Efficient nitrogen doping of graphene by plasma treatment

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1. Introduction

Graphene is a two dimensional carbon nanomaterial with unique mechanical, optical, chemical and electronic properties. It has already been widely used in nano- and optoelectronics, electrochemistry, optics and mechanics. Moreover the potential of graphene applications can be extended through changing of its properties using chemical functionalization or doping. The second approach is based on substitution of a part of carbon atoms by the others, for instance, by boron, nitrogen, sulfur, fluorine etc. The pure graphene is a zero band gap semiconductor and its Fermi level lies on the top of its valence band, where it touches the conduction band. The doping of graphene results in modification of its electronic structure, namely, the Fermi level shifts either in conduction or valence band, depending on the electronic structure of dopants. The most popular dopants for graphene are boron and nitrogen being electron acceptor or donor, accordingly. In this work we concentrated on the synthesis and characterization of nitrogen doped graphene (N-graphene). Recently a couple of methods were discovered for production of N-graphene. The first one is a direct synthesis of doped samples using both carbon and nitrogen precursors such as methane and ammonia or pyridine. The second one is a post-synthesis processing of graphene samples using plasma treatment or chemical reactions. The description of last progress concerning nitrogen doping of graphene is presented in a review paper.

Here we demonstrate an efficient technique for a large scale production of N-graphene. Our process consists of two steps. The first step is synthesis of graphene film on a polycrystalline copper foil using a chemical vapor deposition (CVD) method followed by its transfer onto a desired substrate. The second step is treatment of produced graphene film using radio frequency (RF) discharge in ammonia. Such double step process provides a precise control on each step of procedure and leads to fabrication of N-doped graphene samples with a controllable doping degree. Fabricated samples were described by various methods such as atomic-force microscopy (AFM), scanning electron microscopy (SEM), Raman spectroscopy, optical absorption spectroscopy including Fourier transform infrared spectroscopy (FTIR), X-ray and ultraviolet photoelectron spectroscopy.
spectroscopy, optical absorption spectroscopy including Fourier transform infrared spectroscopy (FTIR), X-ray and ultraviolet photoelectron spectroscopy. The advantages of our approach for N-doped graphene production included the easy way to fabricate the samples for investigations and further applications in electronics or optics. Namely, in some cases it is better to do plasma treatment before transfer and in the others after transfer, also the target substrate should be different for different measurements and applications. In our work we present various processes of fabrication of samples and its investigations. For instance, the Raman spectroscopy and atomic force microscopy measurements were done after synthesis of graphene of copper then transfer onto SiO$_2$/Si substrate and then plasma treatment. The XPS and UPS measurements were done after graphene synthesis on copper, transfer onto Ni/Si substrate and then plasma treatment; on the other hand the FTIR measurements were done after graphene synthesis on copper, plasma treatment and then transfer onto CaF$_2$ substrate. During our experiments we obtained predominate pyrrolic nitrogen impurities which were studied before very poorly [5,9,10]. Our complex of techniques for N-doped graphene investigations should enlarge and clarify the understanding the nitrogen doping process of graphene. Moreover, for the best of our knowledge, the ammonia gas plasma treatment has been used for doping of micromechanical cleavage graphene [4] and of graphene oxide [11] but not for doping of CVD graphene.

2. Synthesis of graphene by a chemical vapor deposition method

A CVD method is a well known technique and is the most promising method for a large scale production of high quality graphene samples. There are many works concerning this method [12]. This approach consists in decomposition of carbon gas precursor (such as methane or acetylene) on catalytic substrate (either nickel or copper) and formation on top of it a graphene film with special parameters. The mechanism of formation has already been studied [13] and in this work we demonstrate the facilities of our home-made equipment for fabrication of graphene.

In our previous works the detailed description of the method and results on synthesis of few layer graphene films both on nickel [14,15] and copper [16] foils were presented. It is well known that the copper foil is better catalytic substrate for fabrication of thin graphene film with the amount of layers less than five, while the nickel foil is more appropriate for production of graphene film thicker than five layers [17]. In this work we focused on fabrication and investigation of thin graphene film and used copper as a catalytic substrate. A brief description of the process is described below. The CVD equipment used in experiments has some advantages comparing with commercial analogues. At first, in this equipment the Joule effect is used for the copper foil heating by a high electric current (up to 70 A) through the copper foil. Such approach provides the opportunity to control heating and cooling rates during synthesis. For instance, it is possible to reach a high temperature (of 800 °C) and then to cool the sample down to the room temperature in a few seconds. The second advantage of our approach is a possibility of direct measurement of the copper foil temperature by the infrared pyrometer with an accuracy of 1 °C. The synthesis was made in a stationary regime without any gas flow.

