

Modification of a graphene–copper substrate in vacuum by femtosecond laser radiation

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Abstract. The effect of intense femtosecond laser radiation on single-layer graphene fixed on a copper fine-meshed grid is studied using a compact femtosecond electron diffractometer. A modification of the graphene–copper substrate is found. The composition of the resulting compounds is analysed. It is shown that the main new products are copper oxides. The prospects of using such a substrate in the method of ultrafast electron diffraction and microscopy are analysed.

Keywords: femtosecond laser radiation, electron diffraction, graphene.

1. Introduction

As is well known, graphene is a two-dimensional layer of carbon atoms and has a number of interesting properties that allow us to consider it as a promising material for various fields of science and technology, including, for example, an alternative to traditional semiconductor electronics – nanoplasmonics, photonics, etc. As a hyperfine substrate, graphene is widely used in the rapidly developing field of research – ultrafast electron microscopy (UEM) [1]. This is primarily due to its unique properties: high mechanical strength, high electrical conductivity, high thermal conductivity, high radiation damage threshold, and good crystallographic ordering. The latter may also prove to be very valuable in obtaining an electron diffractogram from samples under investigation, not distorted by the presence of a two-dimensional substrate made of a very light chemical element. Recall that UEM is based on a combination of an electron microscope and femtosecond lasers to obtain a high spatial-temporal resolution in studying laser-induced processes in matter [2, 3].

With the UEM method development, studies on the effect of high-power femtosecond laser pulses directly on a substrate containing graphene are of particular interest. This is stipulated by the fact that reliable recording of laser-induced

processes in matter (for example, ultrafast phase transformations in a semiconductor) by means of UEM requires sufficiently large energy densities of exciting laser pulses on the order of several mJ cm^{-2} and higher (1 mJ cm^{-2} approximately corresponds to 1 eV \AA^{-2}). Subsequent measurements of the kinetics of processes induced by high-power femtosecond laser pulses are conducted by accumulating a signal at a position-sensitive detector at different delays (after finding the zero point $t = 0$) between the exciting laser pulses and probe electron pulses [4–6]. In this connection, it is necessary to investigate the effect of prolonged intense femtosecond laser radiation on a graphene–copper substrate with attendant recording of an electron diffraction pattern at various time moments. It is also important to analyse the substances obtained as a result of photochemical reactions induced by femtosecond laser radiation.

2. Experiment

The present work was performed on our newly developed femtosecond electron diffractometer utilising an ultrashort electron beam and a highly sensitive scheme intended for its recording (the device is described in detail in [5]). This instrument allowed a thin solid sample irradiated with a femtosecond laser to be probed by photoelectron bunches. Pumping was performed by a Ti:sapphire laser having a wavelength of 800 nm, a laser pulse duration of $\tau \approx 50 \text{ fs}$ and a pulse repetition rate of $f = 1 \text{ kHz}$. To probe the irradiated sample, we used a photoelectron bunch formed by irradiation of a semi-transparent photocathode (thin Ag film) using the third radiation harmonic of the same Ti:sapphire laser. The kinetic energy of photoelectrons was 20 keV, and the photoelectron bunch diameter in the sample region constituted $\sim 0.1 \text{ mm}$. The electron bunch energy was determined by the potential applied to the pulling electrode within the accelerating gap. The electrons were focused by a permanent magnet based lens. A pulsed electron bunch was recorded by a position-sensitive detector consisting of a pair of microchannel plates and a phosphor screen. The signal from the phosphor was recorded by a CCD camera and fed to the computer. The pressure in the vacuum chamber was $\sim 3 \times 10^{-8} \text{ mm Hg}$. The sample–detector distance was about 200 mm.

As a sample we used a single-layered graphene fixed on a copper fine-meshed grid with a cell size of $\sim 6.5 \mu\text{m}$ (TED PELLA, Inc. [7]). In the experiment, the sample was irradiated for $\sim 3 \text{ h}$ by radiation at the fundamental frequency of the Ti:sapphire laser. The laser beam was incident onto the target at an angle of 45° ; the laser radiation intensity I_{las} was $\sim 3 \times 10^{10} \text{ W cm}^{-2}$.

