Wave-vector direction-sensitive photocurrent in laser-induced graphene

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Abstract. Porous graphene film structures were formed in the process of line-by-line scanning by a focused laser beam of \(cw\) \(CO_2\) laser on polyimide film. It was shown that at a power density of 8 W/cm\(^2\) and a scanning speed range of 200-260 mm/s, porous graphene is formed on the surface of a 120-\(\mu\)m-thick polyimide film. The results of the investigation of the longitudinal photocurrent generation in LIG film are presented. Photocurrent excitation was carried out by nanosecond laser pulses at wavelength range of 266-1064 nm. It was found that the photocurrent depends on the direction of the wave-vector of the incident radiation according to the odd law characteristic of the photon drag effect (PDE). It is also shown that the presented method of the LIG film formation leads to anisotropy of its photovoltaic properties.

1. Introduction

Recently, it was shown that it is possible to produce porous graphene (3D graphene), called laser-induced graphene (LIG), using decomposition of a polymer film by pulsed irradiation by \(CO_2\) laser [1–4]. This method of graphene production does not require costly equipment in contrast to CVD method [5] and can be carried out in air under normal conditions. Usually, such a LIG is formed in the process of line-by-line scanning by the focused laser beam on an automated stage, allowing one to draw different figures with high resolution limited to the focused beam diameter. LIG has various perspective applications [2,6,7] (microsupercapacitors, various sensors, electrocatalysts, and microfluidic systems). Meanwhile, graphene as well as nanographite (carbon nanowall) films are shown to be attractive for optoelectronic applications [8–14]. In the studies [15,16] polarization- and wave-vector direction-sensitive longitudinal and transverse photocurrents due to photon drag effect (PDE) [17,18] and surface photogalvanic effect (SPGE) [19,20] were observed in the carbon nanowall films in a broad spectral range.

Here we present results of investigations of longitudinal photocurrent generation in LIG, obtained on the surface of polyimide (PI) film using focused \(cw\) \(CO_2\) laser beam. We have shown that nanosecond longitudinal photocurrent is observed in the synthesized films, dependent on the direction of the wave-vector of the exciting radiation at the wavelengths of the first (1064 nm), second (532 nm), third (354.7 nm) and fourth (266 nm) harmonics of the nanosecond YAG:Nd\(^{3+}\) - laser. We have also shown that the amplitude and duration of the longitudinal photocurrent pulses vastly depend on the azimuthal orientation of the synthesized film relative to the plane of incidence of the exciting radiation on the film.
2. Experimental

2.1. The LIG film production

We have studied LIG films on PI substrate, which were prepared using cw CO\textsubscript{2} laser at a wavelength of 10.6 μm. The LIG was formed during scanning by a focused laser beam. The focal length of the focusing lens was 51 mm. The scanning electron microscopy image of the film is shown in figure 1a. One can see characteristic LIG “strokes” along the direction of laser scanning. To accurately measure the power density of laser radiation at which LIG formation occurs, the radius $r$ of the focused laser beam was determined using the so-called “knife” method or the “sharp edge” method \cite{21}. In this method the power of laser radiation passing by a screen made in the form of a sharp knife or blade, depending on its coordinate when moving along, for example, the $x$-axis lying in the focal plane of the lens (see figure 1b, inset) was measured.

\begin{equation}
 f(s) = \frac{1}{1 + \exp(a_1 s + a_2 s^3)},
\end{equation}

where

\begin{equation}
 s = \frac{\sqrt{2}(x - x_0)}{r},
\end{equation}

and $a_1$, $a_2$ are constants with values $-1.597106847$, $-7.0924013 \times 10^{-3}$, respectively. It should be noted that at $x = x_0$ the edge of the knife or blade is on the axis of the laser beam. Figure 1b shows the power of CO\textsubscript{2} laser radiation depending on the $x$ coordinate, and this experimental dependence is well described by function (1) at $r = 95$ μm. Thus, the diameter of the focused laser beam at the studied film was 190 μm.

