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Graphene oxide layers modified by irradiation with 1.2 MeV He^+ ions

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ABSTRACT

The irradiation with 1.2 MeV He^+ ions to various fluences was successfully used for modification of graphene oxide (GO). The elemental composition of the GO foils before and after He^+ ion irradiation was investigated using Rutherford Backscattering Spectrometry and Elastic Recoil Detection Analysis. The chemical composition and structural changes of the GO foil surface were characterized by X-Ray Photoelectron and Raman spectroscopy and changes in the electrical properties was studied by standard two point method. The obtained data indicate the removal of oxygen functionalities and growth of the graphene domains on the GO surface that leads to the improvement of surface conductivity which is a growing function of the ion fluence.

1. Introduction

Graphene oxide (GO) is a single layer of oxidized graphite with structure similar to the graphene, with the exception that the most of the carbon atoms in GO are sp^3 hybridized due to the introduction of the oxygen containing groups [1]. Since the most of the carbon atoms in the non-reduced GO are sp^3 hybridized the GO is an electrical insulator [2].

The GO has been extensively studied in the recent years due to its perfect mechanical, thermal, optoelectronic and chemical properties and the possibility of further modification opening new huge opportunities for e.g. flexible electronic and optical devices [3–7]. The GO films are applicable as moisture and oxygen barriers and they can also be used for chemical and corrosion protection [8]. The GO prepared by oxidation of graphite contains oxygen groups (carboxyl, epoxy, hydroxyl, carbonyl, etc.), which allowed crosslinking of individual sheets by various types of interactions [9]. Such modification can further improve and control GO properties for its potential application as membrane material [10,11]. The synthesis and electro-optical properties of GO and reduced GO have been extensively studied in the past [12,13].

The ion and electron irradiation is an effective and precision technique for the tailoring of structure and properties of nano-systems [14]. The irradiation with ion microbeam can be used for cutting, patterning and micro-structuring of graphene based samples with a very high spatial resolution [15]. Moreover, the ion irradiation of carbonaceous materials is powerful technique to obtain non-hydrogenated carbon films and new metastable carbon structures [16]. Ion irradiation with controlled ion fluence can lead to increase of number of sp^2 clusters [16] and to the sp^2/sp^3 ratio modification, deoxygenation and band gap reduction which is connected with the change of optical and electrical properties [17]. On the other hand, the ion irradiation leads to creation of radiation defects in the GO samples [18,19]. This is of capital importance especially for GO-based solar cells [20,21]. The great significance of GO based devices is in space application particularly in solar cells, space-based particle detectors, memory devices and battery current collectors [22–27]. In outer space the deterioration of device performance by light energetic particles is expected. So that, laboratory study of stability of G or GO based devices under irradiation with MeV light ions makes sense [28,29]. Moreover, the irradiation of GO with light MeV ions is rarely mentioned in literature and the optical and/or electrical properties of graphene based structures modified by the light energetic ions are still unknown.

In the present work the influence of irradiation with 1.2 MeV He^+ ions on the structural and composition properties of GO foils is investigated by various spectroscopy techniques. Also studied are changes in GO electrical properties as a function of the ion fluence. The results revealed that 1.2 MeV He^+ ion irradiation leads to GO reduction which is accompanied by a surface resistivity decrease. The ions and their energy were selected taking into consideration the results of our previous experiment performed with 5.1 MeV He^+ ions [30]. The obtained data may be of interest for the preparation of GO functionalized for

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potential future applications.

2. Experimental

The graphene oxide (GO) foils were prepared by graphite oxidation utilizing the permanganate oxidation method [31]. 3 g of graphite (2–15 μm, 99.9995%, Alfa Aesar) were mixed with 360 mL H_2SO_4 (96 wt%) and 40 mL of H_3PO_4 (85 wt%). Subsequently, 18 g of $KMnO_4$ were added and the reaction mixture was heated to 50 °C for 12 h. Afterwards, the reaction mixture was quenched in ice (400 g) with 20 mL of hydrogen peroxide (30 wt%), and the formed graphene oxide was separated by centrifugation. GO foils were prepared by suction filtration using a polycarbonate membrane (Nucleopore 0.45 μm/90 mm diameter) and graphene oxide suspension. The GO foils were prepared using aqueous suspension with a concentration of 6.7 mg·mL^{-1}. The prepared GO foils were stored in the paper wrapper due to the reduction of degradation by visible light [32].

The prepared GO foils were irradiated by 1.2 MeV He^+ ions in the implantation chamber installed at the 3 MV Tandetron MC 4130 accelerator and evacuated to the vacuum of about 6.9×10^{-6} mbar. The ion fluences were 1.0×10^{13} cm^{-2}, 1.0×10^{14} cm^{-2} and 1.0×10^{15} cm^{-2}, and the ion current densities vary from 7.5–15.4 nA·cm^{-2}.

Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) were employed for the determination of GO foils composition before and after the ion irradiation. The RBS spectra were measured using 2.0 MeV He^+ ions. An Ultra-Ortec PIPS detector recorded He^+ ions backscattered at a laboratory scattering angle of 170°. The ERDA spectra were measured using 2.5 MeV He^+ ions with the primary beam coming at an angle of 75° with respect to the foil surface normal and with hydrogen atoms recoiled at a scattering angle of 30° registered with the PIPS detector covered by a 12 μm Mylar foil. The typical ion current used during the RBS and ERDA analysis was 5 nA. To reduce the effects of the sample degradation during the RBS/ERDA analysis, several particular spectra were measured on different beam spots and the final spectrum was obtained by summing the individual spectra. RBS/ERDA spectra were evaluated by SIMNRA code [33].