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Received 25 October 2017; revision received 15 December 2017
Kvantovaya Elektronika 48 (2) 145–148 (2018)
Translated by M.A. Monastyrsky

3. Results and their analysis

Prior to irradiation of the sample by high-power femtosecond laser pulses, the electron diffraction pattern from graphene on a copper substrate contained characteristic reflections corresponding to electron bunch diffraction on a carbon sheet (Fig. 1a). However, we noticed that the observed diffraction pattern changed significantly in the course of long-term irradiation (3 to 4 hours). First, an approximately twofold decrease in the brightness of reflections from graphene was recorded. Secondly, additional diffraction rings were observed (Figs 1b and 1c). A decrease in the brightness of reflections from graphene is caused, in our opinion, by breaking of carbon bonds in the process of prolonged sample irradiation by high-power laser pulses and, in principle, does not contradict the results of work [8] in which the radiation stability of graphene in strong laser fields was analysed in detail. It was demonstrated in this work that the characteristic time of graphene structure stability to the action of high-power femtosecond laser radiation decreased proportionally to I_{las}^{-2} , and at $I_{\text{las}} \approx 10^{10} \text{ W cm}^{-2}$ (Ti:sapphire laser, $\tau \approx 50 \text{ fs}$, $f = 1 \text{ kHz}$) constituted 30–40 h. Accordingly, the sample must withstand several hours of continuous operation with the laser radiation intensity threefold increased, which agrees with our measurements. After three to four hours of the experiment, it was possible to reliably record the electron bunch diffraction on graphene. Further irradiation of the test sample for six to eight hours led to the fact that the corresponding reflections became unobservable.

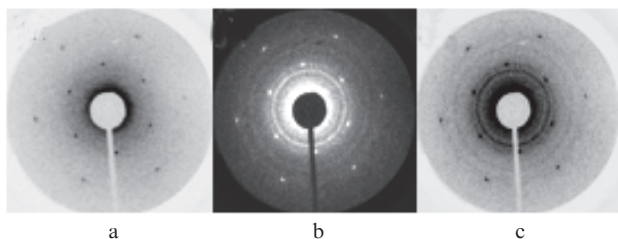


Figure 1. Electron diffraction pattern of single-layer graphene on a copper substrate: before irradiation with high-power laser pulses [(a) negative] and after irradiation [(b) positive and (c) negative]. Negative images are given for better perception of the electron diffraction pattern. The inner circle of the reflections in panel (a) corresponds to the (10) planes, the outer circle – to the (11) planes.

The experimental data obtained (Fig. 1) (in particular, the appearance of diffraction rings) imply that new chemical compounds formed as a result of photochemical reactions induced by high-power femtosecond laser radiation appeared on the sample surface in question. Carbides and oxides of copper can be considered as possible candidates; in this case, the carbon source could be graphene, while the residual oxygen could be present on the substrate in the adsorbed state.

To clarify this question, the obtained electron diffraction patterns were analysed. The positions of reflections and also the dimensions of diffraction rings on the detector screen depend on the basic parameters of the experimental setup (de Broglie wavelength equal to 0.086 \AA for electrons with an energy of 20 keV, and the distance between the sample and screen). To refine these characteristics, the electron diffractometer was calibrated according to the positions of the dif-

fraction maxima for graphene (Fig. 1), since its structure and interatomic distances are well known. As a result, the instrument's parameters were chosen so that the positions of reflections corresponded to the interatomic distance in graphene $r(\text{C} - \text{C}) = 1.42 \text{ \AA}$. In this case, the brightest series of reflections for the (01) planes corresponds to the scattering parameter $s = 2.95 \text{ \AA}^{-1}$, while for the (11) planes $s = 5.11 \text{ \AA}^{-1}$. These reflections are clearly visible in Fig. 1. The next series for the (02) planes corresponds to $s = 5.90 \text{ \AA}^{-1}$ and is located at the detection region edge, whose radius in the same units is approximately 7 \AA^{-1} . After specifying the electron diffractometer parameters, let us pass to the analysis of the diffraction pattern corresponding to the chemical compound formed.

