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Etching of wrinkled graphene oxide films in noble gas atmosphere under UV irradiation

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We have studied the process of UV reduction of wrinkled grahpene oxide films, deposited on silicon substrate from ethanol suspension. In order to avoid destruction of graphene oxide via ozone formation from ambient air, samples were protected by argon atmosphere during UV irradiation. Using the analysis of back scattering spectra for medium energy ions, we have found that the UV irradiation mediated reduction process produced significantly decreased carbon content on the substrate surface. The decrease in the carbon content was accompanied by a smoothing of the films during reduction to graphene. We suppose that the observed effect is related to the oxidation of carbon atoms in the graphene scaffold of graphene oxide to carbon monoxide or dioxide by the oxygen from the graphene oxide (GO) itself. One has to consider this when developing a process for the preparation of graphene films using the UV-mediated reduction of graphene oxide.

Keywords: graphene oxide, reduction, UV irradiation, graphene films.

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1. Introduction

The reduction of graphene oxide is one of the most promising ways to form large scale conducting transparent films for a variety of applications, including solar sells, displays as well as LED light sources and field emitters [1, 2]. Today, effective methods for preparation of high quality large domain graphene oxide in the form of aqueous suspension are ready for industrial application [3]. The only problem still remains is to develop an effective and flexible method for the reduction of graphene oxide (GO) into graphene which obviates the need for high temperature or aggressive reducing agents, such as hydrazine thus avoiding damage to and contamination of the formed graphene film [4]. Using UV irradiation could be a promising approach for the mild preparation of graphene films on a broad variety of substrates [5, 6]. Due to relatively low binding energy of epoxy and hydroxyl groups in GO, excitation of the electron structure, resulting from absorption of UV photons is able to release these moieties from the graphene sheet in the absence of a reducing agent or heating. It is also important for future applications of GO/graphene films that UV irradiation is compatible with photolithography techniques currently available in the electronic industry.

Although the UV method of GO reduction does not require heating of the substrate with deposited GO film or exposing it to active chemical reagents, the probability of incidental photochemical reactions with ambient atmosphere or functional groups present in the GO should be considered when devising a practical UV reduction of GO. Thus, it is reasonable to suppose that the results of UV irradiation could be dependent upon the morphology and the chemical composition of GO. One should also take into account the fact that GO itself does not possess the determined ratio between C–O–C and C–OH groups. The composition of the continuous GO sheet (neglecting the edge) can be described by following formula: $(C_2O)_x(COH)_{(x-1)}$ where

$0 < x < 1$. That's why the samples of GO prepared under different oxidation conditions will possess varying compositions and thus abilities for reduction.

Recently, we have developed the method for preparation the large domain single layer GO sheets with perfect crystalline structure [7]. We have also demonstrated the preparation of single layer GO films on silicon substrates as well as the graphene films obtained by thermal reduction of GO films under a hydrogen atmosphere. However, it was later shown that the applied method of reduction provided partially hydrogenated graphene and consequently, did not allow us to obtain products with sheet resistance less than several $k\Omega/\text{sq}$. The reliable method of *in vacuo* thermal treatment [8] requires temperatures exceeding 900 °C, which makes it incompatible with a majority of potential substrates, including organic polymers. In our search for a more effective and flexible method for the preparation of highly conductive graphene layers, we have chosen the UV irradiation of GO films on the surface of silicon substrates.

The goal of the present work was to study the process of preparation the graphene films using UV irradiation for reduction of GO sheets on silicon substrates.

2. Experimental

Graphite Oxide aqueous suspension was prepared by enhanced Hummers method [9] from natural crystalline graphite. In order to remove small particles and residual graphite, the obtained suspension was centrifuged at 1500 RCF, forming 4 wt% solution, which was subsequently diluted by ethanol at ratio 1:500 to obtain the final suspension, suitable for deposition on substrates. Size distribution of Graphite Oxide particles in initial water and final ethanol suspensions was measured by Optical Diffraction method, using Malvern Mastersizer 2000. Preparation of several layer graphene films on the surface of silicon substrates included deposition the droplets of ethanol suspension to the horizontally-positioned substrates and subsequent drying in air at room temperature. Due to excellent wettability of silicon by ethanol suspension, the surface of each sample was fully covered thus forming a continuous GO film after drying without any additional measures like rotation of the substrate. We assumed that applying the freely-spreading ethanol suspension on a silicon surface will allow us to avoid the use of the complicated Langmuir – Blodgett technique for forming several layer GO films. Graphite Oxide films, formed on silicon wafer, were analyzed by scanning electron microscopy with GEOL GSM3001F instrument.

