



Nanosecond laser treatment of graphene



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ABSTRACT

Laser processing of graphene is of great interest for cutting, patterning and structural engineering purposes. Tunable nanosecond lasers have the advantage of being relatively widespread (compared to e.g. femtosecond or high-power continuous wave lasers). Hereby we have conducted an investigation of the impact of nanosecond laser pulses on CVD graphene. The damage produced by sufficiently strong single shots (pulse width 5 ns, wavelength 532 or 266 nm) from tunable optical parametric oscillator was investigated by the methods of scanning electron microscopy and optical microspectroscopy (Raman and fluorescence). Threshold of energy density for producing visible damage was found to be ~ 200 mJ/cm². For UV irradiation the threshold could be notably less depending on the origin of sample. Surprisingly strong fluorescence signal was recorded from damaged areas and is attributed to the residues of oxidized graphene.

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1. Introduction

The experimental realization of monolayer graphite sheet called graphene has led to an intense investigation of the fundamental properties and potential applications of this new carbon nanomaterial during the last decade [1]. In particular, graphene is expected to have promising optical and optoelectronic applications considering its good transparency which is accompanied with excellent electrical conductivity, saturable absorption and possibility to induce intense luminescence after special treatment [2]. For fast and high-power optical processes the high optical damage threshold is an important characteristic. On the other hand, pulsed lasers can be beneficial for special processing of graphene, such as cutting and patterning with sub-micron resolution. Properly refined laser treatment can also induce more subtle chemical or structural changes such as bandgap tailoring and formation of conductive channels through localized reduction of graphene oxide [3–5] as well as superhydrophobicity and iridescence through biomimetic structuration [6]. Impact of continuous wave (CW) [7] and especially femtosecond [8–10] laser irradiation on graphene has been characterized to some extent. While CW and femtosecond laser beams represent two extreme (and convenient) cases in terms of the involved radiation–matter interaction, lasers operating in

nanosecond regime are somewhat more common and provide a wider choice of wavelengths. Recently, relatively high-power nanosecond lasers have been employed in two-beam interference geometry for large-area patterning of graphene oxide for implementation of a gas sensing device with tunable response time [11].

Hereby we aim to describe the response of large-area (up to cm²) CVD graphene to intense single pulses of nanosecond laser as detected by the methods of optical microspectroscopy and scanning electron microscopy (SEM).

2. Experimental

Since micromechanical cleavage produces generally too small samples for the experimental arrangement described here, we used two different samples of large-area CVD graphene.

The first sample (later referred to as sample S1) was prepared in home-assembled CVD reactor following the receipt described in [12]. Predominantly monolayer graphene was grown on commercial 25- μ m thick polycrystalline copper foils (99.999%, Alfa Aesar). The foils were initially annealed 30 min at 950 °C in Ar/H₂ (both 99.999%, AS AGA Estonia) flow of 100/120 sccm and then exposed to the flow (40 sccm) of the mixture of 10% CH₄ (99.999%, AS AGA Estonia) in Ar at the same temperature for 10 min. Then the sample was cooled at the rate of 15 °C/min to room temperature in Ar flow of 100 sccm. Next, the upper sides of copper foils with graphene were covered with PMMA ($M \sim 997,000$, GPC, Alfa Aesar) in chlorobenzene (Alfa Aesar) solution (20 mg/ml) and the

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copper was removed with warm FeCl_3 (97%, Alfa Aesar) solution (1 mol/l). The PMMA/graphene was washed with deionized water and transferred onto SiO_2/Si substrates. PMMA was dissolved by dichloromethane (Alfa Aesar). Finally, the samples were washed in hot acetone (99.5%, Carl Roth GmbH + CO). In addition to monolayer areas (confirmed by Raman spectra) the sample also contained smaller regions of bi- and triple layer graphene which were easily identified visually under optical microscope by contrast differences.

For comparison, similar experiments were conducted on commercial polycrystalline CVD graphene (Graphene Laboratories Inc.), which was also deposited on SiO_2/Si substrate. This sample will be referred to as sample S2.

The irradiation of graphene was carried out by focusing the radiation from a tunable pulsed optical parametric oscillator (OPO) Expla NT342/1/UVB (pulse width 5 ns) obliquely on graphene (angle of incidence $\sim 60^\circ$) to an elliptical bell-shaped irradiance distribution with FWHM $30 \mu\text{m} \times 10 \mu\text{m}$ (Fig. 1). One UV (266 nm) and one visible (532 nm) wavelength was employed in this study. Only a single pulse was applied with sufficient energy to produce optically visible damage (simultaneously monitored through a microscope). Although the energy of each individual pulse (partly extracted over a quartz plate) was recorded accurately by an energy meter (Ophir Nova II), very accurate determination of damage threshold was complicated due to laser pulse energy fluctuations and some inhomogeneities of the graphene sheet.

