Raman spectroscopy estimation of the carrier concentration and the value of strain in monolayer graphene films grown on 4H-SiC

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Abstract. Comprehensive study of high-quality monolayer graphene samples grown by thermal destruction of the Si-face of the 4H-SiC substrate was carried out. Analysis of the data obtained by Raman spectroscopy and angle-resolved photoemission spectroscopy suggest the need to use the Fermi velocity in the graphene layer under study to obtain a correct estimate of the electron concentration and strain values using Raman data. This statement is valid not only for graphene on the SiC substrate, but for graphene on any other substrate as well, since the Fermi velocity in graphene depends on the dielectric constant of the substrate.

1. Introduction

Graphene (a single layer of graphite) is currently a subject of extensive research. Significant interest to the studies of this material is due to its unique physical properties, which determine a huge potential for creating next-generation devices [1]. Thermal decomposition of the semi-insulating silicon carbide (SiC) substrate is currently considered as one of the most promising technologies for the synthesis of graphene [2]. Such a technology allows one to grow high-quality large-area epitaxial graphene. An advantage of this technology is that there is no need to transfer the grown film onto a dielectric substrate. Structures of this kind can be used in a standard technological line for manufacturing semiconductor devices.

Raman spectroscopy is recognized as an instrument with exclusively broad capabilities for studying graphene structures [3]. Information on carrier concentration and conductivity type of graphene is crucial for electronic and sensory applications. It is known that changes in carrier concentration affect the position and full width at half maximum (FWHM) of graphene’s Raman lines. Thus, this technique is promising for estimating the carrier concentration. Its great advantages are high locality and non-destructive character. As a non-contact optical method, it lacks the disadvantages inherent in Hall effect-based techniques that involve lithography. However, the number of publications containing the results of estimating the concentration of charge carriers in graphene using Raman spectroscopy data is quite limited. Several systematic measurements were performed on exfoliated graphene transferred on a SiO₂/Si substrate [4, 5]. As far as we know, there exist no works containing similar systematic measurements for single-layer graphene on SiC. It is possible that this fact is not accidental, since, as it will be shown for the first time in this work, to reliably determine the electron concentration in...
graphene grown on SiC, it is necessary to take into account such a fundamental characteristic as its Fermi velocity, which is determined by the dielectric constant of the substrate.

2. Experimental

Graphene samples grown at 1800°C on the Si-side of the semi-insulating 4H-SiC substrates by thermal decomposition in an Ar ambient were studied. Their structural, chemical and electronic characteristics were controlled by using Raman spectroscopy, atomic-force microscopy (AFM), low-energy electron diffraction (LEED), angle-resolved photoemission spectroscopy (ARPES) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS) [6].

Raman spectra were measured at room temperature in the backscattering geometry using a Horiba Jobin-Yvon T64000 spectrometer equipped with a confocal microscope, which allowed us to obtain information from the region of a graphene film ~ 1 μm in diameter. Along with local measurements, the measurements of sample areas of 12 × 12 μm² with subsequent plotting of Raman maps of spectral lines parameters were performed. Besides mapping, the histograms of the resulting maps, as well as the graphs illustrating correlations between various parameters of the Raman lines were constructed. To excite the Raman spectra, a Nd:YAG solid-state laser with a wavelength of 532 nm was used. The laser power on the sample was 4.0 mW in a spot with a diameter of 1 μm.

ARPES measurements were carried out at the Resource center “Physical methods of surface investigation” of the Research Park of Saint-Petersburg State University and at the Russian-German beam line of the BESSY II synchrotron radiation facility (Berlin).

According to the data of the complex studies, the graphene films studied in this work were mainly single-layer with a small (~ 10%) fraction of bilayer graphene inclusions.

3. Results and discussion

Figure 1 shows an array of Raman spectra measured in the 1300-2800 cm⁻¹ range on the sample area of 12 × 12 μm², which was obtained after subtracting the interfering contribution of the SiC substrate. The spectra show features appearing upon light scattering from graphene films: G and 2D lines and a weak D line [3].

The G-line in the Raman spectrum of graphene corresponds to the light scattering process involving an optical phonon of the E₂g symmetry with a small wavevector near the Γ-point of the Brillouin zone. The appearance of the 2D line in the spectra is caused by resonant scattering process involving electron states from two nonequivalent K and K’-points of the Brillouin zone (BZ) with the participation of two optical phonons of A₁g symmetry with large wave vectors.

