Research and development of the method of graphene oxide thin films local reduction by modulated laser irradiation

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Abstract. This article describes the reduction process of graphene oxide films deposited on various substrates by 445 nm laser irradiation with exposure time from $4 \times 10^{-3}$ to $3 \times 10^{-1}$ s. AFM images of the deposited films are presented. To obtain a better quality of the reduced graphene oxide films on substrates, we found the optimal ratio of the partial pressures of air and argon in the background environment. Variation of laser irradiation exposure time allowed us to determine its influence on sheet resistance and the ratio of Raman peaks intensities $I_{D}/I_{G}$, $I_{2D}/I_{G}$ of the reduced material. As a result, we demonstrated the possibility of graphene conductive traces formation with a sheet resistance of 188 Ohm/$\square$ at 0.1 um film thickness.

1. Introduction

Graphene is a promising conductive carbon material for the integration into micro- and nanoelectronics processes. Carbon atoms form a two-dimensional hexagonal lattice with $sp^2$-hybridized bonds [1]. It is known that graphene has a high thermal conductivity of $\sim 5 \times 10^3$ W/m$\cdot$K, a transparency of $\sim 97.7\%$, an elasticity of 1 TPa, a mobility of charge carriers of $\sim 2 \times 10^5$ cm$^2$/V$\cdot$s. This material can be applied in the fields of optoelectronics, sensor technology, spintronics.

There are several methods of graphene production, however, they have a number of technological problems. Micromechanical exfoliation allows to obtain graphene flakes of small dimensions. CVD synthesis uses various temperatures and catalysts for graphene production on a metal surface, but the structure transferring from the metal produces a large number of defects in a graphene film. Epitaxial growth on the silicon carbide substrate with 6H-SiC orientation allows obtaining high quality graphene, but the complexity and the high cost of silicon carbide plates preparing make the process uneconomical and difficult to integrate into standard electronics processes.

Nowadays, the reduction from graphene oxide (GO) is one of the cheapest and fastest methods of graphene production. Graphene oxide is a promising material for electronics, optoelectronics and sensorics due to a possibility of its mass production.

There are several methods of graphene oxide production, they involve oxidation and intercalation of graphite with strong oxidants (KMnO$_4$, H$_2$SO$_4$, etc.). The main groups of methods are named after the authors: Staudenmaier, Hammers and Brodie. Graphene oxide is stable in water and in different organic solvents. When its dispersed carboxyl and hydroxyl groups are ionized, as a result, electrostatic repulsive forces prevent adhesion of the particles providing stability of the suspension. After coating a surface with the suspension and removing the solvent, several monolayers of the material remain on the substrate forming a mosaic film with a thickness varying from a few atomic layers to a thick film. Graphene oxide contains $sp^3$ hybridized carbon areas with functional groups that
violate the electrical conductivity making graphene oxide dielectric with a resistance of \( \sim 2 \times 10^3 \text{ Ohm-m} \) [2]. Reduction of graphene oxide is a process of the functional groups removal and C-C bonds in \( sp^2 \) lattice restoration. It allows to receive the reduced graphene oxide layers with lateral dimensions equal to the initial graphene oxide sheets. Despite the fact that the lattice of reduced graphene oxide has many defects and unremoved groups, multilayer films of reduced graphene oxide have a low resistivity, which depends on the method of reduction and may vary from 10\(^{-1}\) to 10\(^{-5}\) Ohm-m [2-4]. Graphene oxide reduction methods should be separated into chemical, thermal and photo ones [4]. Treating in strong reducing agents such as hydrazine and its derivatives, sulfur-containing compounds can be classified as chemical methods. Thermal reduction method involves heating a graphene oxide suspension or deposited material by means of annealing [5]. The last group of methods uses femtosecond lasers as a light irradiation source [6]. A femtosecond pulse causes multiphoton scattering without phonon generation. There is an \textit{ab initio} prediction of energy required for the graphene oxide reduction [7]. Lasers with different wavelengths are widely used for photothermal reduction by local heating (UV: 248 nm [8], visible spectrum: 532 nm [9], IR: 1064 nm [10]).

The reduced graphene is investigated by X-ray photoelectron spectroscopy, Raman spectroscopy. Raman spectroscopy is widely used for studying carbon materials, such as nanotubes, graphene and graphene oxide. The position, width and intensity of the \( I_D \sim 1350 \text{ cm}^{-1} \), \( I_{2D} \sim 2700 \text{ cm}^{-1} \) and \( I_G \sim 1580 \text{ cm}^{-1} \) peaks are determined by composition, defects and numbers of graphene layers. High-quality graphene is characterized by the absence of the \( I_D \) peak and a small width at half-height of the \( I_{2D} \) peak on Raman spectra. The number of layers is estimated by the ratio of the \( I_{2D}/I_G \) peaks intensities [11].

Development of methods for local reduction of graphene oxide thin films by laser irradiation will solve the existing problems.