Raman spectroscopy and XPS measurements were used to get information about structural and elemental modification of the GO foil caused by the ion irradiation. Raman spectroscopy is considered as the powerful method to study carbon based materials due to its specific response to the changes in carbon hybridization state and introduced defects [34]. An inVia Raman microscope (Renishaw, England) was used for Raman spectroscopy measurements. The spectrometer operates in backscattering geometry with a CCD detector. An Nd-YAG laser (532 nm, 50 mW) with 50× magnification objective was used for measurements. Instrument calibration was done with a silicon reference which yields a peak at 520 cm^{-1}. To avoid sample damage, no more than 5% of the total 50 mW laser power was used. The samples were drop-casted on silicon wafer from an isopropanol suspension (1 mg·mL^{-1}).

The high resolution X-ray photoelectron spectroscopy (XPS) offers information about chemical bonds and elemental composition in the very shallow subsurface region of the pristine and irradiated GO foils. The XPS measurements were performed with an ESCAProbeP (Omicron Nanotechnology Ltd., Germany) spectrometer using a monochromatic aluminium X-ray radiation source (1486.7 eV). A wide-scan survey of all elements was performed, with subsequent high-resolution scans of the C 1 s and O 1 s core level spectra. For the evaluation of the carbon-to-oxygen (C/O) ratios from the survey spectra relative sensitivity factors were used. Prior to measurement the samples were pasted onto conductive carbon tape. To eliminate sample charging during measurement (1–5 V) the electron gun was used and acquisition time of all XPS measurement were reduced to minimize possible surface damages by X-ray [35].

The current-voltage (I-V) characteristics of the pristine and irradiated GO foils were studied by the standard 2-point method utilizing the Keithley 6221 current source and Keithley 2128A nano-voltmeter. The Au contacts (50 nm thick) were sputtered on the surface of GO foils for the electrical resistance measurement.

3. Result and discussion

The charged particle penetrating through the matter lost the energy by two mechanisms, by the electronic and nuclear ones, whose interplay is crucial for the compositional and structural changes of the irradiated material. The SRIM code [36] was used for characterization of 1.2 MeV He^+ ions slowing down in GO. Particularly we can calculate range of the 1.2 MeV He ions, ratio of electronic vs. nuclear stopping and approximate depth distribution of vacancies. For 1.2 MeV He ions the S_e/S_n ratio is 910 and the ion-electron interactions are expected to play a decisive role near the GO foil surface and throughout almost the whole implanted layer of GO sample. The electronic stopping leads to excitation and ionization of molecules, creation of free radicals and unsaturated chemical bonds [36–38]. Also the release of gaseous degradation products may occur. Thanks to the electron-phonon coupling the irradiation may result in local heating of irradiated layer [37,38]. All these interrelated processes are responsible for changes in the structure and composition of irradiated samples. The vacancy production strongly depends on the displacement energy of given atoms in mater that is minimum energy which atom must receive in the collision in order to be displaced from the lattice site. The simplest formula to calculate the number of defects is Kinchin-Pease model (K&P) [39]. The K&P is a linear displacement model based on the series of independent two-body collisions with energy transfer given by hard sphere model [40]. The displacement energy of carbon atoms ~22 eV, simulated by molecular dynamics in graphene [41,42], was used in our SRIM simulation. The SRIM default value was used for displacement energy of oxygen. Since displacement energies for O and C in GO are not known, the displacement energy for C atoms in graphene was used as provisional solution. Determination of displacement energies is a complex problem which is out of the scope of the present study. In the Fig. 1, one can see the SRIM calculated depth profiles of the oxygen and carbon vacancies created by 1.2 MeV He^+ ions in the GO foil. The calculation was performed using the full cascade Monte Carlo (MC) simulation with the pristine GO composition obtained from the RBS analysis. Together with C and O vacancies the projected range and energy loss depth profiles of the 1.2 MeV He^+ ions are presented too. It should be noted that the ratio of electronic and nuclear stopping powers S_e/S_n decreases with increasing depth of ion penetration and decreasing ion immediate energy and it achieves a minimum near the ion projected range R_P ~5.8 μm (the SRIM calculated range straggling is $\Delta R_P \sim 1.5$ μm). The maximum of vacancies concentration is found near the ion projected range. The maximum values are $\sim 10^{-2}$ and $\sim 3 \times 10^{-3}$ vac/(ion.Ang) for C and O atoms respectively (see Fig. 1). We note that in the present case the electronic stopping power is higher and the ratio S_e/S_n is lower in comparison with our previous experiment with 5.1 MeV He^+ ions [30]. Therefore more pronounced structural changes in GO could be expected in the present case.

The elemental compositions of GO, pristine and irradiated to different ion fluences, determined by RBS and ERDA methods, are presented in Table 1. The accessible depth for RBS analysis with 2 MeV He ions is about 1 μm. Besides of major elements, carbon, hydrogen and oxygen, additional elements as sulphur and manganese are present which originate from the procedure of GO foils synthesis. It is seen that the atomic ratios C/O and C/H increase with increasing ion fluence. The C/O ratio increases from 2.5 for pristine GO to 3.7 for GO irradiated with the maximum fluence of 1.0×10^{15} cm^{-2}, at the same time the C/H ratio increases from 6.0 to 8.7. The H/O ratio varies slightly around the value ~0.4, thus we can assume the presence of carboxylic acids in GO foils [31]. The changes in C/O and C/H ratios indicate the