![Figure 1. A typical array of Raman spectra of a high-quality single-layer graphene sample obtained by mapping the sample area of 12 × 12 μm². The contribution of the second-order 4H-SiC spectrum is subtracted from the array.](image-url)
phonon corresponding to the $G$ line in the Raman spectrum. With an increase in the concentration of free charge carriers of any sign, this anomaly gradually disappears, resulting in a monotonic shift of the $G$ line towards the high frequencies [7]. An increase in the electron concentration does not lead to a significant change in the position of the $2D$ line in the spectrum, but even a small change in the hole concentration causes the $2D$ line shift to the higher frequency [8]. Different response of the $2D$ line to charge carriers of different signs can be used to determine the conductivity type in graphene.

The position of the lines in the Raman spectrum may also be affected by the elastic strain. In the case of compressive strain, the $G$-line shifts in the same direction as in the case of an increase in the carrier concentration. The method of separation the strain and doping contributions to the Raman spectra of graphene was firstly suggested in Ref. [4]. It is schematically presented on figure 2 (a) for the case of electron doping. The method is based on the assumption that the positions of the $G$ and $2D$ lines depend only on strain values and carrier concentration in the sample. Under this assumption, the analysis of the correlation between $G$ and $2D$ lines allows one to determine the carrier concentration and the value of strain independently. The Raman $G$ and $2D$ lines positions in undoped and unstrained graphene (1581 and 2671 cm$^{-1}$, respectively) determine the reference point. The presence of the compressive strain in graphene without changing its carrier concentration should lead to a blueshift of both the $2D$ and $G$ lines. The ratio of strain-induced shifts of the $2D$ and $G$ lines in the case of pure biaxial strain is 2.8 [9]. However, appearance of an excess electron charge should only lead to the shift of the $G$-line, since an increase in the electron concentration up to $3 \times 10^{13}$ cm$^{-2}$ does not affect the $2D$ line position significantly [8].

Figure 2. (a) A diagram demonstrating the principle of separating the strain and doping contributions to the shifts of the $G$ and $2D$ Raman lines of graphene. Blue arrow corresponds to the strain-induced shift, red arrow to the doping-induced shift, grey arrow to the total shift of the $G$ and $2D$ lines. Red open square denotes the positions of the $G$ and $2D$ lines in the case of undoped and unstrained graphene. (b) Correlation analysis of the $G$ and $2D$ Raman lines positions in the samples under study. Red solid line demonstrates the dependence (1). Red squares show the data from Ref. [5] for graphene on SiO$_2$/Si substrate. The numbers above the red squares denote the values of the electron concentration that can be estimated from the Raman data. Data obtained from Raman mapping of the samples are denoted by triangular and circular symbols. Green stars show the data on the electron concentration obtained by ARPES measurements.

A solid line in figure 2 (b) represents the correlation dependence between the frequencies of the $G$ and $2D$ lines in the Raman spectrum of undoped graphene under biaxial strain [9]. This dependence is described by the following empirical expression:

$$\omega_{2D} = 2671 + 2.8(\omega_G - 1581)$$ (1)
With an increase of the electron concentration in graphene, this dependence shifts parallel to itself to the right. Note that the region to the left of (1) is a region of forbidden values (marked as region II in figure 2 (b)), based on the nature of the G and 2D lines behavior with strain and doping [4].

For quantitative estimation of the carrier concentration from the Raman data, we have tried to use the results of the work [5], which were obtained for single-layer exfoliated graphene transferred on a SiO₂/Si substrate. These results are presented in figure 2 (b) by squares.

Figure 2 (b) also shows the data on the correlation between the positions of the 2D and G lines for seven high-quality single-layer graphene samples grown on 4H-SiC. These data were obtained by processing the arrays consisting of ~170 spectra for each sample. It is seen that the data of all the samples can be well approximated by a set of dependences parallel to (1). The variation of points along the dependence corresponds to the presence of local inhomogeneity in the strain values, while the variation along the X axis indicates presence of local inhomogeneity in the charge carrier concentration. Note that with an increase in the sample number from #1 to #4, only an increase of the G-line frequency is observed, while the frequency of the 2D line remains almost unchanged. Such a situation in the behavior of the G and 2D lines agrees well with what should occur with increasing electron doping level. The results of estimations of the electron concentration by ARPES carried out on samples #1-#4 confirm the above conclusion (ARPES data are presented as triangles in figure 2 (b)).

