Effect of silver doping by ion implantation on graphene nanoplatelets properties

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The structural, electronic and optical properties of thin films based on chemically clean graphene nanoplatelets (GNP) doped by silver ion implantation with relatively low energies have been studied. The silver dopant percentage relatively carbon of 1.18 % has been achieved. The surface of the nanoplatelets was found to be not plane, and there are many areas with different local orientation. Big holes in the GNP surface have been appeared as a result of ion implantation, and metal nanoparticles have been formed. The conductivity of the graphene sheet after ion implantation was found to be lowered by the presence of such graphene lattice defects. It has been concluded that the essential changes of GNP structure occur during the ion implantation process, what is confirmed by electron microscopic, Raman and electrophysical measurements, as well as theoretical consideration.

1. Introduction

Carbon nanomaterials have been continuously increasing interests for science and technology during the past decade. Graphene and graphene nanoplatelets (GNP) are widely studied materials owing to their unique mechanical, thermal, electrical and optical properties [1,2]. Engineering their electronic properties is very important for application in manifold electronic devices. For this purpose, different kinds of physical and chemical functionalization are applied [3]. As a rule, functionalization often results in the decreasing of electrical conductivity. However, physical functionalization does not spoil essentially the electrical conductivity.

One of the interesting ways of physical functionalization of various materials is ion implantation [4]. This technique is clean, efficient, site-selective and suitable for realization of large-scale production at any substrate. It allows an easy control of the dopant selection and its concentration through the ion dose. Moreover, the ion beam can be wide or focused into a little spot and scanned. Colliding with graphene, the ion can interact with the electrons or to be exchanged with a carbon atom. For ion implantation of carbon nanomaterials both light (e.g. N, B, C [5]) and heavy (e.g. Ag and Co [6], Xe [7], etc.) ions are used. Note that ion implantation is a good technique for the synthesis of a high-quality graphene [8]. Depending on the atomic weight, beam energy and dose,

some functionalization or lattice damage can be obtained [9]. Also, changes in the chemical structure or the formation of metal nanoparticles on the graphene surface can be observed [6]. However, it was shown [10] that irradiation of nanostructures does not necessarily destroy them, but it may result in many fascinating phenomena. For example, light boron and nitrogen atoms were found to lead to an effective doping of the graphene sheet [5]. After ion implantation of carbon nanomaterials, a strong increase of the resistivity [10] caused by impurity atoms and especially by carbon lattice defects, appearance of magnetic properties and radiation induced self-organization [11] have been observed.

Such materials can find a lot of applications in electronic devices [12,13]. However, in spite of many achievements, a lot of questions remain still not answered [10]. The main part of such studies was made with carbon nanotubes and fullerenes [6,10]. Not much studies are devoted to graphene. Moreover, typically a reduced graphene oxide [13] which can undergo more strong transformations under ion beam irradiation owing to residual chemical groups in its structure, is used.

The aim of this paper is to implant chemically pure GNP by silver ions and to study the morphology and optical spectroscopic properties of the obtained material. According to our knowledge, the studies on ion implantation of the chemically pure GNP were not made earlier. It was shown before that copper nanoparticles deposited on GNP films by chemical approach were found

[14] to improve conductivity and stability of GNP films. Also, silver nanoparticles on graphene induce large enhancement of the Raman signal from graphene [15]. Noble metals are weakly chemically interacting with carbon atoms and do not change noticeably the graphene surface [16]. We found only few experiments on metal (partially silver) ion implantation of GNP films [6].

2. Experimental

GNP are few layer graphene nanosheets. Our GNP have been prepared by microwave (800 W) exfoliation of ASBURY expandable graphite [17-21] followed by sonication in ultrasonic bath in water-alcohol solution for size reduction, and further enriched by centrifugation. This physical tool posesses to minimize the number of chemical defects. We used a "green" water-isopropanol solvent, because water-ethanol gives sufficient results for graphene dispersion [22]. However, swapping of ethanol to isopropanol, having higher boiling point making difficult a solvent evaporation during nanoparticle synthesis, is expected to be more favorable for NP synthesis. Isopropanol can be easily mixed with water. The ratio of water: isopropanol is 4:1. Graphene nanoplatelets have typical width of 10–20 μm and thickness up to 3 nm.