Knowing the diameter of the laser beam of a CO\textsubscript{2} laser, we determine that the power density at which the formation of LIG occurs is 8 W/cm\textsuperscript{2} at a scanning speed range of 200-260 mm/s. The resulting films had a size of 5×20 mm\textsuperscript{2} and a thickness of about 60 μm. The results of Raman...
spectroscopy and scanning electron microscopy showed that the film consists of graphene layers and has a porous petaline structure, with pores being up to several micrometers in size, and the thickness of the petals about 100 nm [22].

2.2. Photocurrent excitation
Figure 2a shows the schematic diagram of line-by-line LIG films formation using CO2 laser, both along the long and short sides, to study the generation of photocurrent, which will be called x-stroke film and y-stroke film respectively. Both of them were provided with two parallel electrodes (A and B) attached along the short sides of the film and oriented with the long side perpendicular to the plane of incidence \( \sigma \) (see figure 2b). The sheet resistance of the film was 24 \( \Omega/\square \). The experiments were carried out with a single-mode YAG:Nd\(^{3+}\) - laser with passive Q-switching [23] at wavelengths \( \lambda = 1064, 532, 354.7, \) and 266 nm with pulse durations \( \tau_{in} \) of 19.5, 13.2, 13.5, and 9.4 ns (FWHM), respectively. Excitation laser pulse durations \( \tau_{in} \) were measured using a SIR-5 high-speed photodetector (ThorLabs) and a Tektronix TDS7704B digital oscilloscope with a 7 GHz bandwidth. The films were placed on a special goniometric device, which was capable of performing smooth changes of the angle of light incidence \( \alpha \) on the film. The energies of nanosecond laser pulses \( E_{in} \) incident on the films under study were measured using the ES111 pyroelectric energy meter via the PM100USB interface (ThorLabs). In the experiments the extreme values of voltage pulses \( U_x \), as well as their duration \( \tau \) (FWHM), arising between the measuring electrodes A and B, pressed to the film surface (see Figure 2b) using a four-channel digital oscilloscope (Tektronix TDS7704B) were measured. The longitudinal photocurrent \( i_x \) (hereinafter, the photocurrent) flowing in the direction parallel to the plane of incidence \( \sigma \) was determined by the formula \( i_x = U_x/r \), where \( r \) is the input impedance of the oscilloscope.

![Figure 2](image)

Figure 2. (a) The schematic diagram of LIG “strokes” formation: at the top - the “strokes” are formed perpendicular to the electrodes (x-stroke), at the bottom - in parallel (y-stroke); (b) experimental setup for studying the generation of photocurrent in LIG films when they are irradiated with nanosecond laser pulses; (c) the shapes of the pulses of the photocurrent obtained on LIG films, the "strokes" of which are applied: above - perpendicular to the electrodes, below - parallel to the electrodes.

3. Experimental results and discussion
The experiments showed that in the synthesized film structures with an oblique incidence of nanosecond laser pulses, photocurrent pulses are generated that depend on the angle of incidence. In x-
stroke films, photocurrent pulses of nanosecond duration appear (see figure 2c, top inset), depending on the angle of incidence according to an odd function. The photocurrent pulses obtained in y-stroke films are more complex. They, in essence, are the sum of two pulses, significantly differing in duration (see figure 2c, bottom inset). A second pulse with a duration of more than 1 μs is superimposed on the first leading short pulse of nanosecond duration. These pulses are rather distinguishable since the amplitude of the nanosecond leading pulse depends on the angle of incidence. The amplitude and time shape of the microsecond pulse, i.e. the second component of the photocurrent pulse arising in the y-stroke film is practically independent of the angle of incidence \( \alpha \) and the polarization of the laser radiation. At the same pulse energy of the exciting laser, the amplitude of the nanosecond pulse that appears in the x-stroke film is about 1.5 times higher than the amplitude of the nanosecond lead pulse that appears in the y-stroke film. Thus, from the point of view of creating high-speed photodetectors, the most interesting is the study of x-stroke films, in which the generation of unipolar nanosecond pulses takes place. Therefore, x-stroke films, i.e. films that were synthesized by scanning a CO\(_2\) laser along the long side of the film (see figure 2a) and in which the photocurrent was measured in accordance with the schematic diagram in figure 2b, were used in further experiments.