The synthesis process included few steps. At first, the copper foil was annealed in a gas mixture (with ratio Ar:H$_2$ = 4:1) at pressure of 500 mbar. The annealing process was carried out at temperature of 840 °C during 20 min. Then methane was injected into the chamber in portion of 7 mbar. The graphene film formation lasted 20 min. Finally the copper foil was cooled down to room temperature very fast, within 10 s. The most important parameter of the synthesis was the relative percentage of methane and the velocity of its injection. The methane was injected into the chamber with the flow rate of 280 sccm during 6 s. Changing the methane flow rate leads to formation of graphene films with different thicknesses containing different amount of defects. The detailed description of CVD synthesis of graphene on the copper foil and the transfer of graphene from the copper foil onto an arbitrary substrate is presented in our previous work [16]. After transfer process the graphene films were cleaned by sonication in isopropanol and deionized water. In Fig. 1a a photograph of graphene transferred onto a silicon substrate covered with 300 nm of silicon dioxide is shown. A microscope image of graphene is shown in Fig. 1b. Raman spectroscopy was used for confirmation of fabrication of thin graphene film (Fig. 1c). The Raman spectrum of graphene has the ratio of I(2D)/I(G) = 2.4, and 2D band has the position of 2679 cm$^{-1}$ and the bandwidth around 35 cm$^{-1}$. A D peak is induced by defects in graphene film. The atomic force microscopy (AFM) was used to study the surface of graphene film and the corresponded images are shown in Fig. 1d–e. The size of graphene grains is around 10 μm. The step height on graphene is around 1 nm which corresponds to the graphene thickness of 2 or 3 layers plus the contaminations between the graphene film and the substrate kept after the transfer process (chemical etching of copper foil). This method of graphene synthesis has already been used for fabrication of graphene samples for different optical applications [18–21] and have been confirmed as an efficient approach for graphene production.

3. Plasma treatment of graphene samples

After synthesis of graphene on copper foils it was transferred onto Si/SiO$_2$ substrate and onto silicon substrate with 200 nm of nickel layer. Further the sample was treated by RF-discharge plasma in ammonia gas. The other order of experiments was used as well. The graphene film was synthesized on copper foil then it was treated in ammonia plasma followed by transfer onto CaF$_2$ substrate.

Fig. 2(left) illustrates the scheme of plasma-chemical reactor [22,23]. The working chamber was preliminary evacuated to pressure 10$^{-2}$ Torr and then filled with ammonia. The composition of plasma generating media was constantly monitored during experiment using mass-spectrometer HALO 201-RC (Hiden Analytical, UK). The gas flow rate and the pressure of plasma generating gas were automatically controlled by mass flow and pressure controllers (MKS Instruments, USA) as it presented in Fig. 2(left).

After the pressure stabilization in the working chamber to a proper value the capacity coupled RF-discharge plasma was generated using the RF frequency generator Genesis GHW-12 (MKS Instruments, UK). The RF generator operated at the standard industrial frequency 13.56 MHz and the adjustable nominal power up to 200 W. The graphene sample was placed on the plane electrode, which was subjected to RF-voltage while the ring electrode was grounded. The graphene temperature was controlled during the treatment by a non-contact infrared pyrometer Optris LS (Optris GmbH, Germany) and did not exceed 40 °C.

The treatment conditions were as follows:

- an effective RF-power 10 W, 20 W and 50 W,
- NH$_3$ pressure in the working chamber 0.1–0.5 Torr,
- NH$_3$ flow rate 5 sccm (standard cm$^3$ × min$^{-1}$),
- a treatment time 2–80 min.

In ammonia glow-discharge plasmas NH$_3$, NH, H, excited NH$_3$ radicals and ions NH$_4^+$, NH$_2^+$, H$^+$ are formed due to collisions of
NH₃ molecules with the energetic electrons produced in the RF-discharge [24–26]. Some major chemical reactions occurred in ammonia gas under RF-discharge conditions are given in Table 1. These active N-containing species could react with carbon free radicals which are produced in graphene film in RF-discharge plasma and form the covalent C–N bounds or substitute C atoms in graphene structure.