Within the framework of the analysis, we calculated electron diffraction patterns of polycrystals of copper and its oxides, the structure of which is well known. (Note that we do not have data on the structure of copper carbides.) The calculations were conducted in two ways. The first method assumes the formation of a crystalline cluster of several thousand atoms and electron diffraction pattern calculation according to known electron diffraction techniques. In this case, the electron diffraction pattern appears as a set of peaks with widths determined by the cluster size. The second method relies on the calculation of the positions of reflections for different crystal orientations with subsequent averaging over all possible orientations, which corresponds to the limiting case of large crystallites.

As is known from the literature [9–12], copper forms a cubic face-centred lattice with a cube side of $3.58\text{--}3.62 \text{ \AA}$ (the scatter of values can be related to the difference in temperatures at which experiments were performed). In the unit cell of Cu, there are four atoms with crystallographic coordinates $(0, 0, 0)$, $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$ and $(0, 1/2, 1/2)$.

The copper oxide crystal Cu_2O (I) also has a cubic structure with a cell size of $4.25\text{--}4.27 \text{ \AA}$. In the unit cell, two oxygen atoms with crystallographic coordinates $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$ and four copper atoms with coordinates $(1/4, 1/4, 1/4)$, $(1/4, 3/4, 3/4)$, $(3/4, 1/4, 3/4)$ and $(3/4, 3/4, 1/4)$ are present.

Of all the substances under consideration, copper oxide CuO (II) has the most complicated crystal structure. It belongs to a monoclinic crystal system with cell parameters $a = 4.684 \text{ \AA}$, $b = 3.423 \text{ \AA}$, $c = 5.129 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 99.54^\circ$, $\gamma = 90^\circ$ [12]. In the unit cell there are four copper atoms with crystallographic coordinates $(1/4, 1/4, 0)$, $(3/4, 1/4, 1/2)$, $(3/4, 3/4, 0)$, $(1/4, 3/4, 1/4)$ and four oxygen atoms with coordinates $(0, 1/2 - u, 1/4)$, $(0, 1/2 + u, 3/4)$, $(1/2, 1 - u, 1/4)$, $(1/2, u, 3/4)$, where the experimentally determined value of u is 0.083. The comparison of the calculation results with the corresponding experimental data is shown in Fig. 2.

Note that the experimental cross section does not pass through graphene reflections (Fig. 1). Calculations of the electron diffraction patterns from polycrystals were performed with clusters of the following characteristic sizes: 5.4 nm (Cu), 6.4 nm (Cu_2O) and 6.0 nm (CuO). The size of clusters for calculating the diffraction curves from copper and its oxides was chosen from the requirement that the peak widths obtained, which depend on the cluster size, would approximately correspond to 0.1 \AA^{-1} , as on a real electron diffraction pattern. Note that the size around 5 nm is quite typical for polycrystals.

Because of the complexity of the crystal structure, in this case there are a large number of closely spaced rings which are not always resolvable in experimental conditions. Table 1 lists

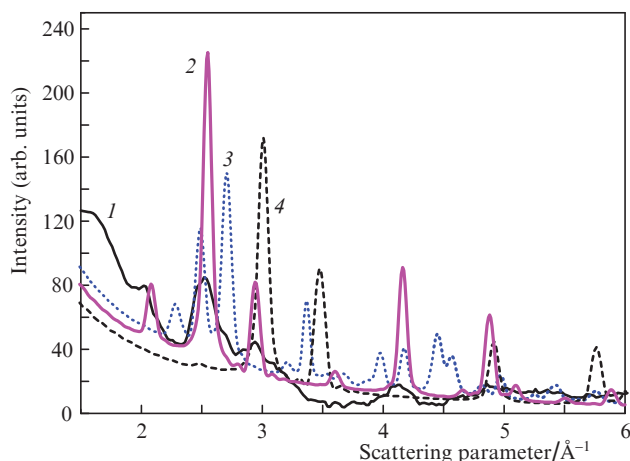


Figure 2. Radial intensity profiles for cross sections of electron diffraction patterns obtained in the experiment (1), and the calculated values of (2) Cu_2O , (3) CuO and (4) Cu .

the radii of the main diffraction rings, both experimentally recorded and calculated for copper and its oxides.