As follows from figure 2 (b), a quantitative estimation of the carrier concentration in the sample #1 gives us the value of \((1.0 \pm 0.3) \times 10^{12} \text{ cm}^{-2}\). However, according to the ARPES data, the charge carrier concentration in this sample is \((5.4 \pm 0.5) \times 10^{12} \text{ cm}^{-2}\). Moreover, the estimations of the carrier concentration for the other samples, obtained by using Raman and ARPES data, also demonstrate a large difference between the data of these two methods.

![Figure 3](image-url) **Figure 3.** Histograms of the Raman maps of the G-line FWHM for the sample #5 (a) and for the sample #1 (b).  

The reason of the observed significant discrepancy in the electron concentration estimates can be determined by analyzing the Raman data presented in figure 2 (b) for the samples #5-7. These samples were grown on 4H-SiC and, according to the data of comprehensive studies, are also high-quality single-layer graphene films. The data for these three samples are very close, well fitted by the dependences parallel to (1), however, all of them fall into the region of forbidden values.

It was predicted theoretically and then confirmed experimentally that an increase in the charge carrier concentration in graphene should lead to the narrowing of the G-line due to an increase in the lifetime of the \(E_{2g}\) phonon resulting from blocking its possible decay pathways [7]. Figure 3 (a) represents the histogram of the FWHM of the G-line for one of the samples from this group (histograms for the remaining samples are similar). Figure 3 (b) shows the histogram for the sample, the concentration of electrons in which is \((5.4 \pm 0.5) \times 10^{12} \text{ cm}^{-2}\) according to ARPES. It is seen that
the FWHM of the $G$-line is substantially larger for the samples whose data fall within the region of forbidden values, which indicates significantly lower concentration of electrons in these samples.

![Diagram](image)

**Figure 4.** (a) A diagram demonstrating resonant Raman processes responsible for the appearance of the $2D$ line. Red and blue solid lines display the dispersion of electronic states for two different Fermi velocities. Solid arrows denote the acts of absorption and emission of a photon, dashed arrows denote the phonon scattering events. (b) ARPES data for a typical graphene/SiC sample under study measured at the K point of the BZ. The momentum axis is perpendicular to the ΓK direction. $E_F$ and $E_D$ denote the positions of the Fermi energy and of the Dirac point, respectively.

The appearance of the $G$ and $2D$ lines in the forbidden region II can be understood if we consider a process of resonance Raman scattering which leads to the appearance of the $2D$ line in the spectra. It is represented schematically in figure 4 (a) and occurs with the participation of electron states from the K and K’ points of the Brillouin zone, and two optical phonons with large wavevectors of identical magnitudes but opposite directions. Near these points, the graphene band diagram can be represented by two Dirac cones. The dispersion of the electron bands in graphene near the K and K’ points can be described by the following expression:

$$E = \pm \hbar v_F k$$  \hspace{1cm} (2)

According to this expression, the tangent of the inclination angle of the Dirac cone is proportional to the Fermi velocity ($v_F$) in graphene. The need to fulfill the resonance conditions leads to the fact that such a scattering process is very sensitive to the changes in the Fermi velocity. The Fermi velocity in graphene grown on SiC is substantially smaller than in graphene deposited on SiO$_2$/Si substrate: it equals $v_F = 0.90 \times 10^6$ m/s in the former case and $v_F = 1.09 \times 10^6$ m/s in the latter, according to the ARPES data from the literature [10, 11]. As the Fermi velocity decreases, the magnitude of the wave vector of the phonon participating in the scattering process also decreases. Analysis of the dispersion dependence for the A$_{1g}$ phonon near the K point shows that a decrease in the magnitude of the phonon’s wave vector should lead to an increase in its energy [12]. As a consequence, the $2D$ line should experience a blueshift with decreasing $v_F$. The shift of the $2D$ line ($\Delta \omega_{2D}$) is connected to the relative change in the Fermi velocity by the following expression [13]:

$$
\Delta \omega_{2D} = \frac{\hbar}{M} \left( \frac{1}{v_F(1)} - \frac{1}{v_F(2)} \right)$$
This expression allows us to estimate the required value of the change of the Fermi velocity to match the ARPES and Raman data on the electron concentration. Blue open squares on Figure 5 show the result of the adjustment procedure. The best agreement between the data of the two techniques is observed when the 2D line is shifted by ~20 cm⁻¹, which corresponds to a ~9% reduction (from 1.09 × 10⁶ to 1.00 × 10⁶ m/s) of the Fermi velocity. Note that the change in the Fermi velocity does not affect the G line position due to a non-resonant nature of the process responsible for its appearance in the Raman spectra.

