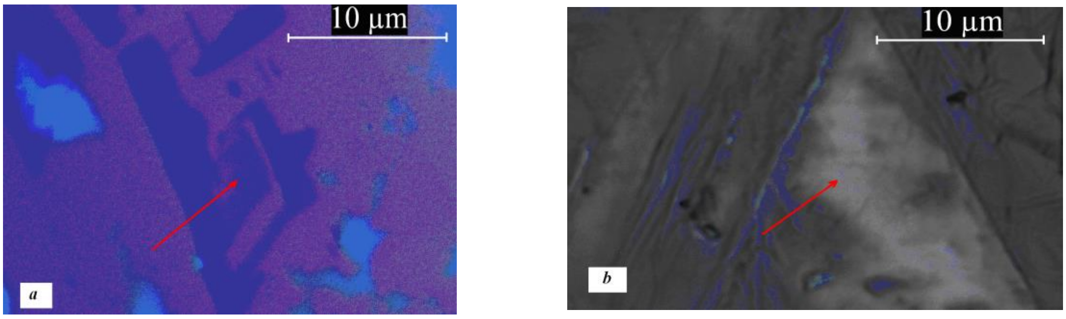
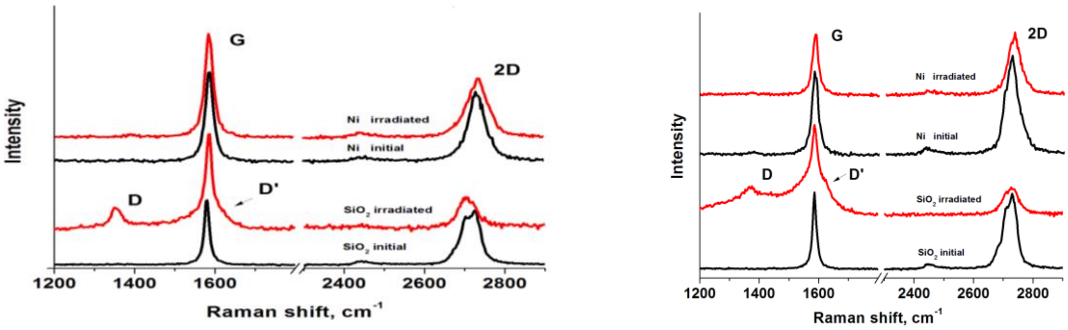
http://www.techno-press.com/?journal=anr&subpage=7 ISSN: 2287-237X (Print), 2287-2388 (Online)



(a) (b)

Fig. 1 Representative optical images of 2-layer graphene (shown with arrows) on different substrates: (a) SiO_2, (b) Ni



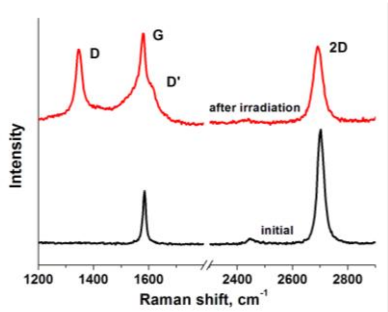
(a) (b)

Fig. 2 (a) Typical Raman spectra from 3- layer graphene, arranged on SiO_2 and Ni surface before and after irradiation by 30 keV beam; (b) a panel of Raman spectra from 2-layer graphene, irradiated by 2 keV beam on SiO_2 and Ni substrates

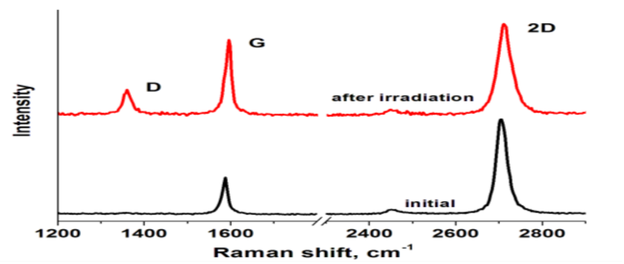
defects, which can be produced by irradiation can essentially improve mechanical and physical properties of FLG nanostructures. Therefore, special selected irradiation can be used as a technological tool of modification of such carbon nanostructures In this paper, in order of better understanding of the physical mechanisms of damaging process in such nanostructures, we performed irradiation of FLG arranged on different substrates (dielectric and metallic) in the wide interval of SEM beam energies and used the Raman spectroscopy as the basic technique of inspection of structural changes.

