The study of optical properties of graphene intercalated with ferric chloride for application in terahertz photonics

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Abstract. The investigation and development of new functional two-dimensional materials is one of the most important challenges for terahertz (THz) photonics and optoelectronics. These materials allow to dynamically manipulate the properties of the THz radiation. Graphene and graphene-based materials are the promising candidates for this task as they are efficient and fast-acting in the THz frequency range. In this work we have experimentally studied the properties of novel material based on few-layered graphene intercalated with ferric chloride (FeCl₃-FLG) in the THz frequency range. In particular, the influence of infrared optical pumping intensity (using 980 nm continuous-wave (CW) laser) on the spectral properties of FeCl₃-FLG was investigated. The experimental results have shown the efficiency of the suggested method of radiation characteristics control.

1. Introduction

Terahertz (THz) waves are defined as the electromagnetic radiation in the frequency from 0.1 to 10 THz. This spectral domain has low frequency crystalline lattice vibrations and other intermolecular vibrations in many chemical and biological materials, including explosives, drugs, and other biomolecules. Therefore this radiation has become very popular in the wireless communication [1-3] and biomedicine [4-6]. Since graphene invention, two-dimensional (2D) materials have attracted increasing interest in research community both from the point of view of fundamental physics studies, also from the point of view of application in the field of THz science and technology. The vast majority of the works are devoted to the first 2D material, graphene [7], because there are very few materials that can effectively interact with the THz radiation. However, graphene has some disadvantages, such as absence of a band gap and low efficiency of control by optical pumping. To overcome these disadvantages, other 2D graphene-based modifications were proposed in recent researches [8, 9]. In this work, we perform measurements of optical properties of FeCl₃-FLG using THz time-domain spectroscopy (THz-TDS) system under an external infrared (980 nm) continuous-wave excitation.

2. Sample preparation and the THz conductivity measurements

For the samples under investigation, the CVD (chemical vapor deposition) graphene grown on Ni substrate was used. Then, the Ni substrate underneath of few-layer graphene film was etched. After that, graphene film was transferred to the glass substrate. Graphene on the glass substrate was placed in the furnace tube with FeCl₃ powder and was intercalated at 300 °C. Basically, molecules of FeCl₃...
were inserted between atomic layers of graphene. Then, the intercalated graphene was transferred from the glass to PET and quartz substrates. The measurements of transmission spectra of FeCl$_3$-FLG on PET and quartz substrates for the different pumping intensities were performed using typical THz-TDS system. The scheme of this setup is shown in Fig. 1. The 980 nm CW laser was used as the infrared optical pumping source. To obtain complex sheet conductivity dispersion it is appropriate to use an effective medium model and a thin-film approximation [10]:

$$\frac{\hat{E}_{\text{sam}}(\omega)}{\hat{E}_{\text{sub}}(\omega)} = \frac{n + 1}{n + 1 + Z_0 \theta(\omega)},$$

where $\hat{E}_{\text{sam}}(\omega)$ and $\hat{E}_{\text{sub}}(\omega)$ are the complex amplitudes of the signals transmitted through the sample on a substrate (full structure) and bare substrate correspondingly, $n$ is substrate refractive index, $Z_0 = 377$ Ohm is the free space impedance. The measured waveforms for the graphene on PET and quartz substrates for the different optical pumping intensities are shown in Fig. 2 (there are also shown the waveforms for the corresponding bare substrates). The photos of the used samples are depicted in Fig. 3.

The complex conductivity dispersions were extracted from the experimental data using an Equation 1. The dependencies of the real and imaginary parts of the complex sheet conductivity of the samples on the infrared continuous-wave 980 nm pumping intensity are shown in Fig. 4 (PET substrate) and Fig. 5 (quartz substrate) for the different frequencies of the THz radiation.

