

Mid-IR reflectance spectrum of multilayer graphene: Influence of adsorbate at the graphene–substrate interface

V.D. Frolov, P.A. Pivovarov, V.G. Plotnichenko, V.I. Konov

Abstract. Water adsorbate at the interface between graphene and SiO₂/Si substrate is found to affect the reflectance spectra of (3–6)-layer graphene in the mid-IR range ($\lambda = 2\text{--}16\ \mu\text{m}$). The sample under study was previously kept in acetone vapour to remove water adsorbate from the graphene–substrate interface. The graphene reflectance in the range of 8–16 μm tends to decrease with recovery of water adsorbate layer at the graphene–substrate interface at room temperature and relative air humidity RH = 40%–60%. The observed effect is most likely caused by the blue shift of the absorption edge at interband transitions due to the change in the Fermi level position in the graphene valence band under the influence of the charge induced in graphene by the water adsorbate film.

Keywords: graphene, optical properties, IR spectroscopy, water adsorbate.

1. Introduction

The interaction of electromagnetic radiation with graphene structures in a wide wavelength range is surprisingly pronounced (see, for example, Refs [1, 2]). Indeed, the radiation absorption is rather strong ($\sim 2.3\%$) even in single-layer graphene, due to which graphene monolayers can be found by visualising surfaces in an optical microscope [3]. This property makes optical spectroscopy an efficient tool for probing the unique physical properties of graphene.

Two main channels of mid- and near-IR absorption in graphene can be distinguished. The studies in this field showed that interband transitions dominate in the optical absorption spectra of graphene at photon energies above $2E_F$ (E_F is the Fermi energy of graphene, counted from the top of the valence band) [4]. The interband transition probability does not change with an increase in the radiation frequency ω (photon energy E), and the optical response, being practically independent of frequency, is equal to some universal value, determined by fine-structure constant e^2/hc of the initial graphene

(see, e.g., [5]). At the same time, the transition probability at photon energies lower than $2E_F$ decreases. In practice, the absorption at energies below $\sim 0.5\ \text{eV}$ does not correspond to the universal value and changes from sample to sample. This behaviour is believed to be caused by electric charge variations in graphene layers [1].

As experiments showed, the optical response in graphene can be controlled by changing deliberately its charge state, for example, by applying a positive or negative voltage to an electrostatic gate [6, 7]. As a result, one can shift the Fermi level by several hundred meV, thus either inducing interband optical transitions or blocking them in view of the Pauli exclusion principle.

According to the dipole mechanism of the effect on graphene [8, 9], the polar molecules adsorbed on the graphene–substrate interface determine the graphene charge state. This refers to both inorganic adsorbates (for example, water and nitrogen dioxide) and organic ones (dichloromethane, ethanol, hexane, and toluene). This is the most likely reason for the spontaneous (uncontrolled) increase in the electric charge, which was observed many times in graphene layers deposited on a Si/SiO_x substrate [10, 11].

It was established that the adsorbate-induced changes in the charge state are accompanied by variations in the graphene work function (which looks quite obvious, because the latter is directly related to the Fermi level position E_F). A direct dependence of the graphene work function on the thickness of water adsorbate layer on the graphene–substrate interface was established in [12, 13]. Specifically, the work function was found to decrease with decreasing adsorbate thickness. This was confirmed by our measurements (using scanning probe microscopy methods) of the surface topology and energy characteristics of graphene when removing water adsorbate from the graphene–substrate interface by a series of low-intensity nanosecond laser pulses [14, 15]. The studies showed also that the adsorption of polar molecules of organic liquids (such as ethanol and acetone) by graphene samples leads to removal (replacement) of water adsorbate molecules on the graphene–substrate interface, thus reducing significantly (by up to 150 meV) the graphene work function with respect to its initial level [16–18]. It was also found that the graphene work function monotonically increases during subsequent sample exposure under normal conditions in air due to the recovery of water adsorbate layer on the graphene–substrate interface.

In addition to the charge mechanism, we should note another way in which adsorbate may affect graphene. As was mentioned in [19], the presence of water adsorbate on graphene surface may change the graphene band structure: ‘open’ the band gap (i.e., make it larger than the thermal potential) due to the induction of strong electrical field on the

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graphene–substrate interface. For example, water adsorption from atmosphere was found to increase the graphene band gap E_g up to ~ 0.2 eV [19].