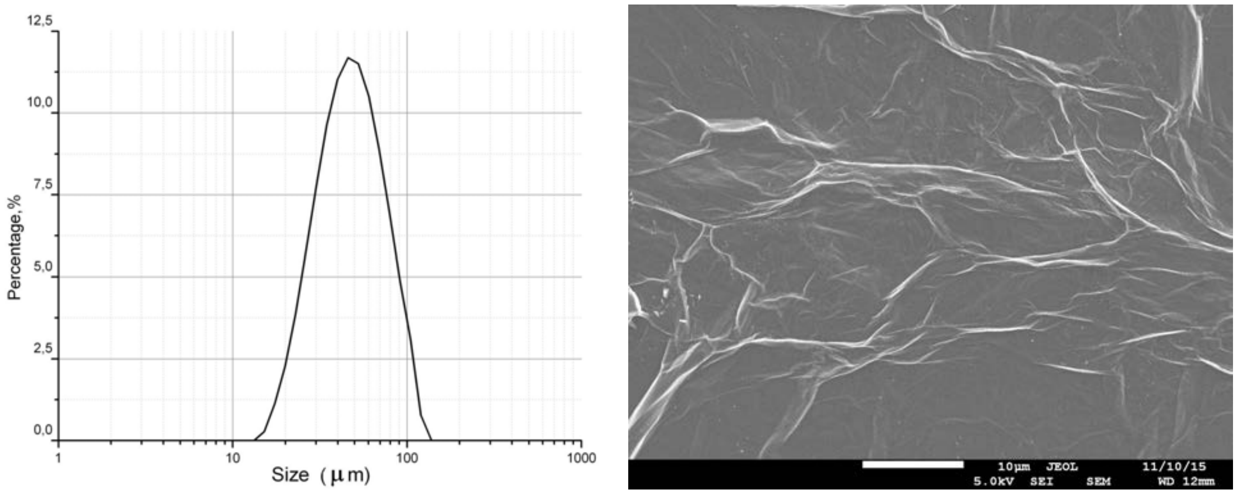
As a source of UV irradiation, we applied the 30 W deuterium lamp with quartz window with wavelengths ranging from 186 – 360 nm. Samples were placed at 5 mm behind the quartz window of lamp in the quartz cylinder with pure argon gas flow at normal pressure. Noble gas is necessary in order to avoid the generation of ozone by UV irradiation from ambient oxygen and therefore prevent damage to the reducing graphene film by the reaction with active oxygen species.

Argon gas also played role of coolant to avoid significant increasing of sample temperature under irradiation. Adjusted gas flow was at 150 cm^3 per minute and the duration of UV irradiation was 1 hour.

Reduction of Graphite Oxide films under UV irradiation was analyzed using: UV-Vis spectroscopy, performed on a Shimadzu UV 2450; IR-spectroscopy, performed on Infralum 08 FTIR spectrometer with attenuation total reflectance attachment, and by analysis and reciprocal modeling of reverse backscattering spectra of medium energy ions (RBS). Medium Energy Ion Spectrometry combined with ion channeling method also provided possibility to estimate the element (C,O) amounts. In our previous work [10], we have demonstrated the usability and high efficiency of applying RBS for observing the structure and composition of atomically thin films on the surface of perfect crystals as a result of the channeling effect.

3. Results and discussion

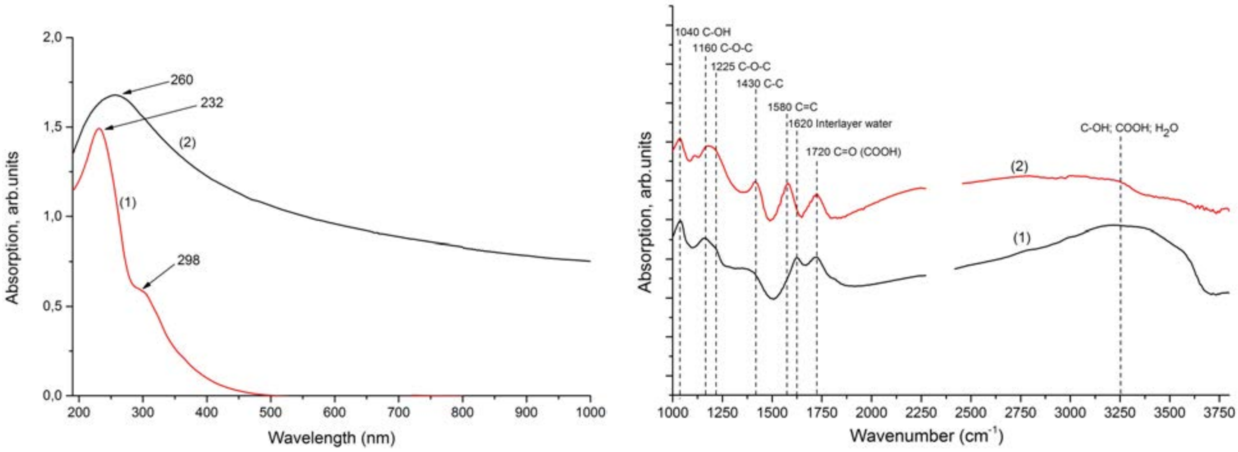
Figure 1 demonstrates the size distribution of separate graphite oxide platelets in prepared suspension, measured by optical diffraction method (OD), and structure of formed GO film on silicon substrate. One sees, that the average size of graphite oxide particles is about 50 μm, much larger than that usually obtained using the common Hummers method [11]. This is rather important, especially in the case of following formation of large scale conducting transparent films, due to the decreasing of degree of platelets boundaries influence on optical and electronic properties. A SEM image of the prepared graphite oxide film on silicon wafer, presented at Fig. 1b demonstrates presence of wrinkles on GO flakes deposited onto the silicon surface. However, the presence of wrinkles is unlikely to contribute to the overall resistance of reduced graphene film because, as estimated from the SEM image, the curative radius in each wrinkle is incomparable to the thickness of a single layer of graphene film.