4. Results and discussion

After plasma treatment the prepared samples were characterized by several techniques. Raman spectroscopy (spectrometer Jobin Yvon S-3000 with an excitation by Ar–Kr “Spectraphysics” laser with λ = 514.5 nm) was measured from the samples on SiO₂/Si substrates. X-ray photoelectron spectroscopy (XPS) (“Thermo Fisher Scientific Theta Probe” with monochromatic radiation of AlKα with energy 1486.6 eV) was measured from the samples on Ni/Si substrates to avoid charging effect. The valence band of N-graphene was examined by X-ray photoelectron spectrometer, equipped with a UV radiation source (He-II radiation with energy 40.8 eV). The FTIR measurements were carry out on PerkinElmer Spectrum 100 FTIR Spectrometer from the graphene films.
transferred onto CaF2 substrates. The optical absorbance measurements in UV–Vis–NIR wavelength range were done using PerkinElmer Lambda 950 Spectrometer from the graphene films transferred onto CaF2 substrates.

In Fig. 3 (left) the survey XPS spectra of graphene film before and after ammonia RF-discharge plasma treatment during 20 min are presented. A presence of the peak around 400 eV in the spectrum corresponds to the appearance of nitrogen atoms in graphene lattice. To understand better the influence of ammonia plasma on graphene and to find the optimal parameters for fabrication of desired samples a series of experiments using different treatment time and different effective power of RF-generator have been done.

In the series of experiments on fabrication of N-doped graphene the parameters of plasma treatment were the following: the temporal period of plasma treatment was varied from 2 min up to 80 min and the power of plasma generator was 10 W and 20 W. Also it was found that the effective power of RF-generator around 50 W is enough to remove the graphene film in 5 min 20 min is necessary to remove graphene film using 20 W and the treatment with the effective power of RF-generator of 10 W should be longer than 80 min to remove the graphene completely. The concentrations of nitrogen atoms in graphene films have been estimated from the survey XPS spectra of each sample. In Fig. 2 (right) these dependencies are presented. In case of treatment by RF-discharge with higher effective power the concentration of nitrogen increased more rapidly with the treatment time than in case of the lower effective RF-power. Moreover, it was found that the concentration of N atoms in graphene gets the fixed value and does not exceed it. For example, the graphene treatment using the effective RF-power of 20 W provides the maximum concentration of nitrogen of 2.2 atomic % in case of the plasma treatment during 10 min, while the treatment of graphene film using RF-discharge with the effective RF-power of 10 W during 20 min leads to introduction into graphene 3 atomic % of N atoms. Further increasing of treatment time (up to 20 min) results in the same concentration of N atoms but in different distribution of types of nitrogen.

In Fig. 3 (right) the difference in C 1s lines of graphene before and after plasma treatment is shown. The main peak corresponded to C–C bond with sp2 hybridization has the binding energy around 284.5 eV ± 0.2 eV and confirms the graphene presence. This peak decreases after plasma treatment due to damaging of the crystalline carbon lattice by particles with a high energy appearing during the plasma generation in reactor. The other components of the C 1s peak, which have the positions 285.5 eV, 286.8 eV, 289.0 eV ± 0.2 eV, corresponded to the C–C bond with sp3 hybridization, C–O and C==O bonds respectively. The increasing of C–C bond with sp3 hybridization confirms increasing of organic compounds, which appeared on the edge of defects of graphene film after plasma treatment.

Further the graphene samples, treated in RF-discharge with 10 W effective RF-power, were studied more carefully by SEM and Raman spectroscopy. The latter has shown that the amount of defects significantly increased after the plasma treatment. In Fig. 4a there is a comparison of Raman spectra of graphene films before and after the plasma treatment during different periods (from 2 min to 20 min). It is well seen that D peak around 1350 cm−1 is few times increased after plasma treatment and does not influenced by the treatment time. But the other peak around 1617 cm−1, called as D' and corresponded also to the defects in the graphene crystalline lattice, increased with the increased treatment time. This means that the amount of defects increased. The SEM images (Fig. 4b, c) of graphene films before and after plasma treatment were obtained for visualization of damaging of graphene. In Fig. 4b the graphene before plasma treatment is shown. The dark area corresponds to graphene and bright – to substrate. A couple of cracks in graphene are observed before treatment and its amount strongly increases after plasma treatment.