The composite solution was drop-casted on Si substrate, followed by heating under vacuum at 100°C for 30 min, what is sufficient for solvent removal. Before deposition, the substrates were ultrasonically cleaned in acetone for 15 min, dried in a nitrogen flow, and then irradiated with oxygen plasma for 15 min to remove any organic contamination. The film thickness was 400-500 nm. A Solver P47 atomic force microscope in tapping mode was used to measure the thickness of the films.

Ion implantation has been carried out by Ag^+ perpendicularly to the sample surface with ion accelerate ILU-3 in vacuum of 10^{-5}Torr, with ion energy 30 keV, beam current 2 μA/cm^2, and dose range of 5.10^{15}-2.0×10^{16} ion/cm^2. This energy and dose are enough to penetrate essentially to the depth of GNP film. According to calculation by TRIM programme [23] a penetration depth of silver ions in carbon materials is about 80 nm, and so all implanted Ag ions was collected in near GNP film surface without doping of silicon substrate. The beam kinetic energy corresponds to the energy of electrons of about 0.15 eV being thermal.

The morphology of the GNP film surface was examined using a LEO-1455VP scanning electron microscopes (SEM). Elemental composition has been determined with X-ray spectral analyzer RONTEG. Raman spectra have been registered with a Raman microscope Nanofinder High End (Tokyo Instruments).

3. Modeling

Molecular mechanics force field implemented in MM2 program [24] was applied to simulate the interaction between silver ions, silver NP and the first layers of GNP. In molecular dynamics simulations by the force field method, the functional type and parameters are used to calculate the potential energy of a system. Chemical interactions between atoms linked by covalent bonds, and physical interactions describing the long-range electrostatic and Van der Waals forces are taken into account in the terms of potential energy. The MM2 extension of the force field method was designed primarily for conformational analysis of hydrocarbons and adds to potential energy a torsional energy term describing rotations around single bonds. Graphene nanoplatelet has been approximated by a single layer plane sheet containing 10×10 elementary cells. In order to simplify calculations, Ag nanoparticle has been presented as the lowest cluster consisting of 14 atoms, with the face-centered cubic symmetry structure.

The resistance measurements were made by standard four-point method using precision LCR Agilent E4980A set-up.

4. Results and discussion

Fig. 1 represents electron microscopy pictures of GNP films before and after Ag-ion implantation, at two resolutions. It can be seen (Fig. 1, a) that pure GNP (before implantation) are more than 10 micrometer sized sheet-like structures, similar to other exfoliated graphene flakes reported in the literature [25]. High-resolution SEM pictures reported in the works [17-21] show that such GNP have a typical thickness of from single layer up to 3 nm. Also, from the same images [17-21], it appears that the considered GNP in our case are few-layered planar structures, rather than plane sheets, with zigzag-like and bended edge sites. Such edges essentially prevent separate sheets from aggregation. It can be noticed (see Fig. 1a) that GNP are aligned mainly along the surface. Spectral analyzer registered only carbon with silicon and little amount of oxygen adsorbed on the substrate. Silver ion implantation with a dose below 2×10^{16} ion/cm^2 did not change essentially the morphology of the GNP film surface (see Fig. 1b). However, it is possible to notice more or less big oval holes (1) in the nanoplatelets (Fig. 1c), and spherical structures (2) of different diameters on the nanoplatelet surface (Fig. 1c). The big holes with a diameter from 100 to more than 1000 nm can be appeared due to breaking lattice bonds resulting in further weakening of the graphene lattice.

SEM image (Fig. 1c) indicates the formation of synthesized implantation spherical nanoinclusions (light blemishes 2) in the structure of GNP film with an average size of ~5-20 μm. Since heavier chemical elements registered by the detector of backscattered electrons are revealed in SEM microphotographs in a lighter tone than for a composite material composed of carbon atoms alone and implanted silver, it is possible to conclude that light (white) regions observed on a dark background (signal from carbon) are determined by the formed metal silver in the form of nanoparticles (Fig. 1c). In this case it could be note that silver atoms do not form any chemical compounds with carbon. Actually, silver nanoparticles are easily formed in different materials [4]. Spectral analyzer