In this paper, we report the results of studying the optical response of (3–6)-layer graphene on a SiO_2/Si substrate: the mid-IR reflectance spectra recorded under conditions of water adsorbate accumulation at the graphene–substrate interface. The experiments were carried out using the fact that, according to our experimental data, acetone as an adsorbate removes efficiently water adsorbate from the internal graphene–substrate interface [18].

2. Experimental

The experimental samples were polycrystalline graphene sheets, CVD grown on a copper foil and transferred to a SiO_2/Si substrate. The thickness of the SiO_2 film on silicon was ~ 300 nm. The experiments were performed with samples of (3–6)-layer graphene, selected with the aid of micro-Raman spectroscopy. Water adsorbate was removed by keeping graphene samples in acetone vapour for 30 days. After the exposure in acetone, water adsorbate layers were gradually recovered on the graphene–substrate interface from the air atmosphere under normal laboratory conditions at a relative humidity $\text{RH} = 40\%–60\%$ [18].

Spectral measurements were carried out in the range of $600–5000\text{ cm}^{-1}$ using a Bruker IFS-113v vacuum IR Fourier spectrometer equipped with a reflection microscope. During each measurement cycle the radiation from a source was focused on the same portion of graphene surface into a spot $400\text{ }\mu\text{m}$ in diameter. The measurements were carried out in several stages: immediately after the exposure in acetone vapour ($t = 0$), 5 or 65 min after the exposure, and a week after the exposure. The spectrometer resolution was $\sim 2\text{ cm}^{-1}$. The reflectance spectrum of a «pure» (i.e., without a graphene layer) SiO_2/Si substrate was used as a reference one. During each measurement the spectral response was fixed multiply (64 scans), accumulated, and then averaged. The spectral dependences were plotted based on averaged data.

The spectral data were normalised to the reflectance spectra of a silver film deposited on an epitaxial silicon wafer. This normalisation was performed immediately prior to or after each measurement stage in order to reduce the influence of the spectrometer sensitivity drift on the reflectance spectra. With allowance for the noise and drift of the beam incident on the sample analysed and the spectral sensitivity of the IR detector, the statistical error in measuring signals over the entire spectral range was $\sim 1\%$.

3. Results and discussion

Figure 1 shows the reflectance spectrum R_{gr} of graphene on a SiO_2/Si substrate, recorded immediately after the sample exposure in acetone vapour, and, for comparison, the substrate reflectance spectrum.

A comparison reveals a significant contribution of the substrate to the reflectance spectrum of the graphene– SiO_2/Si structure. The most pronounced evidence is the occurrence of a peak at $\lambda \approx 8.6\text{ }\mu\text{m}$, which is characteristic of the SiO_2 film [20]. To reveal the optical signals directly related to graphene, we plotted the spectral dependences of the ratio of the reflectance of graphene on the substrate, $R_{\text{gr}}(\omega)$, to the reflectance of pure SiO_2/Si substrate, $R_{\text{sub}}(\omega)$.

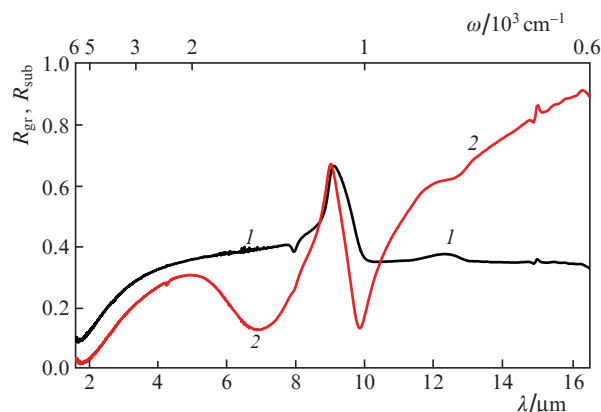


Figure 1. Reflectance spectra of (1) SiO_2/Si substrate, R_{sub} , and (2) graphene on substrate, R_{gr} .