Figure 5. The red solid line and red filled squares demonstrate the dependence (1) and the data from Ref. [5] for graphene on SiO₂/Si substrate, respectively. Blue dashed line and blue open squares demonstrate dependence (1) and data from Ref. [5] corrected for the Fermi velocity value of 1.00 × 10⁶ m/s. The numbers above the red and blue squares denote the values of the electron concentration estimated from the Raman data.

Table 1 contains the estimates of the electron concentration from the ARPES data for four of the seven samples under study. The electron concentration estimates for the graphene films on 4H-SiC obtained by using the Raman data for graphene on SiO₂/Si [5] and by using the Raman data corrected for the change of Fermi velocity in graphene grown on SiC are also presented in table 1. It is seen that the first method of estimation gives us values underestimated 2.5–3 times in comparison to those given by the second one.

Using the method of separation of strain and doping contributions (figure 1 (a)), we also estimated the magnitude of the strain from the shift of the G-line in the Raman spectra. In this case, the evaluation was as well carried out using two approaches, without and with an account on the Fermi velocity change. Table 1 shows that the strain values obtained using the first approach are almost 40% higher than those given by the second one. A good agreement between the Raman data obtained using the second approach and the ARPES data allows us to suggest that the estimates of the strain, obtained...
upon taking into account the Fermi velocity in graphene on SiC, should be more reliable, since the $G$-line shift is determined simultaneously by the magnitude of strain and the value of the electron concentration.

Difference between the value of Fermi velocity of graphene on the SiO$_2$ substrate and the value measured in graphene on SiC substrate may be explained if one takes into account the renormalization of the $v_F$ by the electron-electron interaction. The effect of the Coulomb interaction on the electron spectrum near Fermi level is known to be large [14]. For the suspended graphene layer (when the surrounding media has the dielectric constant $\varepsilon = 1$), Coulomb interaction increases the Fermi velocity for about 20% as compared with the bare electron velocity. Screening of the Coulomb interaction by the surrounding media with high dielectric contrast $\varepsilon > 1$ leads to lower contribution of the electron-electron interaction to the spectrum, and, consequently, to the decrease of the Fermi velocity value. The effect of the dielectric screening may be taken into account quantitatively for by the equation [14]:

$$v_F^* = v_F + \frac{\alpha}{4} \ln \frac{\Lambda}{k}$$

Here $v_F$ is the bare Fermi velocity without the electron-electron interaction, $v_F^*$ is the renormalized Fermi velocity, $\Lambda$ is the momentum cutoff (parameter of the model, $\Lambda \approx 1.75$ Å$^{-1}$), $k$ is the wave vector and $\alpha \approx 2.2/\varepsilon$ is the fine structure constant of graphene. For graphene placed on the substrate, the average dielectric contrast should be taken $\varepsilon = (\varepsilon_{\text{subs}} + 1)/2$ [15].

Dielectric constant of SiO$_2$ is $\varepsilon_{\text{SiO}_2} = 3.90$ [16], and for 4H-SiC it is $\varepsilon_{\text{SiC}} = 6.52$ [17]. As a result, according to Eq. (4), the value of Fermi velocity in graphene on 4H-SiC substrate should be lower than the $v_F$ value in graphene on SiO$_2$ substrate as a result of the change of substrate dielectric constant. This is in a qualitative agreement with our results.

4. Conclusion

Systematic studies of the effect of the electron concentration on the Raman spectra of single-layer graphene films grown by thermal destruction of the Si-face of the 4H-SiC substrate have been carried out. It is established that the estimation of the electron concentration for graphene grown on SiC, based on the results of Raman studies of single-layer graphene on SiO$_2$/Si substrate, leads to large errors. It is shown that taking into account the value of Fermi velocity in graphene on SiC leads to good agreement between the estimates of the electron concentration obtained using Raman and ARPES data for the same samples. The analysis of the results obtained suggest the need to consider the Fermi velocity in the graphene layer under study to obtain a correct estimate of the electron concentration and strain values using Raman data. This statement is valid not only for graphene films grown on SiC, but also for graphene on any other substrate, since the value of the Fermi velocity depends on the dielectric constant of the substrate.

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