of implanted GNP surface shows 60% of carbon and 0.71% of silver atoms (Table 1), and the achieved dopant percentage relatively carbon (considering only carbon and silver) is 1.18%, though these values can be considered as estimated data, taking into account measurement accuracy and depth inhomogeneous of ion implantation. This silver doping percentage is comparable with copper nanoparticles percentage in GNP-silver composite obtained by chemical synthesis [14]. The other part of element signal in Table 1 occurred apparently owing to some little admixtures during implantation process. Higher resolution (Fig. 1c) reveals also that the surface of the nanoplatelet is not planar, and there are many areas with different local orientation (3 in Fig. 1c). It points that the structure of nanoplatelets undergoes essential changes. These areas do not contain any visible nanoparticles or they are ultrasmall, thus these changes are owing to interaction with silver ions.
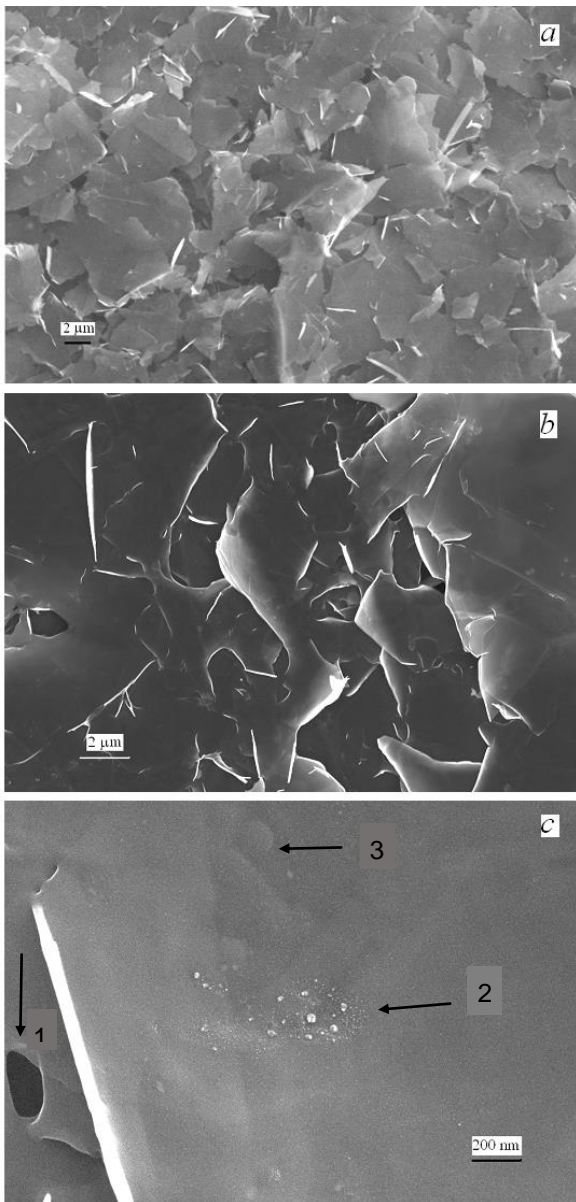
Table 1. Element distribution in Ag implanted film on Si substrate

Element	Weight%	Atomic %	Ethalon
C	58.66	60.00	C Vit
O	2.17	1.66	SiO_2
Si	85.73	37.50	SiO_2
S	0.21	0.08	FeS_2
Cl	0.14	0.05	NaCl
Ag	6.27	0.71	Ag
Sum:	153.18	100.00	