The dependence $R_{\text{gr}}/R_{\text{sub}}$ for the instant directly after the exposure in acetone vapour (i.e., at a minimum concentration of water adsorbate on the graphene–substrate interface and, therefore, a minimum induced charge in the graphene) is presented in Fig. 2.

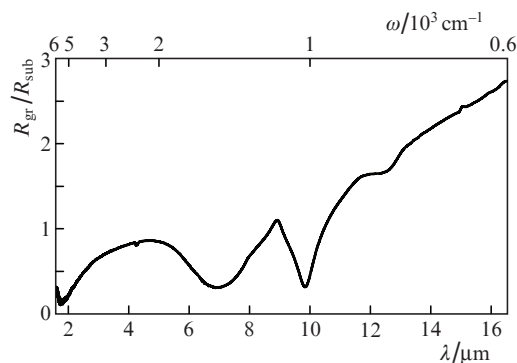


Figure 2. Spectral dependence of the normalised reflectance of graphene on a substrate $R_{\text{gr}}/R_{\text{sub}}$, recorded immediately after the exposure in acetone vapour (the signal is normalised to the reflectance $R_{\text{sub}}(\omega)$ of «pure» SiO_2/Si substrate, see Fig. 1).

This dependence exhibits a minimum at $\omega = 5500\text{ cm}^{-1}$ and a number of features, including a peak at $\omega \approx 1200\text{ cm}^{-1}$, corresponding to the light photon energy of ~ 0.15 eV.

Figure 3 shows the relative changes in the spectral signal $\Delta R_{\text{gr}}/R_{\text{sub}} = [R_{\text{gr}} - R_{\text{gr}}(0)]/R_{\text{sub}}$ that occurred during the recovery of water adsorbate layer on the graphene–substrate interface [here, $R_{\text{gr}}(0)$ is the graphene reflectance spectrum recorded immediately after the exposure in acetone vapour (see Fig. 1) and R_{gr} is the reflectance spectrum in a chosen region of graphene sample after a certain time (from 5-min to 1-week sample exposure under normal laboratory conditions in air atmosphere)].

The spectral dependences in Fig. 3 demonstrate the following: about 5 min after the exposure in acetone vapour, the graphene reflectance tends to increase (by $1\%–1.5\%$) relative to the initial spectrum (i.e., immediately after the end of acetone vapour effect) in the entire measured spectral range. A reverse effect – decrease (by $2\%–3\%$) of the graphene reflectance in the range $\lambda \approx 10–14\text{ }\mu\text{m}$ (energy $E \approx 0.09–0.12$ eV) –

is observed 1 h after the exposure in acetone vapour. The conditional short-wavelength edge of this spectral region is denoted by an arrow at $\lambda \approx 10 \mu\text{m}$. An additional (by even more $\sim 1\%$) decrease in the graphene reflectance in this region is observed 1 week after the exposure in acetone vapour. In addition, there is a relative falloff of the spectral dependence (by $\sim 2\%$) in the range $\lambda \approx 8\text{--}10 \mu\text{m}$ (at $E \approx 0.14\text{--}0.15 \text{ eV}$). The short-wavelength edge of this spectral region is indicated by an arrow at $\lambda \approx 8 \mu\text{m}$ in Fig. 3. Note also that a small falloff ($\sim 0.5\%$) was observed previously ($t = 1 \text{ h}$) in the same spectral region.

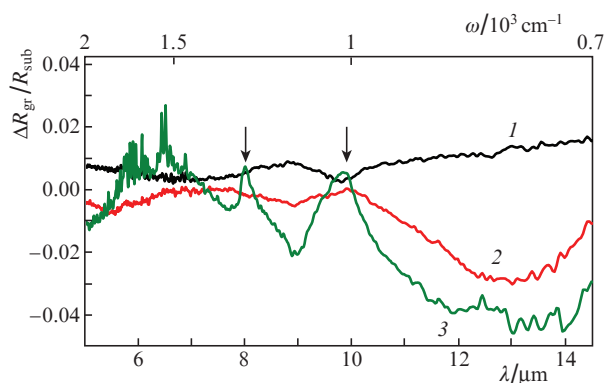


Figure 3. Relative changes in the graphene reflectance spectrum, $\Delta R_{\text{gr}}/R_{\text{sub}}$, in comparison with the spectrum recorded after the exposure in acetone vapour ($t = 0$): measurements performed $t = (1)$ 5 and (2) 65 min after and (3) 1 week after.

