Polarization-sensitive terahertz spectroscopy of graphene nanostructures

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Abstract. Efficient devices for control temporal and spatial properties of electromagnetic waves are essential for the development of terahertz (THz) technologies. But despite the great progress achieved in a study of graphene, the influence of the number of graphene layers on its optical and electrical properties in the THz frequency range has not yet been sufficiently studied. In this work, we experimentally studied optical and electrical properties of multilayer graphene (MLG) thin films in the frequency range 0.2–0.8 THz (corresponding to a wavelength range ∼1.5–0.37 mm), at a controlled room temperature of 291 K, and a relative humidity of 40 %.

Using our custom-made THz time-domain spectroscopic polarimetry system, we obtained spectra of the complex relative permittivity and the electrical conductance of the chemical vapor deposition graphene with ∼14, ∼40, and ∼76 layers of graphene on borosilicate glass substrates. It is shown that the conductance increases nonlinearly with an increase in the graphene layer number and reaches, for ∼76 layers, 0.06 S for the real, and 0.03 S for the imaginary part, respectively. Our results show that by using MLG it is possible to create tunable devices that can be used in the advanced areas of THz photonics.

Keywords: graphene, multilayer thin films, chemical vapor deposition, raman spectroscopy, terahertz time-domain spectroscopy, permittivity, electrical conductivity, polarization of light.

1. Introduction
In recent years, there has been a real breakthrough in the study of all possible carbon allotropes—fullerenes, carbon nanotubes, graphene and their heterostructures [1,2]. The latest nanotechnology allows us to engineer materials at the atomic level and create dynamically-controlled nanostructures for their real integration into all areas of our life, from genome editing to hyper-speed wireless Internet networks. And therefore, advanced fundamental and applied science is less and less within the rigid boundaries of the classical fields, and more and more becomes truly interdisciplinary [3].

One of these topical complex areas is the terahertz (THz) photonics of low-dimensional nanostructures. In connection with the development of sources and receivers of THz radiation, it became possible to develop compact systems for data transmission for the next generation of communication networks. But the problem of efficient manipulation of the temporal and spatial parameters of electromagnetic (EM) waves in the THz range in open space remains unresolved.
A promising method for solving this problem is the use of graphene, a material with proven unique optical and electronic properties, as an active medium for THz wave control devices [4,5]. But despite the great progress achieved in the theoretical and experimental study of graphene-based nanostructures, the question of the influence of the graphene layer number on its fundamental properties has not yet been resolved, and there are still many dark spots in this scientific field.

The aim of our work was to experimentally study a room-temperature layer-number effect of multilayer graphene (MLG)-on-glass structures on its electrical conductance via polarization-resolved THz time-domain spectroscopy.

In this work, we experimentally studied optical and electrical properties of MLG thin films in the frequency range 0.2–0.8 THz (corresponding to a wavelength range ∼1.5–0.37 mm), at a controlled room temperature of 291 K, and a relative humidity of 40%. We found that the conductance of the MLG increases nonlinearly with an increase in the graphene layer number and reaches, for ∼76 layers, 0.06 S for the real, and 0.03 S for the imaginary part, respectively. Our results show that by using MLG it is possible to create tunable devices that can be used in the advanced areas of THz photonics.

2. Materials and methods

2.1. Sample preparation
For our study, we selected three samples of MLG thin films with different number of graphene layers. Our graphene thin films were synthesized by the modified chemical vapor deposition (CVD) method [6] on the nickel foil. The samples were synthesized in a specially designed home-made system [7] that allows continuous monitoring of each synthesis parameter, including temperature and pressure. Such control makes it possible to obtain graphene samples with a high repeatability and a certain predetermined number of layers. Then the films were transferred onto the commercially available borosilicate cover glass substrates [8] with a thickness of ∼150 µm.

2.2. Raman spectroscopy
To study the structural properties and qualitative composition of graphene films, we performed the Raman spectroscopy [9]. Experimental data were obtained using a standard commercially available confocal Raman microscope ‘inVia™’ (Renishaw, UK) using an excitation wavelength of 488 nm [10] in the backscattering geometry. The spectra were recorded at a room temperature, in the range from ∼103 cm⁻¹ to ∼3503 cm⁻¹, with a step of ∼2 cm⁻¹.

