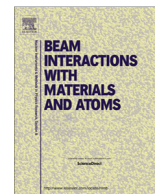




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Graphene defects induced by ion beam

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ABSTRACT

The CVD graphene deposited on the glass substrate was bombarded by molecular carbon ions C_3^+ , C_6^+ hydrocarbon ions $C_3H_4^+$ and atomic ions He^+ , C^+ , N^+ , Ar^+ , Kr^+ , Yb^+ . Size and density of ion induced defects were estimated from evolution of relative intensities of Raman lines D (~ 1350 1/cm), G (~ 1600 1/cm), and D' (~ 1620 1/cm) with ion fluence. The efficiency of defect generation by atomic ions depend on ion mass and energy similarly as vacancy generation directly by ion predicted by SRIM simulations. However, efficiency of defect generation in graphene by molecular carbon ions is essentially higher than summarized efficiency of similar group of separate atomic carbon ions of the same energy that each carbon ion in a cluster. The evolution of the D/D' ratio of Raman lines intensities with ion fluence was observed. This effect may indicate evolution of defect nature from sp³-like at low fluence to a vacancy-like at high fluence. Observed ion graphene interactions suggest that the molecular ion interacts with graphene as single integrated object and should not be considered as a group of atomic ions with partial energy.

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1. Introduction

The ion solid interactions have been widely investigated for many years as the ion implantation is a one of standard technologies used in manufacturing of solid state devices. However, the main efforts were focused on the ion energy loss mechanisms in the target volume. The graphene is a one atom thick membrane composed of carbon atoms organized in a honeycomb like hexagonal structure. So, the ion transfer through the graphene is reduced to the interaction with a single atomic layer. Hence, secondary cascade in the graphene is possible only in graphene plane and seems very rare because of the atomic thickness of the graphene membrane. Carbon atom displaced from their lattice positions in graphene structure is most probably irreversibly lost. There are some positions located between graphene membrane and the substrate which can be occupied by ejected carbon atom however, probability of occupation of these sites seems rather small. Moreover, there is a more fundamental difference between ion energy loss in a volume of solid target and ion interaction with graphene layer. In case of graphene layers, both free standing and deposited on the substrate, only first atomic layer interacts with the ion. Hence, graphene interacts with the ion at its original kinetic and potential energy. Subsequent interactions between ion and target material may modify ion charge and energy. This effect may be important in case of chemically bonded molecular ions. Interaction of molecular ion with solid target may leads to decomposition of

the molecule on the components in the form of atomic ions which next simultaneously penetrate the solid with partial energy proportional to its partial mass of whole molecule. However, the molecular ion starts to interact with the first atomic layer as whole molecule with its charge, potential and kinetic energy and size. Usability of ion beams for modification of graphene properties has been reported by many authors. For example following effects were reported: graphene cutting by ion beams [1], graphene doping [2,3], modification of electrochemical activity of graphene [4], graphene perforation to produce nano-sieves available for water desalination [5], improving of graphene-metal contact by helium ion bombardment [6].

The molecular ions implantation is utilized in solid state devices fabrication. For example shallow junctions in silicon device may be produced by following molecular ions: BF_2^+ [7], decaborane $B_{10}H_{14}^+$ [8] [9], octadecaborane $B_{18}H_{22}^+$ [10] or molecular phosphorus P_4^+ [11,12]. In case of boron rich molecules high ion mass allows one to use ions of higher energy (easier beam handling) comparing to the atomic boron B^+ ions and to create a shallower boron doped junction [10]. In all these cases boron profile may be estimated under assumption that every atomic component of the molecule travels in the solid target volume independently with partial initial energy proportional to its partial mass of the whole molecule. However this approach seems to be inappropriate to ion bombardment of graphene because of graphene interacts with whole molecular ion as it is.

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The quality of graphene structure may be estimated with by using Raman Spectroscopy. Usability of this method was presented in [13] and [14]. The effective method for quantifying of ion beam induced defects in graphene was proposed in [15]. The proposed in [15] method is based on analysis of evolution of proportion of so called Raman lines D to G with ion fluence.

