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Modification of graphene by ion beam

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ABSTRACT

Ion induced defect generation in graphene was analyzed using Raman spectroscopy. A single layer graphene membrane produced by chemical vapor deposition (CVD) on copper foil and then transferred on glass substrate was subjected to helium, carbon, nitrogen, argon and krypton ions bombardment at energies from the range 25 keV to 100 keV. A density of ion induced defects and theirs mean size were estimated by using Raman measurements. Increasing number of defects generated by ion with increase of ion mass and decrease of ion energy was observed. Dependence of ion defect efficiency (defects/ion) on ion mass end energy was proportional to nuclear stopping power simulated by SRIM. No correlation between ion defect efficiency and electronic stopping power was observed.

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1. Introduction

Graphene is a one atom thick carbon material of hexagonal crystalline structure. Its exceptional mechanical strength allows transfers and deposition on various substrates. The set of parameters like electrical conductivity, high charge carrier mobility, optical transparency, mechanical durability and low chemical activity promise its application in electronics, optics and materials engineering in composites, ceramics or polymers. However in many practical applications modification of graphene parameters may be required. Perfect graphene structure is responsible for its low chemical activity, but always for its low adhesion to the substrate, and causes problems with tailoring of its electrical parameters. Ability of ion beam bombardment to modify structure of target material seems to be promised method for tailoring of graphene properties. The application of ion beam for modification of graphene was examined for graphene cutting and perforation [1], doping in electronic applications [2–3], modification of electrochemical activity for batteries [4] and fabrication of sieves with nano-pores for water desalination [5]. In all these cases, the formation of defects in the graphene was used for changing of its properties. Thus the better knowledge of ion interactions with graphene may have very useful practical aspects. The interaction between ion and bulky solid can be effectively simulated using models based on loss of ion energy in elastic and inelastic processes. Energy transfer from ion to target atoms usually generates secondary processes which create secondary recoil cascade of target atoms detached from its positions. In case of graphene membrane there is no volume to produce a cascade of secondary atoms. For this reason ion-graphene interaction is usually reduced to the first hit of the ion to the target material. The ion impact may rearrange the crystalline structure of the graphene or create a vacancy by detach of carbon atom from graphene structure or simply excite electrons and increase the target temperature. Usually no excess carbon atoms are in close vicinity to the graphene defect available to supplement the lost carbon atom. Therefore the effect of ion impact to the graphene may differs from effects observed in bulky materials. Especially defect generation and its preservation in graphene may differ from bulky target due to lack of recoil cascade in graphene and low probability of vacancy recombination with a neighboring carbon atom.

Graphene crystallinity may be effectively studied by using Raman spectroscopy, including the defects detection. A pioneer works on Raman application for ion beam induced defect identification in graphene has been presented in [6] and [7]. A method of graphene defects quantifying has been proposed in [8]. This analysis allows one to identify kind and number of defects induced by ion bombardment taking into account proportions between so called line D at about 1350 cm^{-1} and line G at about 1600 cm^{-1} of Raman spectra. It opens unique and perhaps the first available opportunity for the investigation of ion beam collisions with a first atomic layer of irradiated solid. However it should be pointed out that role of interaction of graphene with the substrate on ion-graphene collision process is not clear. Graphene membrane is weakly bonded to the substrate via van der Waals bonds essentially weaker than interatomic bonds in solid bulk. So the ion induced secondary cascade may evolve differently on the graphene-substrate interface than in bulky target volume.

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2. Experimental and methods

The graphene grown on Cu foil using chemical vapor deposition method (CVD) and then transferred onto a glass substrate was used in presented experiments. The samples composed from graphene membrane deposited on the glass were irradiated with He^+, N^+, Ar^+ and Kr^+ ions at energy 100 keV, Kr^+ ions at energy 37 keV, N^+ ions at energy 50 keV and 25 keV and C^+ ions at energy 25 keV. In all processes ion beam was directed at right angle to the target surface. The ion beam current was always kept under 0.1 μA/cm^2 to avoid excess heating of the sample and to ensure uniformity of the ion fluence on all over the sample surface using XY scanner with kHz frequency.

Raman spectra were recorded at room temperature using a Renishaw inVia Raman Microscope. The excitation at the 532 nm wavelength from Nd:YAG laser with an average power of the laser spot below 0.5 mW was applied. The laser spot of a size of about 0.5 μm was focused on the sample using a ×100 lens and a numerical aperture NA = 0.9 in backscattering geometry. The Raman spectra of graphene excited by 532 nm wavelength exhibit two main lines: the one -phonon mode of wavenumber about 1600 cm^{-1} originating from the center of the Brillouin zone usually called G mode (E2g symmetry), and a two-phonon mode of wavenumber about 2700 cm^{-1}, originating from the K point of the Brillouin zone usually called 2D (A1 g symmetry). Presence of defects in graphene activates new modes: D mode positioned at 1350 cm^{-1} and D′ mode at 1620 cm^{-1} which are not observed in pristine graphene of good quality. Both of these lines D and D′ were observed after ion implantation. According to [8] intensity ratio of D and G modes ID/IG depends on graphene defects density and defect size. The proposed in [8] relation between Raman lines end defect density and size was applied it this work to determine the density and dimension od ion induced defects.