2.3. Polarization-resolved transmission terahertz spectroscopy
To study the optical and electrical properties of graphene thin films in the THz range, we used an upgraded spectroscopy system [11,12]. This system is based on the THz radiation generation using a InAs crystal in a static magnetic field [13], and the detection using a CdTe crystal with the electro-optic sampling. Using a system of high-precision passive THz polarizers, we have added the ability to perform polarimetric measurements [14–16]. The spectra were recorded at a room temperature, a relative humidity of 40%, in the range from 0.2 THz to 0.8 THz, with a step of ∼0.03 ps.

3. Results and Discussion

3.1. Structural properties
Raman spectroscopy results are shown in Figure 1 (a). The obtained results of the Raman spectroscopy clearly show that with an increase in the number of graphene layers, an enhancement of the G-peak at ∼1580 cm⁻¹, and a suppression of the 2D-peak at ∼2710 cm⁻¹ occurs, which indicates a transformation from two-dimensional carbon-based nanostructures to quasi-bulk graphite-like ones. The absence of a strong D-peak at ∼1360 cm⁻¹ in the spectrum indicates a high structural integrity of graphene films, despite the relatively large number of layers.
Figure 1. (a) Raman spectra of the MLG thin films; (b) scheme of the THz-TDSP setup (ADC—analog-to-digital converter; BP—balanced photodetector; DAC—digital-to-analog converter; GTP—Glan–Taylor prism; HW—half-wave plate; IF—poly(tetrafluoroethylene) \((C_2F_4)n\) infrared cut-off filter; L1, L2—lenses; LD—laser diode driver; LIA—lock-in amplifier; LR—femtosecond Yb:KYW 1040 nm laser; OC—optical chopper; OCC—optical chopper controller; ODL—optical delay line; P1, P3—static polarizers; P2—rotatable polarizer; PC—personal computer; PS—balanced detector power supply; QW—quarter-wave plate; TD—THz radiation detector based on the CdTe crystal; TS—THz radiation source based on the InAs crystal; WP—Wollaston prism); typical temporal waveforms of the THz signals at P2 polarizer rotation angle of (c) 0°, and (d) 45°; the real part of the electrical conductance of the MLG thin films at P2 polarizer rotation angle of (e) 0°, and (f) 45°; and the imaginary part of the electrical conductance of the MLG thin films at P2 polarizer rotation angle of (g) 0°, and (h) 45°.
3.2. Terahertz properties
Terahertz spectroscopy results are shown in Figure 1 (c)–(h). For the analysis of the obtained waveforms of the THz waves transmitted through the samples we used a basic Tinkham thin-film calculations [17] and a modernized data processing techniques [18]. The use of THz polarizers (see Figure 1 (b)) with a higher extinction ratio relative to our previous work described in Ref. [19] made it possible to abandon strong signal noise reduction and, thus, to obtain more accurate results. We managed to obtain the electrical and optical properties, including the complex electrical conductance of the MLG thin films [20], based on THz polarimetric measurements. The results show that the conductance of the MLG films increases nonlinearly with an increase in the graphene layer number and reaches, for ~76 layers, 0.06 S for the real, and 0.03 S for the imaginary part, respectively. And the use of calculations at two angles of the P2 polarizer rotation makes it possible to determine the difference of these changes.

4. Conclusions
In this work, we experimentally studied optical and electrical properties of MLG thin films in the frequency range 0.2–0.8 THz (corresponding to a wavelength range ~1.5–0.37 mm), at a controlled room temperature of 291 K, and a relative humidity of 40 %. Using our custom-made THz-TDSP system, we obtained spectra of the complex relative permittivity and the electrical conductance of the CVD graphene with ~14, ~40, and ~76 layers of graphene on borosilicate glass substrates. Our results show that by using MLG it is possible to create tunable devices that can be used in the advanced areas of THz photonics.

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Author contributions
A. K.: Conceptualization (lead); Data curation (lead); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Methodology (lead); Project administration (lead); Validation (lead); Visualization (lead); Writing—original draft (lead); Writing—review and editing (lead). M. R.: Formal analysis (equal); Investigation (equal); Resources (lead). A. Z.: Formal analysis (equal); Investigation (equal). Software (lead). K. B.: Formal analysis (equal); Investigation (equal). D. Z.: Formal analysis (equal); Investigation (equal). E. O.: Supervision (lead).

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