2. Experimental

In order to compare the defect formation efficiency induced by ions containing different number of C atoms the carbon ions C^+ having 25 keV energy were used as a reference. The molecular ions C_6^+ and C_3^+ at energies 150 keV and 75 keV respectively were applied as examples of molecular ions. At these energies the partial energy of every carbon atom of molecular ion is 25 keV, i.e. the same as reference atomic carbon ions. It allows for a direct comparison of bombardment effects in graphene induced by three or six atomic carbon ions with effects of bombardment by one molecular ion composed from three or six carbon atoms. Additionally graphene was subjected to the ion bombardment by C_6^+ ions at energy 100 keV to estimate effect of ion energy. The carbon ions were generated from decomposition of CO_2 plasma in discharge chamber of the ion source. Molecular ions C_6^+ were generated in the Nielsen type ion source from benzene vapor, and C_3^+ ions were generated using the same ion source fed with propane. Beside the carbon molecular ions the hydrocarbon molecular ions were detected in the ion beam which leaves the ion source with different number of bonded hydrogen atoms from one up to maximum number of hydrogen atoms specific for given hydrocarbon. The molecules composed only from carbon atoms without hydrogen component were selected by using mass spectrometer. In case of C_3^+ there is only one possible carbon atoms configuration in the form of the v shaped chain. The angle between carbon–carbon bonds in propane is estimated about 111.7° a bit more than the tetrahedral angle 109.5° . Increase of angle between carbon–carbon bonds in propane is due to interaction with bonded hydrogen atoms. However, in case of pure C–C–C chain the angle between carbon bonds may be closer to tetrahedral angle. In both cases the angle between carbon atoms in C–C–C chain is smaller than angle between carbon bonds in graphene hexagon which is equal 120° . It makes the C_3 molecule a bit larger than distance between closest parallel sides of the graphene carbon hexagon. In case of C_6 molecule there are possible two basically different configurations of carbon atoms: the first one is benzene-like hexagonal ring and the second one is a chain of six carbon atoms formed by breaking of one carbon–carbon bond of carbon hexagon. Carbon chain usually forms a zig-zag configuration. Any form of such chain is larger than carbon hexagon of graphene structure. However it should be stated that this is not possible to separate these two different C_6 forms by using mass spectrometer.

In our experiments several other atomic ions were applied for defects generation in graphene for comparison with applied molecular ions. The graphene were bombarded by He^+ , N^+ , Ar^+ , Kr^+ and Yb^+ ions at energy 100 keV, N^+ ions at energies 25 keV and 50 keV and Ar^+ ions at energy 37 keV as well.

The graphene used in experiments was grown on copper foil in chemical vapor deposition process (CVD) and then it was transferred onto the borosilicate glass substrate. The applied graphene was mostly single layer with a network of long, narrow wrinkles always observed in such material and with a few small islands of multilayer graphene of 1–2 μm diameter.

The effects of ion bombardment on graphene properties were evaluated using Raman spectroscopy. The main advantage of this method is its very good selectivity allowing investigation of one atom thick graphene without interference from the substrate. For

our experiments we chose graphene on the glass substrate taking into account its negligible interference with Raman graphene signal. The method proposed in [15] allows for the estimation of graphene defect density and size utilizing Raman spectra. So, it allows to determine the ion efficiency of defect creation and estimation of the ion induced defect area. Such approach may provide information about differences between defects generated in graphene by different incident ions. The main aim of this work was experimental checking of difference between graphene interaction with atomic and molecular ions.

In all cases the sets of Raman spectra were measured to select the signal from single layer graphene. The Raman spectra were recorded using a Renishaw inVia Raman Microscope. The Nd:YAG laser of wavelength 532 nm with average power below 0.5 W focused on a spot of about 0.5 μm was used for Raman spectra excitation. Fig. 1 shows the Raman spectra of graphene both pristine and bombarded by C^+ 25 keV ions at selected fluencies. Similar evolution of Raman spectra after graphene irradiation by C_3^+ 75 keV ions for a number of selected ion fluencies was presented in the Fig. 2. A similarity of Raman spectra evolution in both cases can be noted. The Raman spectra of defect-free graphene measured at these conditions consist of two main lines: the one-phonon mode so called G line originating from the center of Brillouin zone centered at about 1600 cm^{-1} and a two-phonon mode so called 2D line originating from the K point of Brillouin zone of wavenumber about 2700 cm^{-1} . Defects in graphene activate additional two lines: the so called D mode centered at about 1350 cm^{-1} and D' mode at about 1620 cm^{-1} . Raman spectra of pristine graphene in our experiments consisted from two main lines G and 2D. In some measurements traces of D line a little over noise level were observed. After ion implantation both D and D' lines were detected. The ion fluency dependent evolution of D/G lines intensities rate was observed for all applied ions. Quantitative dependence of the ratio of D/G lines intensities on the mean distance between defects and defect size was proposed in [15]. We applied this model for estimation of efficiency of defect generation by ion and estimation of ion induced defect radius. The proposed in [15] formula (1) is based on the idea that incident ion creates circular structurally defected area S of radius r_S surrounded by a ring shape activated area A of radius r_A . The area A consists of unchanged graphene from which generation of the D and D' lines was activated by close vicinity of the structural defect edge.

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

where L_D is a mean distance between defects in nm, C_A and C_S – are the constants defined in [15]. 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:

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

According to the model [15] the graphene surface consists of three areas: the native unaffected graphene surface from which lines G and 2D originate, the sum of structurally defected areas S which doesn't contribute to the graphene Raman signal, and total area of activated regions A which is a source of lines D and D'. At low density of defects separated from each other by a distance far higher than defect size increasing of defect density leads to increasing of the area A and decreasing of the unaffected graphene surface proportionally to the increasing number of defects. Consequently intensity of D line growth comparing to the intensity of line G with increasing of defect density. At higher defect density areas S and A of separate defects start to overlap and relationship of lines intensities ratio D/G with respect to defect density reached

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