The numerous isolated islands of double graphene layer on the background of the continuous single graphene layer were observed with scanning electron microscope (SEM) on the samples. Therefore, in order to provide Raman measurements of a single layer the maps of Raman spectra were recorded and then the Raman signal from single layer area only was taken into account in next steps.

SRIM simulations were carried out for estimation of number of vacancies produced by ion graphene collisions and for estimation of electronic Se and nuclear Sn stopping powers. The simulations were carried out using Monolayer Collision Steps/Surface sputtering procedure. A graphite and quartz substrate data from SRIM compound dictionary were applied. The SRIM simulations were done at graphite thickness 0.3 nm close to the thickness of monoatomic graphene membrane. Binding energy of carbon atoms in graphene was set at 22 eV according to value determined experimentally in [9]. The total depth of plotting window of SRIM simulation was set at 30 nm. Under these conditions the first simulated layer is composed from carbon atoms only and no carbon atoms are included in next layers. The simulated number of vacancies induced by ion in the first carbon layer of 0.3 nm thick was taken as the simulated amount of graphene vacancies caused by incident ion.

3. Results and discussion

Examples of Raman spectra of graphene both pristine and after krypton and nitrogen ion bombardment at energy 100 keV and 50 keV respectively up to the few different fluences are presented in the Fig. 1. Raman spectrum of pristine graphene exhibits only two lines: so called G line located at wavenumber about 1600/cm and 2D line centered at wavenumber about 2700/cm. Such

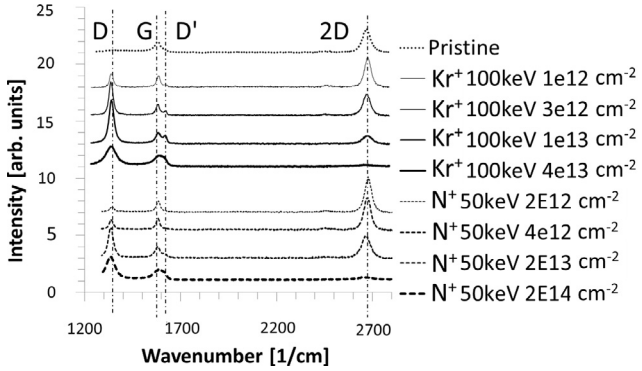

Fig. 1. Raman spectra of graphene pristine and subjected to ion bombardment with krypton ions Kr^+ at energy 100 kev up to fluencies 1x10^{12} cm^{-2}, 3x10^{12} cm^{-2}, 1x10^{13} cm^{-2}, 4x10^{13} cm^{-2}, and nitrogen ions N^+ at energy 50 keV up to fluencies 2x10^{12} cm^{-2}, 4x10^{12} cm^{-2}, 2x10^{13} cm^{-2}, 2x10^{14} cm^{-2}. All spectra were normalized to G line amplitude and shifted vertically to better visualization of graphs.

Raman spectrum indicates that defect density in initial sample graphene material is below detection threshold of the method. After ion bombardment the D line positioned at about 1350/cm was observed. Intensity of this line first increases with ion fluence and then steadily decreases. So, dependence of intensity rate of D and G lines ID/IG on ion fluence has a maximum at some fluence specific for each applied ion-energy combination (Fig. 1). In all examined ion – energy combinations the Raman spectra transformations were qualitatively similar. However the fluencies at which changes of Raman lines intensities were observed were specific for each ion mass-energy combination.

The quantitative relation of ID/IG ratio on defect density in graphene has been proposed in [8]. This method is based on idea that each defect cause the circular structural disorder area of radius r_S (S-region), which is surrounded by so-called activated region A of radius r_A ($r_A > r_S$). The region between r_A and r_S contribute most strongly to the D band, whereas the rest of graphene sheet outside S-region contribute to the G band (see the theoretical explanation in [8]). Structural disorder region S contribute weakly to the D band due to breakdown of the lattice structure itself. Defects generated by ions at low fluence are mostly separated one from another at mean distance many times higher than defect size. The distance between defects gets closer with increasing of ion fluence. Some of defects may overlaps and probability of this process grows with defect density leading ultimately to covering the graphene surface with structurally disordered carbon material. Changes in mutual relations between this areas are responsible for evolution of the Raman spectra with ion fluence. The proposed in [8] formula describes the relationship between the defects distance L_D and the ratio between the lines D and G:

$$\mathrm{ID/IG} = C_A[(r_A^2 - r_S^2)/(r_A^2 - 2r_S^2)][\exp(-\pi r_S^2/L_D^2) - \exp(-\pi(r_A^2 - r_S^2)/L_D^2)] + C_S[1 - \exp(-\pi r_S^2/L_D^2)]; [8] \quad (1)$$

where r_S is a radius of structurally disordered graphene region S, r_A is a radius of activated graphene area A surrounding the structurally disordered area S, L_D is a mean distance between defects in nm, C_A and C_S – are the constants defined in [8]. In our estimations we applied $C_A = 5.43$ and $C_S = 0.87$.

The formula (1) can be expressed in terms of the defect density N_D using expression [8]:

$$N_D = 1/L_D^2 \quad (2)$$

This transformation seems more convenient to evaluate the effect of ion beam bombardment as ion fluence is usually expressed in units cm^{-2}.

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