![Figure 1](image-url)  
**Figure 1.** (a) Scheme of the experimental setup; (b) Sample optical pumping scheme (the parameters of the THz wave transmitting through the structure are controlled by optical pumping of the sample).
Figure 2. Measured THz waveforms of FeCl$_3$-FLG on PET (left graph) and quartz (right graph) substrates under infrared optical pumping of different intensities.

Figure 3. The samples of FeCl$_3$-FLG on PET (bottom – two left samples) and quartz (top – two left samples) substrates. The corresponding bare substrates are placed at right side.

Figure 4. The dependencies of the real (left graph) and imaginary (right graph) parts of complex sheet conductivity of FeCl$_3$-FLG on the infrared pumping intensity (three-point curves) for the different frequencies of the THz radiation (PET substrate).
Figure 5. The dependencies of the real (left graph) and imaginary (right graph) parts of complex sheet conductivity of FeCl$_3$-FLG on the infrared pumping intensity (three-point curves) for the different frequencies of the THz radiation (quartz substrate).

It can be clearly seen that conductivity behaviour of FeCl$_3$-FLG under optical pumping depends on the substrate type. The significant changes in real and imaginary parts of complex sheet conductivity are observed under infrared optical pumping. There is also a saturation of changes in complex conductivity under relatively low optical pumping. The tuning of the complex conductivity depends on the frequency of the THz radiation: the greatest changes are achieved at higher frequencies (0.8 THz, in case of this work).

For FeCl$_3$-FLG on PET substrate, the changes mostly in real part of sheet conductivity are observed. For the pumping intensities in range from 0 to 8.33 mW/mm$^2$, the change in real part of complex sheet conductivity is equal to 3.52 mS at 0.8 THz and 0.58 mS at 0.4 THz. There are also significant changes in imaginary part of complex conductivity, which are equal to 3.67 mS at 0.8 THz and 2.65 mS at 0.4 THz. It means that FeCl$_3$-FLG on PET substrate can be used for the efficient amplitude modulation of the THz radiation at frequencies around 0.8 THz, and phase modulation of the THz radiation at different frequencies in range 0.4-0.8 THz. The losses in this structure are low.

For FeCl$_3$-FLG on quartz substrate, the changes mostly in imaginary part of sheet conductivity are observed. For the pumping intensities in range from 0 to 8.33 mW/mm$^2$, the change in real part of complex sheet conductivity is equal to 1.55 mS at 0.4 THz and 0.85 mS at 0.8 THz. The losses in this structure are high, because the real part of complex sheet conductivity has a values of about 0.12-0.14 mS. There are significant changes in imaginary part of complex conductivity, which are equal to 5.76 mS at 0.4 THz and 11.52 mS at 0.8 THz. The FeCl$_3$-FLG on quartz substrate can be used for the efficient phase modulation of the THz radiation at different frequencies in range 0.4-0.8 THz.

The change of parameters of the structures at 1.67 mW/mm$^2$ pumping intensity is from 77% to 85% relative to the full change (at 8.33 mW/mm$^2$ pumping intensity).

These structures can be used in high-speed communication systems, spectroscopy, contactless diagnostics, visualization systems, and in medicine (including tomography of the surface layers of the body), as the active components that modulate the amplitude and phase of the THz radiation.

3. Conclusions
In summary, we have experimentally demonstrated the efficient optical properties tunability of FeCl$_3$-FLG on different substrates by relatively low-intensity infrared optical pumping. It was shown that tunability character depends on the substrate type. The FeCl$_3$-FLG on PET substrate can be used for...
the efficient amplitude modulation of the THz radiation at frequencies around 0.8 THz, and phase modulation of the THz radiation at different frequencies in range 0.4-0.8 THz. The FeCl₃-FLG on quartz substrate can be used for the more efficient phase modulation of the THz radiation at different frequencies in range 0.4-0.8 THz in comparison to the FeCl₃-FLG on PET substrate. The proposed material can be used in high-speed, efficient and tunable THz photonic and optoelectronic systems.

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