a b

FIG. 1. a) size distribution of GO particles in aqueous suspension; b) SEM image of the GO film deposited on the surface of silicon substrate

Reduction of the graphite oxide film was confirmed by UV-Vis spectroscopy and FTIR spectroscopy, which are presented in Fig. 2. The UV-Vis spectrum of the initial graphite oxide contains two peaks – at 300 nm, attributed to n-π* transitions in C=O, and 230 nm attributed to π-π* transitions of C=C in amorphous carbon system [12] – and absence of absorption at wavelengths from 500 to 1000 nm. However, the UV-Vis spectrum of graphite oxide film after 1 hour UV irradiation has specific changes, in particular, the peak at 300 nm has disappeared, the peak at 230 nm has shifted to 260 nm, and absorption at wavelengths from 500 to 1000 nm have significantly increased, which confirms reduction of the sample. In order to prove this fact, we measured IR spectra of initial graphite oxide and graphite oxide film after 1 hour of UV irradiation. The IR spectrum of the initial GO has several distinguishing features, determining presence of functional groups: region at 3000 – 3700 cm^{-1}, corresponding to hydroxyl groups and water molecule deformations, peaks at 1720 cm^{-1} (carboxyl), 1620 cm^{-1} (interlayer water), 1040 and 1365 cm^{-1} (hydroxyl groups), 1160 cm^{-1} and shoulder at 1220 cm^{-1}, corresponding to epoxide groups [13,14]. After treatment, the IR spectrum has significant changes – absorption at 3000 – 3700 cm^{-1} (hydroxyls, water and carboxyl) are significantly decreased, the peak for interlayer water (1620 cm^{-1}) also disappears and peaks at 1580 and 1430 cm^{-1}, corresponding to C=C and C–C vibrations, increases. However, peaks that correspond to epoxide and hydroxyl functional groups still remain almost unchanged. This observation can be explained by the fact that the formed film has a several-layered structure and reduction of the film by UV irradiation occurs only for a finite number of the top layers. During reduction, light absorption of these uppermost layers significantly increases due to the transition from GO to graphene electronic structure. Consequently, the intensity of UV radiation reaching the bottom layers isn’t enough to reduce them. As a result, the underlying layers of GO still remain unreduced and maintain their contribution to the averaged data of the FTIR spectrum.



a

b

FIG. 2. UV-Vis spectra (a) and IR spectra (b) of initial graphite oxide (1) and reduced graphite oxide (2)

These results are in good agreement with data, reported in [15]. Actually, the energy of UV photons of wavelengths ranging from 186 – 360 nm is enough to overcome the energy barrier for the removal of OH as well as CO groups from the surface of graphene sheet.

For further investigation of structural and chemical changes during reduction process, we utilized Medium Energy Ion Spectrometry with analysis of energy spectra of 96 keV protons, back scattered to 120 ° from the structure under investigation (silicon single crystal having a natural SiO_2 surface layer of about 1 nm thickness on which GO layer was deposited).