Figure 3 shows the shapes of the incident laser pulses and the pulses of the photocurrent measured in x-stroke films at different wavelengths. The photocurrent pulses duration in the LIG film are listed in table 1. One can see from figure 3 and table 1 that at all wavelengths, the duration of the photocurrent pulses exceeds the duration of the pulses of the exciting radiation. Moreover, as can be seen from figure 3, the rise and fall times of the photocurrent pulses also exceed the corresponding pulse times of the exciting laser. Note that the extension of the temporal parameters of photocurrent pulses can be significantly affected by the capacitive load arising in the volume of the film between graphene petalines.

![Figure 3](image)

**Figure 3.** Temporal shapes of incident laser pulses and pulses of the photocurrent generated in x-stroke LIG films under excitation by radiation at wavelengths of (a) 1064, (b) 532, (c) 355 and (d) 266 nm.

**Table 1.** Photocurrent pulses duration in x-stroke LIG film at different excitation wavelengths.

| Excitation wavelength | 266 nm (ns) | 355 nm (ns) | 532 nm (ns) | 1064 nm (ns) |
|------------------------|-------------|-------------|-------------|--------------|
| Excitation pulse duration \( \tau_{\text{in}} \) | 9.4         | 13.5        | 13.2        | 19.5         |
| Photocurrent pulse duration \( \tau \) | 14.5        | 20.5        | 24.7        | 34.5         |
Figure 4a shows that the $i_x$ photocurrent linearly depends on the pulsed power of the $P_{in}$ laser at all studied wavelengths, where $P_{in} = E_{in} / \tau_{in}$ at an angle of incidence of $45^\circ$. This allows us to use the conversion factor $\eta$ of the laser power into the photocurrent, determined by the formula $\eta = i_x / P_{in}$. Figure 4b shows the dependence of $\eta$ on the angle of incidence $\alpha$ at wavelengths of 266, 355, 532, and 1064 nm. It can be seen from it that there is no photocurrent during the normal incidence of radiation on the film, and when the sign of the angle of incidence is changed, the direction of the photocurrent changes. The obtained arrays of experimental data are well approximated by the dependence $\eta = \eta_0 \sin^2 \alpha$, where $\eta_0$ is the value of the coefficient $\eta$ at an angle of incidence of $45^\circ$, which is characteristic of the generation of the photocurrent arising due to PDE in two-dimensional structures (see, for example, [24]). Typically, the PDE photocurrent occurs simultaneously with the photocurrent due to the surface photovoltaic effect (SPGE) [25]. Our additional studies showed that the angular dependences $\eta(\alpha)$ obtained at a specific wavelength are independent of polarization. This indicates the absence of a longitudinal SPGE photocurrent, which disappears at $s$-polarization [15,20], in the synthesized film structures.

For wavelengths of 1064, 532, 355, and 266 nm, the $\eta_0$ value is 3.20, 3.35, 3.40, and 3.50 mA/MW, respectively, and it can be seen that the conversion coefficient increases with decreasing wavelength. This agrees with the data for CVD nanographite films on silicon substrates [15,26].

4. Conclusions

Thus, we showed that line-by-line scanning $cw$ CO$_2$ laser beam with a diameter of 190 $\mu$m and a power density of 8 W/cm$^2$ can be used to obtain a porous graphene film on the surface of a polyimide film. Photocurrent pulse generation is observed in the synthesized rectangular 5x20 mm$^2$ films irradiated by nanosecond laser pulses at a wavelength range of 266 - 1064 nm. The amplitude-time characteristic of the generated photocurrent pulses substantially depends on the azimuthal orientation of the synthesized films relative to the plane of incidence. When measuring the photocurrent along the plane of incidence perpendicular to the scanning direction of the CO$_2$ laser beam, the generation of a pulse of complex shape consisting of two pulses of nanosecond and microsecond duration is observed. Moreover, the amplitude of the nanosecond pulse is an odd function of the angle of incidence, and the microsecond pulse duration does not depend on the angle of incidence. The photocurrent pulse, measured along the plane of incidence, coinciding with the scanning direction of the CO$_2$ laser beam, has a nanosecond duration and its amplitude is an odd function of the angle of incidence characteristic.
of PDE. The obtained results show the possibility of using LIG films for the development and creation of orientation sensitive high-speed photodetectors operating in a wide spectral range.

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