The Raman spectra are usually reliable for monitoring any defects in carbon nanomaterials [26]. It can be seen that Raman spectrum of unimplanted GNP (Fig. 2, curve 1) does not contain the D specific peak at about 1360 cm^{-1}, thus pointing out the absence of structural defects. It contains only G at ~ 1580 cm^{-1} (caused by the E2g phonon in the graphitic material), and the 2D peak at ~ 2700 cm^{-1} (defect-related, breathing mode of A1g). However, the spectrum of the Ag implanted GNP (Fig. 2 curve 2) is very different from the virgin film (Fig. 2, curve 1). For implanted sample, very wide D and G peaks, and an additional unusual peak at ~1850 cm^{-1} are observed. The overall intensity of this spectrum of implanted sample is much lower than that of virgin one, though the laser excitation intensity is 100 times higher for Ag doped material. Note that our measurements showed that 100 times increase of the laser intensity do not change significantly the shape of the Raman spectrum. It is known [27] that heavy enough dose of implantation of graphene results in Raman bands broadening and the formation of the amorphous carbon. The latter is known to contain a number of wide peaks in the 1000-2000 cm^{-1} region [28]. Taking into account this information that wide bands with maxima at 1430 and 1588 cm^{-1} can be apparently attributed to the essential transformation of graphene into amorphous carbon. The nature of peak at 1853 cm^{-1} is not clear yet. This peak has been also appeared in the Raman spectrum of graphene under strong flux increase of the irradiation of low energy N$^+$ ions [29]. Note, that surface enhanced Raman scattering (SERS) peaks at some species can be also observed in the implanted sample containing silver nanoparticles [29] obtained by magnetron sputtering. Additionally, incorporation of Ag nanoparticles results in a very efficient n-type doping of graphene [30] that can strongly widen and shift bands in Raman spectra. Generally, the nature of the obtained peaks is not clear yet, however, it can be concluded that the structure of the graphene lattice is strongly changed as a result of ion implantation.

The resistance of the sample after ion implantation is also strongly changed comparing to virgin film. When the resistance of the unimplanted sample is about 200 Ω/□, the resistance of implanted one increases up to more than 30 kΩ/□, and essentially different over the sample area (up to two-fold). It means possibly that GNP lattice undergo essential changes similar to those observed in such experiments with reduced graphene oxide.
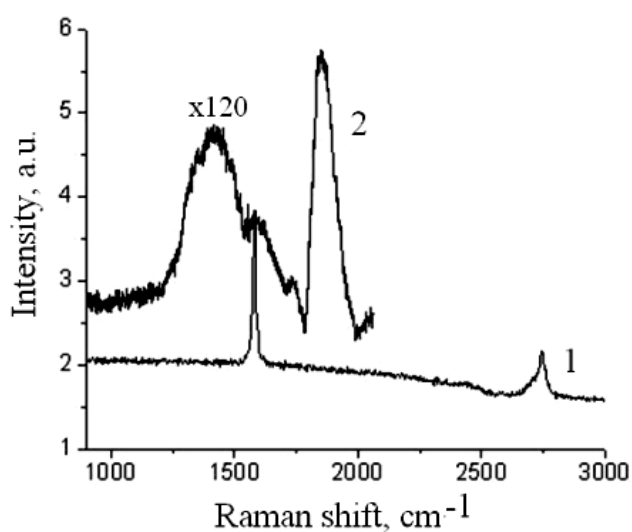

Fig. 1. Micrographs of unimplanted (a) and Ag implanted (b,c) GNP with different resolution

Fig. 2. The Raman spectra of undoped (1) and Ag doped (2) (120 fold increased) GNP samples. 1 - laser excitation with 473 nm and 800 µW radiation with a spot diameter of 600 nm, 600 line/mm grating and 30 s exposition; 2 - laser excitation with 532 nm and 100 mW radiation with a spot diameter of 600 nm, 600 line/mm grating and 30 s exposition

Comparing the above results between virgin and implanted samples, it can be concluded that inspite of relatively little amount of the attached silver atoms and silver nanoparticles to the GNP surface (1.18%), the essential changes of GNP structure occurs during the ion implantation process, apparently breaking the structure of π-electron system of GNP that could be suggested from by microscopic, Raman and electrophysical measurements.

Simulation of interaction of silver atoms and nanoparticles with graphene was fulfilled in order to reproduce the effect of ion implantation of silver atoms in graphene nanoplatelets. For this purpose, different configurations were considered. Firstly we have introduced a silver atom to the graphene structure; secondly we have simulated the interaction of graphene and silver nanoparticle; finally we have simulated interaction of graphene and silver nanoparticle direct link with substituted silver on graphene structure. The case of breaking bonds by silver ions, resulting to the formation of holes in plane graphene structure is too simple and not considered. The results of calculations are presented in Fig. 3.