2. Experimental

In this paper we used the graphene oxide suspension produced by «SIC Graphene» Ltd. This material was prepared by the modified Hammers method [12]. We used monocrystalline silicon plates KDB-7.5 with (100) orientation with natural oxide (< 5 nm) and polyethylene naphthalate films (PEN) as substrates. Deposition was performed by drying 80 \( \mu \)l of 0.8 mg/ml graphene oxide suspension on a square of 1 cm\(^2\) at 22°C for 24 hours. Vertical withdrawal of the substrate from the suspension with a speed of 0.1–10 mm/min was performed to obtain monolayer GO films. Modification of GO was carried out in a climatic chamber filled with a mixture of air and argon at atmosphere pressure and room temperature. The sample was treated with a 2 W solid-state laser working at the 445 nm wavelength with the 5 nm spectral width. Output laser power was regulated by PWM of DPSS laser current with a 30 kHz sampling rate. The laser power was calibrated with a silicon photodiode FDS-155 Rus, the calibration curve was plotted. The laser was focused on the samples by microscope lens with a numerical aperture of 0.11 and 4.7x optical multiplicity in a 30 \( \mu \)m circle. For the automated processing, the samples were fixed on a motorized XY table. To study the samples by Raman spectroscopy, a Centaur U HR spectrometer «Nano Scan Technologies» Ltd. was used. The quality of graphene oxide films reduction was estimated by the relative intensity of the \( I_D \), \( I_G \), \( I_{2D} \) peaks that characterize graphene. To achieve representativeness of the data, we obtained Raman spectra from different areas of samples and averaged out the results. Measurements of the reduced graphene oxide sheet resistance were performed by the four-probe station and a digital multimeter Agilent 34401A. The deposited graphene oxide films were investigated by an AFM (Solver Pro company «NT-MDT»).

3. Results

Withdrawal of the substrate from the suspension at a speed of 0.1–10 mm/min allowed to receive GO films deposited on the substrate. Atomic Force Microscopy of the deposited material confirmed the
presence of a significant number of single-layer flakes of graphene oxide with lateral dimensions greater than 1 μm and a thickness of about 1.2 nm (figure 1 (a)) that is consistent with experimental data from other works [13]. The optimal speed providing a high density of oxide graphene monolayers on surface (~ 90% covering) was determined to be ~ 5 mm/min (figure 1 (b)).

![Figure 1. AFM images of graphene oxide (a) monolayer flakes; (b) a few-layer thin film on natural silicon oxide](image)

Drying the suspension at room temperature was used for deposition of homogenous thick films up to 1.5 μm thick. Drying at increased temperatures (80–90°C) caused the appearance of the inhomogeneity and defects on the film surface. These graphene oxide films were locally treated under different conditions.

In air atmosphere, oxidation of carbon occurred with CO₂ formation due to the presence of oxygen. The lattice recovery of the carbon did not occur. Reduction of the background intensity in Raman spectrum after treatment (curves 1,2 in figure 2(a)) indicates removal of organic matter remained after the film deposition process. Intensities of the characteristic peaks of carbon ID, I₂D and IG in this case changed negligibly. The sheet resistance reduced from > 10 MΩm/□ to ~ 40 kΩm/□ due to the sintering processes between GO flakes. The Ar/Air partial pressure ratio changed in 10 % steps in the range 0–100 %. This experiment revealed that the most efficient reduction process of GO occurs at 90 % Ar and 10 % Air, that corresponds to 2 % of O₂.

Reducing the partial pressure of atmosphere oxygen in the chamber led to the shift of the process towards graphene oxide reduction: the removal of functional groups and restoration of the hexagonal lattice structure, which is confirmed by Raman spectra (figure 2).

Reduction of ID and increase of I₂D peaks intensities occurred due to increase of argon partial pressure in the chamber (figure 2(b)). After argon pressure had exceeded 90 % (at an oxygen content of < 2 %), several blue shifted peaks merged with IG appeared, that can indicate the presence of amorphous carbon on the surface (curve 5 in figure 2(a)). Oxygen released during reduction was not sufficient for the removal of amorphous carbon from the film surface.

Amorphous films showed the highest conductivity, but they had lower structural perfection, low adhesion and they are not suitable for practical use as a functional material in micro- and nanoelectronics. Measurement of the sheet resistance of the material demonstrates its linear decrease to 101.17 Ohm/□ (figure 3).
Figure 2. Raman spectra demonstrate the structural change of the material during processing (a); relative intensity of the Raman peaks $I_D/I_G$ (square) and $I_{2D}/I_G$ (triangle) as a function of the argon/air partial pressure ratio in the chamber (b).

We have experimentally obtained the dependence of sheet resistance and the $I_{2D}/I_G$, $I_D/I_G$ ratio (which characterizes the structural perfection of films) on the laser irradiation exposure time. The exposure time of the laser beam on the sample was defined by the formula: $\tau = (d/V) \cdot D$, where $d$ is the laser beam diameter, $V$ is the laser movement speed, $D$ is the control signal duty ratio. The exposure time varied from $4 \cdot 10^{-3}$ to $3 \cdot 10^{-1}$ s (figure 4).

Figure 3. Sheet resistance as a function of the argon/air partial pressure ratio in the chamber. Recovery occurred at a constant exposure time of $4.29 \cdot 10^{-2}$ s.

The laser speed influence on reduction process was studied (within a range from 150 to 1500 $\mu$m/s, at 100% power) (figure 5). Existence of the critical exposure time of $\sim 4 \cdot 10^{-2}$ s is observed in all experiments. When we exceeded the critical time of exposure, the material reduction did not occur because the excess energy broke the carbon lattice bonds.

When the exposure time was less than the critical one, reduction of the material occurred that was confirmed by Raman spectra (increasing intensity of the $I_{2D}$ peak, decreasing intensity of the $I_D$ peak) and improving conductivity of the film. Further reduction of the exposure time resulted in a slight improvement of the material quality.
4. Conclusions
Processes of films and monolayers graphene oxide deposition on silicon and PEN substrates were practiced in this work. The effect of laser irradiation on the graphene oxide films was studied. We found the optimal ratio of argon to air (9:1) for the high-quality graphene films production. The dependence of material sheet resistance and its structural perfection on the laser irradiation exposure time and the laser movement speed was revealed. We found the critical exposure time required for graphene oxide reduction, which is $\sim 4 \cdot 10^{-2}$ s. We obtained the conductive traces with a sheet resistance of $\sim 200$ Ohm/$\square$ and a thickness of 0.1 um, isolated by graphene oxide.

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