We compared our spectrum $R_{\text{gr}}(\omega)/R_{\text{sub}}(\omega)$ (Fig. 2) with the reflectance spectrum $R(\omega)$ of a sample of gapless ($E_{\text{g}} = 0$) graphene on a SiO_2/Si substrate (in the form of a transistor structure), normalised to the substrate reflectance $R_{\text{sub}}(\omega)$, which was taken from [6]. Note that the latter spectrum $R(\omega)/R_{\text{sub}}(\omega)$ of the graphene structure ([6], Fig. 1a) was measured in the state of charge neutrality, i.e., at a gate voltage corresponding to the minimum dc conductivity and zero density of total charge in graphene and, correspondingly, under the conditions close to the case considered here. Our spectrum in Fig. 2 and the spectrum from [6] look similar in main details: they both contain a wide band $\omega = 1600\text{--}8000 \text{ cm}^{-1}$ with a minimum at about $\omega = 5500 \text{ cm}^{-1}$ due to the interference effects in SiO_2 , and a series of spectral features in the range $\omega = 600\text{--}1600 \text{ cm}^{-1}$. The similarity of the spectral dependences suggests that $E_{\text{g}} \approx 0$ in graphene immediately after its exposure in acetone vapour.

The charge state of graphene was increased in [6] by increasing the gate voltage; this rise is accompanied by a decrease in the graphene reflectance in the long-wavelength range to 3%–5% relative to the neutral level. In particular, a spectral minimum is initiated, which undergoes a blue shift with an increase in the gate voltage, starting with $\omega \approx 2000 \text{ cm}^{-1}$ ($E \approx 0.1 \text{ eV}$) ([6], Fig. 1b). Thus, the changes in the IR spectra occurring during water adsorbate recovery on the graphene–substrate interface (see Fig. 3) are similar to those in the spectra of graphene structure reported in [6] under an electrical bias, both in their sign and in the effect magnitude (1%–5% in [6]).

Proceeding from the similarity of the spectral changes, the observed effect can be explained as follows: while water adsorbate returns to the graphene–substrate interface, the Fermi level increases relative to the top of the valence band

(to $2E_{\text{F}} \approx 0.15 \text{ eV}$ in our experiment) due to the deviation of the charge state from the neutral one (the Dirac point) and activation of intraband transitions [1]. It is noteworthy that the shift of the Fermi level ($\sim 0.15 \text{ eV}$) coincides in magnitude with the increase in the work function of experimental graphene sample after the end of its exposure in acetone vapour and subsequent long-term exposure in a wet atmosphere, which was observed by us previously [18].

At the same time, one cannot exclude the possibility of another mechanism of changes in the graphene optical response. The decrease in the reflectance of graphene structures may be caused by the blue shift of the interband absorption edge due to the expansion of the graphene band gap, induced by the strong electrical field across the graphene–substrate interface, which, however, should also increase the work function. Indeed, as follows from the Forouhi–Bloomer dispersion relations [21], the extinction coefficient k is proportional to the energy difference $E - E_{\text{g}}$. The blue shift of the interband absorption edge means a decrease in the extinction coefficient k at a specified energy and, therefore, a decrease in the reflectance R ; specifically this behaviour was observed experimentally.

4. Conclusions

The study of the mid-IR ($\lambda = 2\text{--}16 \mu\text{m}$) reflectance spectra of graphene showed that water adsorbate accumulation at the graphene– SiO_2/Si interface reduces the optical reflectance of graphene (approximately to 3%–4%) in the spectral range of 8–14 μm . The fixed change in the optical reflectance has the same sign as the change in the optical reflectance of graphene in this spectral range under electric impact, and the magnitudes of these changes are comparable. The found changes in the optical response are presumably due to the blue shift of interband absorption edge under the influence of the electric charge induced in graphene layers as a result of water adsorbate accumulation. At the same time, one cannot exclude that this effect is caused by the expansion of the graphene band gap. Further investigations in this field should clear up which of these two mechanisms is dominant.

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