2. Experiments

Graphene and few-layer graphene specimens were produced by CVD technique. CVD method was based on using argon-benzene mixture with Ni substrate heated by resistive method at 900-1000^{o}C under atmospheric pressure. After structures formation a part of specimens was transferred to SiO_2 substrates (purchased by Graphene Supermarket) for examination and irradiation, while other specimens were studied and irradiated directly on Ni – substrate surface. All specimens were selected by optical microscopy (Leica DM6000) and Raman spectroscopy (NT-MDT NTegra



(a)



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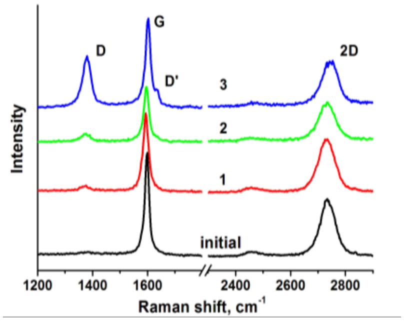


(c)

Fig. 3 Typical Raman spectra from graphene on SiO_2 before and after irradiation by: (a): 500 eV; (b): 200 eV beam; (c): Panel of Raman spectra from 3-layer graphene irradiated on SiO_2 by 30 keV beam with different intensities ($I_1:I_2:I_3 \approx 1:10^3:10^4$)

Spectra). All irradiation procedures were performed in SEM Quanta 3D 200i dual beam system with electron beam energies ranged from 0.2 to 30 keV, with typical current value ~1nA, under oil-free vacuum conditions ~10^{-4} Pa.

Fig. 2(a) presents Raman spectra from 3-layer graphene arranged on SiO_2 and Ni surfaces before and after irradiation by 30 keV beam. In Fig. 2(b) Raman spectra from 2-layer graphene specimens also arranged on both SiO_2 and Ni substrates after irradiation with 2 keV beam are presented. One can see for both cases the obvious changes appeared in Raman spectra from specimens, irradiated on SiO_2.

Fig. 3(a)-(b) present Raman spectra from graphene on silicon oxide irradiated by electrons with very low energies (0.5 and 0.2 keV) correspondingly. Fig. 3(c) illustrates very essential effect of the electron beam intensity (30 keV).

3. Discussion

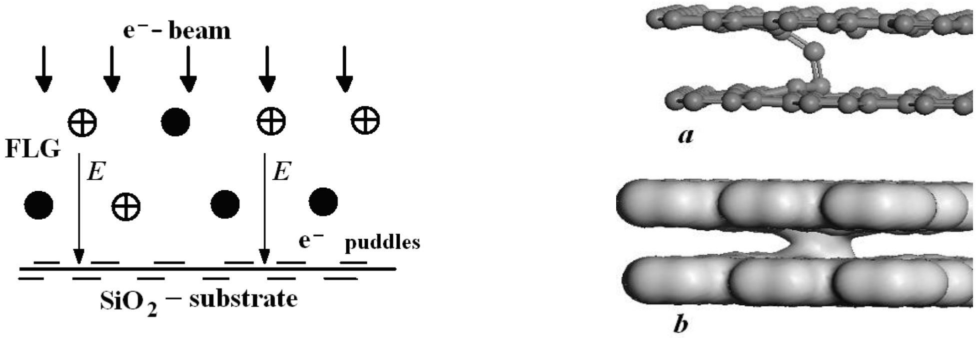
The data presented above were obtained in the relatively wide interval of SEM beam energies (30–0.2 keV). In Fig. 2 and Fig. 3 one can compare the Raman spectra from few-layer graphene, arranged both on SiO_2 and Ni substrates, irradiated with 30 and 2 keV beam correspondingly. Obviously one can see the essential changes in Raman spectra from specimens irradiated on SiO_2 substrate, while in the case of specimen irradiated on the Ni substrate there are no noticeable differences. Similar changes were observed for few –layer graphene irradiated on SiO_2 with the beam energies 15, 0.5 and 0.2 keV. The main features in Raman spectra from graphene and few-layer graphene after irradiation on insulator in all cases are the following: the appearance of the *D* peak and weak step-like feature *D'* at the right side of *G* peak Ferrari (2006). Above presented results give the weighty grounds to suppose that electron irradiation caused structural defects in graphene and few-layer graphene even at very low energies if these specimens are arranged on insulator surface. It should be noticed, that even maximum value of SEM energies 30 keV is too low for production radiation defects in graphene by commonly considered mechanism of elastic collisions of fast electrons with a carbon atoms in graphene structure. It is known, that maximum energy $E_{\max}$, which can be transferred from electron with the kinetic energy E_0 to a scattering atom can be obtained from the expression (1)