Fig. 3a shows the substitution of carbon atom with silver, in graphene lattice structure. It is visible a loss of aromaticity of graphene system: in fact, the resonance structure is interrupted by the presence of silver, that induced a modification on flatness of structure. Furthermore, a slight deformation is visible on the edge of structure, probably due to out of plane silver presence.
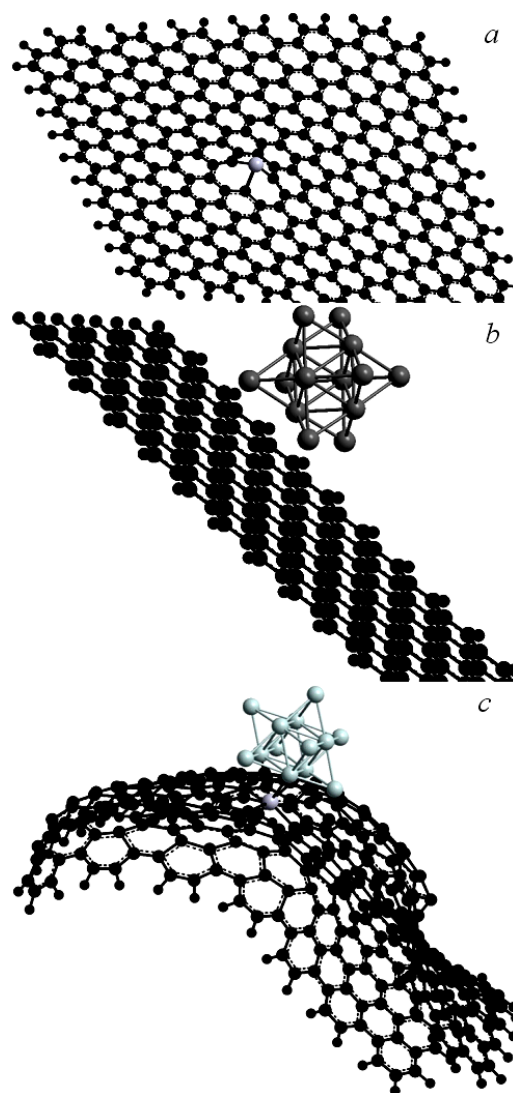

Fig. 3. Graphene surface after the introduction of Ag ions into graphene lattice (a), outside silver nanoparticle (b), and lattice bonded nanoparticle (c)

The simulation of the independent silver nanoparticle nearby the graphene surface showed (Fig. 3b) that no visible interaction between both parts of this system and no graphene sheet deformation is observed. On the other hand, silver nanoparticle can be grown from the substituting silver atom on the graphene surface. In this case we have simulated silver nanoparticle linked by central and apex atom of nanoparticle to the graphene surface. Huge modification has occurred in this configuration: although aromatic system is still present, morphological modifications are clearly observed (Fig. 3c). Silver nanoparticle orientation is quite unperturbed, a slight modification of the structure has occurred, with a loss of symmetry of silver nanoparticle. Futhermore, a loss of graphene flatness is clearly visible. The observed transformations are in some accordance with simulation data, and application to several layers graphene sheets will essentially diminish calculated morphological modifications.

5. Conclusions

Thin chemically clean GNP films were functionalized using silver ion implantation technique, and their structural, Raman and electrophysical properties have been studied. The evaluative dopant percentage of 1.18% has been achieved. It was shown that part of silver ions led to the formation of nanoparticles. The surface of the nanoplatelet was found to be not plane, and there are many areas with different local orientation. Big holes in the GNP surface have been appeared as a result of ion implantation. The conductivity of the graphene sheet was found to be lowered due to the presence of such lattice defects. It has been concluded that in spite of relatively little amount of the attached silver atoms and silver nanoparticles to the GNP surface, the essential changes of GNP structure occur during the ion implantation process, apparently breaking the structure of π-electron system, that is confirmed by microscopic, Raman and electrophysical measurements. Several possible results of interaction of silver ions with GNP has been theoretically analyzed. It was shown that irradiation of even chemically clean GNP by silver ions with relatively low energies implement not only physical, but also chemical functionalization, resulting in morphological and structural changes, amorphization, etc. that is similar to those observed in such studies of reduced graphene oxide. Further experiments for dose and ion energy optimization are required.

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