The obtained spectra are presented in Fig. 3. Curve 1 corresponds to the GO film before UV irradiation, while curve 2 corresponds to the film after UV irradiation. The measurements were performed in channeling regime and therefore the signal from bulk silicon was suppressed for about 30 times compared to that in ‘random’ orientation regime. The level of bulk silicon signal is depicted in Fig. 3 by dashed curve. On this pedestal there are three peaks: carbon (73 – 76 keV), oxygen (77 – 80 keV) and silicon (83 – 86 keV), corresponding to amorphous phases of structure. The ion back scattering yield from these phases is insensitive to measurement regime (channeling or ‘random’). Note that besides signal from Si atoms of amorphous SiO_2 layer, the silicon peak contains that from Si atoms, forming so-called surface peak.

Comparison of the carbon peaks in curves 1 and 2 shows a 3-fold carbon content decrease, whereas the corresponding value for oxygen is only 1.2-fold. This is because the basic part of oxygen belongs to SiO2 layer and is therefore insensitive to UV radiation.

Comparison of the carbon peaks obtained from the films before and after UV irradiation demonstrates the noticeable etching the GO film simultaneously with its reduction. The observed effect can be explained by the fact that graphene oxide is an intermediate state of carbon oxidation. The functional groups that terminate the dangling π-bonds on the surface of graphene

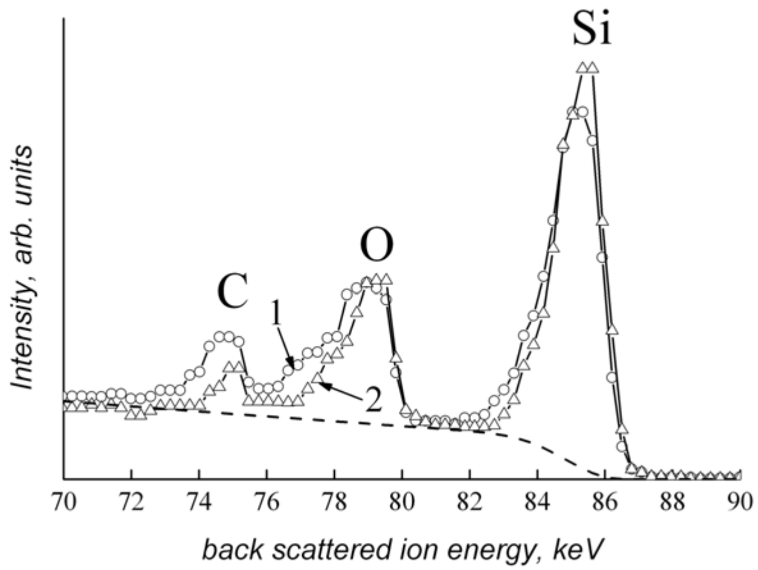


FIG. 3. The energy spectra of H^+ ions having the initial energy of 96 keV back scattered from GO deposited on Si single crystal before (1) and after (2) the UV irradiation

sheet like hydroxyl (OH) and epoxy (C_2O) can be simply removed by excitation in the following process:

$$(\mathrm{COH})_x + \hbar\omega \to \mathrm{C}_x + \frac{1}{2}x\mathrm{H_2O} + \frac{1}{4}x\mathrm{O_2}$$
$$(\text{ or } \quad (\mathrm{COH})_x + \hbar\omega \to \mathrm{C}_x + x\mathrm{OH}^* \quad \text{and} \quad 2\mathrm{OH}^* \to \mathrm{H_2O} + \mathrm{O}^*)\,.$$

As it was demonstrated in [16], this path is related to the extraordinary strength of σ-bonds between carbon atoms inside the graphene plane. The presence of wrinkles or edges can significantly affect the hardness of C–C bonds and give rise for probability of alternative paths for the process in GO films under UV irradiation:

$$\mathrm{C}_x\mathrm{C_2O} + \hbar\omega \to \mathrm{C}_{x+1} + \mathrm{CO},$$

or even

$$\mathrm{C}_x(\mathrm{COOH})_4 + \hbar\omega \to \mathrm{C}_{x+2} + 2\mathrm{H_2O} + 2\mathrm{CO}.$$

The observed smoothing of the carbon film under UV irradiation shows that the process related to recession of carbon from the graphene film takes place specifically at wrinkles formed by GO during the deposition process.

4. Conclusions

We have demonstrated the successful reduction of GO films by UV irradiation in argon gas atmosphere on silicon substrates at room temperature. We have also observed the effect of smoothing the wrinkled GO films accompanied by the noticeable decrease in the carbon content of the GO film subsequent to UV irradiation. The probable explanation of the observed etching of wrinkled GO films is in further oxidation of the graphene plane of GO by its own oxygen with formation of carbon monoxide or carbon dioxide gases under UV excitation. This effect can be applied for simultaneous smoothing the graphene films while preparation them for optical and electronic applications. It should also be noted that the UV reduction of GO can be used for the preparation of 3D graphene for energy storage of electrochemical applications.

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