Analysis of the diffractometry data (Fig. 2, Table 1) allows a conclusion that all the diffraction rings that result from the sample irradiation by high-power femtosecond laser pulses can be explained by the appearance of copper oxides. According to the diffractometry data, the main contribution is made by Cu_2O . The contribution of bivalent cuprous oxide CuO , according to these data, turned out less. Thus, in case of prolonged irradiation of the sample, a decrease in brightness of graphene reflections was accompanied by the appearance of diffraction rings corresponding to copper oxides.

Table 1. Experimentally obtained and calculated radii of diffraction rings.

Experiment	Radii of diffraction rings/ \AA^{-1}		
	Calculation		
	Cu	Cu_2O	CuO
2.05		2.0898	2.2849
2.55		2.5595	2.4845 2.4907 2.7063 2.7206
2.95	3.0105	2.9554	3.3666
	3.4762		3.9768
4.1–4.2		4.1796	4.1748 4.4332 4.4595
4.6			4.5596 4.5697
4.9	4.9161	4.9010	4.9690 4.9814
			5.4126 5.4367
	5.7646		5.7589

4. Conclusions

We have investigated the impact of intense femtosecond laser radiation ($\lambda = 800 \text{ nm}$, $I_{\text{las}} \approx 3 \times 10^{10} \text{ W cm}^{-2}$) on a commercially available graphene–copper substrate under vacuum conditions ($\sim 3 \times 10^{-8} \text{ mm Hg}$). To diagnose the sample, the electron diffraction method was used, which made it possible to perform real-time measurements. It turned out that, as a result of prolonged irradiation of the sample with high-power laser pulses, the observed electron diffraction pattern experienced qualitative changes. As our analysis showed, this effect was stipulated by the formation of copper oxides and the reduction of the signal from graphene. A drop in brightness of reflections from graphene itself can be attributed to the breaking of carbon bonds and concomitant formation of nanocrystallites, which does not contradict paper [8]. To increase the duration of experiments and reduce the effect of copper oxide, it is advisable to perform measurements after preliminary annealing of the sample under conditions of ultrahigh vacuum.

A practically significant result of the work is the disclosure of possibilities and analysis of limitations in employment of a graphene sheet in the methods of ultrafast electron diffraction and microscopy in studying solid samples. Such a hyperfine substrate, being transparent for electrons with a kinetic energy of several tens of keV, can be used in a desktop device for observation of time-resolved electron diffraction. (For comparison, it is very problematic to form a metal film with a thickness of less than 10 nm, which does not have a fractal structure.)

A graphene sheet is a convenient platform for combining optical and electron pulses in space and time: an indicator of this can be the response associated with the Debye–Waller effect (the growth of the mean square stochastic displacement of atoms after pulsed laser excitation of the sample), with an accompanying sharp decrease in the diffraction signal. This will solve the problem of determining the initial time moment ($t = 0$) in the methods of ultrafast diffraction and microscopy [2, 3], which cannot be done, for example, using a standard streak camera.

As shown in the present study, experiments with a graphene sample irradiated in vacuum with high-power laser pulses (an energy density of several mJ cm^{-2} and a repetition rate of 1 kHz) are limited to several operation hours, after which the pattern of electron diffraction from the substrate becomes significantly more complicated.

With the number of 10^3 electrons in one probe pulse, the time resolution of our desktop electron diffractometer is $\sim 400 \text{ fs}$ [5], and a step of 100 fs in the study of laser-induced dynamics is completely justified. At a pulse repetition rate of 1 kHz, 10^6 electrons will be incident onto the detector per second, which is sufficient for reliable registration of one electron diffraction frame [3]. This means that in the course of a few hours it is possible to observe the dynamics of laser-stimulated processes in the sample under study with a high degree of detail over a wide time range (from hundreds of femtoseconds to hundreds of picoseconds).

Acknowledgements. The work was supported by the Ministry of Education and Science of the Russian Federation (Project No. RFMEFI61316X0054).

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