Interesting results have been achieved after a long-time
treatment (more than 20 min) because in this case the amount of nitrogen atoms was fixed while the doping type was changed. In Fig. 5a the XPS spectra of N1s peak are presented. The study of N1s line with binding energy around 400 eV in XPS spectra of samples treated with different times has revealed a redistribution of intensities of all components of the band during a long-time treatment. The peaks with energies $398.7 \pm 0.2$ eV and $402.0 \pm 0.2$ eV corresponding to pyridinic-N and quaternary nitrogen or graphitic-N accordingly [29,9] decrease, while the other component with energies $400.1 \pm 0.2$ eV, corresponding to a pyrrolic-N [29,9] increases. It is caused by a strong influence of ammonia radicals (such as NH$_2$ and NH), created in plasma on
The ultraviolet photoelectron spectroscopy (UPS) of the valence band for pristine graphene and for nitrogen-doped graphene have been performed (Fig. 5b, d). The valence band structure of N-graphene was studied both theoretically [30–32] and experimentally [29,33–35] but the shift of valence band maximum (VBM) has not been clearly described yet. In our experiments the investigated graphene films have a couple of layers thickness and some contaminations and were measured by UPS. Two types of experiments were done for better understanding of N-doped graphene electronic structure. At first, the graphene film was transferred onto metallic substrate, then treated in ammonia plasma and then the UPS measurements were performed. In second approach, the synthesized on copper foil graphene film was treated in ammonia plasma and characterized by UPS without transfer. The valence band structure of the samples before and after plasma treatment are presented in Fig. 5(b, d). It should be noted that after the ammonia plasma treatment resulting into the predominant pyrrolic nitrogen doping of graphene. This type of nitrogen impurities has not been studied theoretically, but it is well known that a graphitic nitrogen is a donor of electrons and a pyridinic nitrogen is an acceptor of electrons [28,31,33]. Thereby here we demonstrate graphitic nitrogen is a donor of electrons and a pyridinic nitrogen is a pyrrolic nitrogen graphene [10]. The FTIR measurements of pristine and N-doped graphene with 20 min of 10 W plasma treatment (left). The opening of the band gap was not observed but the decreasing of transmittance of N-doped graphene around 0.4 eV corresponds to absorption of N-graphene with the double energy of the shift of valence band maximum equivalent to 0.2 eV. This proves the changes in electronic structure of graphene after treatment in ammonia plasma discharge. Moreover, the optical absorption spectroscopy in UV—Vis-IR range shows the typical optical absorbance spectra of graphene without any changes before and after plasma treatment (Fig. 6(right)) as it was described earlier [36]. The doping affects on electronic structure of graphene and results in shift of Fermi level of pristine graphene. In case of pyridinic or nitric nitrogen impurities N-graphene becomes p-type semiconductor [37] where the Fermi level shifts to valence band and in case of graphitic or pyrrolic N-bond types the N-doped graphene becomes n-type semiconductor where the Fermi level shifts to conduction band [37,10].

5. Conclusion

In this work we presented the effective method for graphene synthesis by a chemical vapor deposition on copper foil using home-made cold wall equipment. The Raman spectroscopy and atomic-force microscopy were used for confirmation of fabrication of graphene. Using RF-discharge treatment of graphene in ammonia gas the nitrogen doped graphene samples have been obtained. The doping degree of N-doped graphene was controlled

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**Fig. 6.** The FTIR measurements of pristine and N-doped graphene with 20 min of 10 W plasma treatment (left). The IR-VIS-UV transmittance measurements of pristine and N-doped graphene with 20 min of 10 W plasma treatment (right). (A color version of this figure can be viewed online.)
by the time of plasma treatment. A maximum concentration of 3 at % of nitrogen has been achieved. The X-ray photoelectron spectroscopy was used for studying the samples fabricated. The long-time plasma treatment results in increasing of pyrocl nitrogen impurity type, namely: a 60 min treatment leads to mostly pyrocl N. With UPS the shift of the valence zone maximum in N-doped graphene has been revealed. It was caused by an influence of nitrogen atoms on graphene as the donors of electrons resulting in graphene has been revealed. It was caused by an influence of nitrogen atoms on graphene as the donors of electrons resulting in graphene has been revealed. It was caused by an influence of nitrogen atoms on graphene as the donors of electrons resulting in graphene has been revealed. It was caused by an influence of nitrogen atoms on graphene as the donors of electrons resulting in graphene has been revealed. 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