$$E_{\max} = 2E_0 \cdot \left(\frac{E_0 + 2mc^2}{Mc^2} \right) \quad (1)$$

where *m* and *M* are correspondingly masses of electron and atom, *c*-speed of light. Obviously, production of a structural defect caused by this mechanism is possible only if $E_{\max}>E_d$, where E_d– the energy of displacement of an atom from the structure. Some recent theoretical estimations for graphene Fei *et al.* (2012) gave approximately E_d=20 eV, while for E_0=30 keV and for *M*=12 a.u. (carbon) $E_{\max}$=5 eV. The mentioned above process of collision cannot cause production of structural defects in graphene. Therefore we need another physical mechanism for explaining observed above damaging of graphene structures. First of all, it must be taken into account that process of ionization of carbon atoms is possible at all beam energies used. For example, it has been proved by Ilyin and Golovanov (2006) in UHV Auger Spectroscopy experiments that maximum cross section for *K* level corresponds approximately to 1-1.5 keV. Therefore, in our experiments the main part of electron beam even with low energies passed through few layer graphene and reached the substrate surface (Fig. 4). Results presented show that the effect of under threshold energy damaging was revealed only in few-layer graphene, specimens arranged on dielectric surfaces and no signs of damaging were observed in specimens, arranged on conducting metal surfaces. It is reasonable to assume that during irradiation in subsurface and surface region of the insulator the negatively charged puddles can be formed. Obviously, the depth of the subsurface volume depends on the electron beam energy. The grounded assumption can be advanced, that on conducting surfaces such effects are impossible. The electric potential originated from this charge distribution in general can be obtained as a solution of Poissons equation for a film charged Ilyin *et al.* (2013). In this study much more wide interval of beam energy 0.2-30 keV and focusing on low energy irradiation allow us to suggest a model based on surface uniform charge distribution. It is also reasonable to neglect time variations of the charge surface density and consider electric field originates from these puddles as a stationary flat electrostatic field which can be determined as

$$E = \frac{\sigma}{2 \cdot \varepsilon_0} \quad (2)$$

where σ is surface charge density, ε_0- the electric constant. All our experiments were performed by the beam current nearly to 1 nA, by the size of focus about 20 nm, therefore the value of the surface charge density can be estimated as large as 10^2 C/m^2. One can see in Fig. 4(a) the main physical features of the system studied, in particular, that ionized carbon atoms of graphene sheets



(a) (b)

Fig. 4 (a): Scheme of electron irradiation of graphene structures. Black marks are carbon atoms, crossed circles - ions of carbon atoms. *E* is the electric field originates from negative charged puddles. (b): Computer model of a bridge-like radiation defect in two - layer graphene. (a) the atomic structure, (b) calculated electron charge distribution (shown for the density of charge 0.4 el / Å ^{3}) in the zone of the defect

are exposed to action of the field *E*. Under this conditions the electrostatic field caused by charged puddles reached instant values as large as 50-100 V/Å . Obviously, this field is able just pull out carbon ions from the structure with forming defects. The most probable defects expected by electron irradiation in few layer graphene are vacancies and interstitial atoms. In the paper Eckman *et al.* (2012) was supposed, that nature of structural defects in graphene can be defined with using relation between amplitudes *I*(*D*) / *I*(*D'*). Based on these data we suppose, that in our experiments defects observed in graphene were vacancies. But for 2- and 3-layer graphene relations *I*(*D*) / *I*(*D'*) are very different, therefore, we interpret these defects as bridge-like defects (BLD), which, physically can exist only in FLG, but not in graphene. A typical atomic configuration of a bridge-like defect, built by computer simulation and density functional theory calculations in 2-layer graphene is presented in Fig. 4(b).

These defects consists of interstitial atom arranged between two vacancies in both graphene planes. Such a defect links graphene sheets together and makes few-layer graphene more stiffer. Moreover, one can see, that dense electron charge bridge is also formed between two sheets. Besides, our quantum mechanical calculations with using density functional theory (Delley 1990) show that there is a large contribution of p_z – electrons of conduction band in this electron charge bridge, and it can be considered as creation of electric and thermal cross-conductivity between graphene sheets. This feature can be very important, for example, in the case of application such few-layer graphene nanoparticles modified with bridge-like defects as filler elements in composite materials that increase the isotropy of physical properties.

4. Conclusions

Few-layer graphene specimens placed on dielectric and conducting substrates were irradiated in SEM with the low- and middle electron beam energies, ranged by 0.2 -30 keV. The essential changes in Raman spectra from graphene and few-layer graphene after irradiation were observed only for specimens placed on dielectric surfaces. It was revealed, that the effect of the electron beam intensity was much more noticeable than that of beam energy. Results obtained allow to suppose a possible physical mechanism of under threshold energy structural defects production, based on forming the surface negatively charged puddles. Results of the work point that much more attention should be paid as to possible changes in few-layer graphene structures, which can appear even after conventional SEM examinations with relatively low-energy electron beam as well to substrate effects.

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