Raman spectra were recorded by using a Renishaw inVia micro-Raman spectrometer (spectral resolution 2 cm^{-1}) employing the 514 nm line of an argon-ion laser for excitation and a $50\times$ objective for focusing of the laser beam and collecting the backscattered Raman signal.

Microluminescence measurements were carried out on home-assembled setup consisting of Olympus BX41M microscope combined with Andor iXon DU-897D camera for fluorescence imaging and fiber-coupled Andor SR303i spectrometer equipped with Andor Newton DU970P-BV camera for spectral measurements. 532 nm DPSS laser was correspondingly used for either wide-field or point excitation. Dichroic beamsplitter in combination with a band-pass or high-pass filter was used to reject the excitation. The setup also permits employing the OPO at lower intensities for oblique excitation of fluorescence at arbitrary wavelength and confocal detection [13].

X-ray photoelectron spectroscopy (XPS) measurements were performed in UHV chamber with a SCIENTA SES-100 spectrometer using the $\text{Mg K}\alpha$ X-ray source (photon energy 1253.6 eV, FWHM 0.7 eV). The error of measured absolute energies is less than 0.1 eV.

High-resolution scanning electron microscopic (HR-SEM) images were acquired by using HeliosTM NanoLab 600 (FEI) system operated at probe electron energies of 1–5 keV and current of 21 pA. Secondary electron images of the sample were acquired with TLD (Thru-the-Lens Detector).

3. Results and discussion

Laser-induced formation of optically clearly visible damage area in the graphene layer was observed typically for peak energy densities above $\sim 200 \text{ mJ}/\text{cm}^2$. Exceptionally, the home-grown sample S1 appeared much more sensitive to UV pulses with damage threshold as low as $25 \text{ mJ}/\text{cm}^2$. A possible explanation is that the damage mechanism involves absorption of UV radiation by some adsorbed species which are present at higher concentration on the CVD samples grown in our lab. Moreover, it is known that the absorption of graphene itself becomes markedly stronger around 270 nm [2]. This fact has to be combined with the possibility that due to the peculiarities of the transfer process applied to commercial graphene, it has much better thermal contact with substrate leading to more efficient dissipation of absorbed energy. This is partially suggested by the fact that under UV pulses the visible damage in the commercial graphene sheet (S2) appears nearly at the same intensities as the damage in the underlying SiO_2/Si substrate. Therefore the details of the damage process under UV and visible irradiation may be slightly different and influenced by the presence of substrate.

In order to check the possibility of chemical difference between the samples, XPS measurements were carried out. Due to the large beam size of the used XPS apparatus only untreated graphene areas could be characterized by this method. XPS scans of the C 1s core level peak are depicted in Fig. 2. It was possible to deconvolute the spectra into four Gaussian components. The strongest peak centered at 284.8 eV corresponds to C 1s in sp^2 configuration (i.e. graphene). The remaining peaks at 285.6, 286.4 and 288.5 eV belong most probably to C–OH, C–O and C=O bonds [14]. Differences in the oxidation level are relatively small (some interplay between the amount of single and double C–O bonds). It appears that the peak corresponding to C–OH is almost completely missing

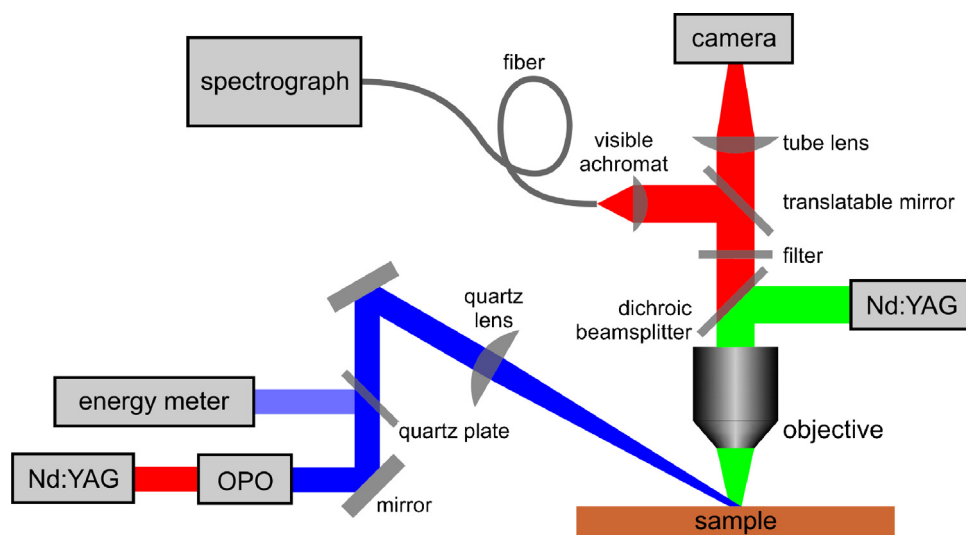


Fig. 1. Experimental setup used for irradiation of graphene and for fluorescence microspectroscopic measurements. Additional optics inserted for wide-field excitation is omitted for clarity.

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