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Raman spectroscopy of graphene: doping and mapping

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Abstract
In this study, graphene samples prepared by mechanical exfoliation were examined by Raman spectroscopy. The Au electrical contacts, fabricated using photolithography, allowed the application of a gate voltage between graphene and the Si substrate. In the Raman spectra of the sample, we observed shifts of position, changes of intensity and the width variations of the G and 2D peaks with the change of the gate voltage. Spatial Raman mapping of the samples was performed showing variations in intensities of the Raman peaks in different flake regions.

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(Some figures may appear in color only in the online journal)

1. Introduction

Graphene is a two-dimensional carbon material with a honeycomb lattice. Since its discovery, graphene has been explored for many practical applications including field-effect transistors [1]. The back-gate voltage is linearly related to the charge carrier density. The minimum observed in the conductance is called charge neutrality or the Dirac point. Electrons in graphene are sometimes referred to as massless Dirac fermions due to the linear energy–momentum dispersion relation [1, 2].

Raman spectroscopy is a very useful tool for probing the electronic and structural characteristics of graphene [3]. It gives information about the number of graphene layers, doping, defects, strain, chemical modifications and graphene edges [4, 5]. The main features in the Raman spectra of graphene are the G peak (1580 cm^{-1}) and the 2D peak (2700 cm^{-1}) [3]. Electrical doping plays a major role in graphene physics as it considerably modifies the transport properties of the device based on this material. It changes the Fermi surface of graphene and also has a strong influence on the electrons and phonons in graphene. Consequently, the intensity, position and width of the prominent Raman features vary by changing the applied gate voltage [5–8].

Here, we investigated the dependence of the Raman spectrum on doping at two positions of the sample (figure 1(a)). The electron concentration was directly controlled by applying a gate voltage, in back-gate configuration (two-point probe) [9], which produces a shift of the Fermi energy (figure 1(b)). In an ideal graphene sample, the Fermi energy is located at the Dirac point. However, in experiments the graphene samples are doped by the environment (mainly adsorbed water molecules) [1] so the Fermi energy is brought back to the Dirac point with the application of a finite gate voltage. The shift of Fermi energy causes strong electron–phonon coupling which gives rise to Kohn anomalies in phonon dispersions of graphene [5]. The result of these are shifts of the prominent features in the Raman spectrum.

We performed Raman mapping of the G and 2D peaks and observed variations of their intensities throughout the sample. Spatially resolved Raman measurements, which were used to monitor peak intensities, provide information about homogeneity of the sample [10].

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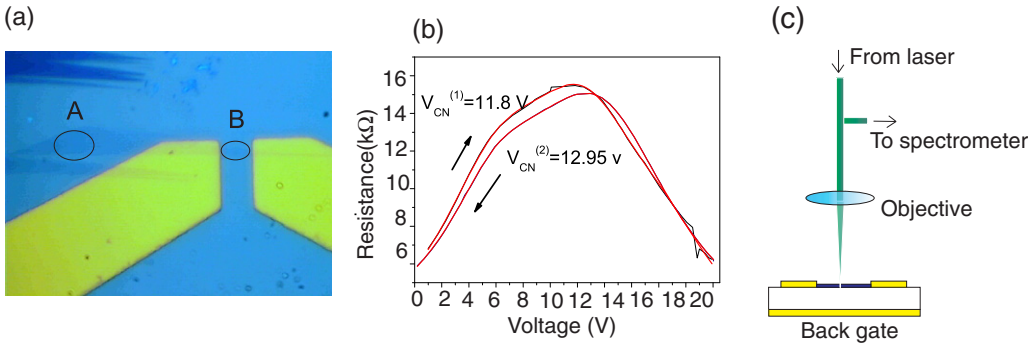

Figure 1. (a) The measured sample, top view using an optical microscope (40× magnification) and two positions of measuring—A and B. (b) Transport measurements. The applied gate voltage was in the range of 0–22 V and the Dirac point moved from 11.8 to 12.95 V. (c) Schematic view of the experimental setup for Raman measurements with applied gate voltage.

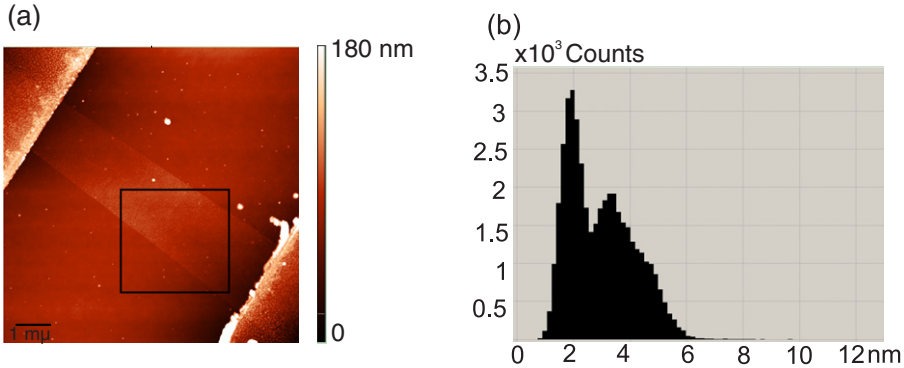

Figure 2. (a) AFM topography image (marked region—4 × 4 μm). (b) AFM height histogram of graphene and substrate in the marked region.

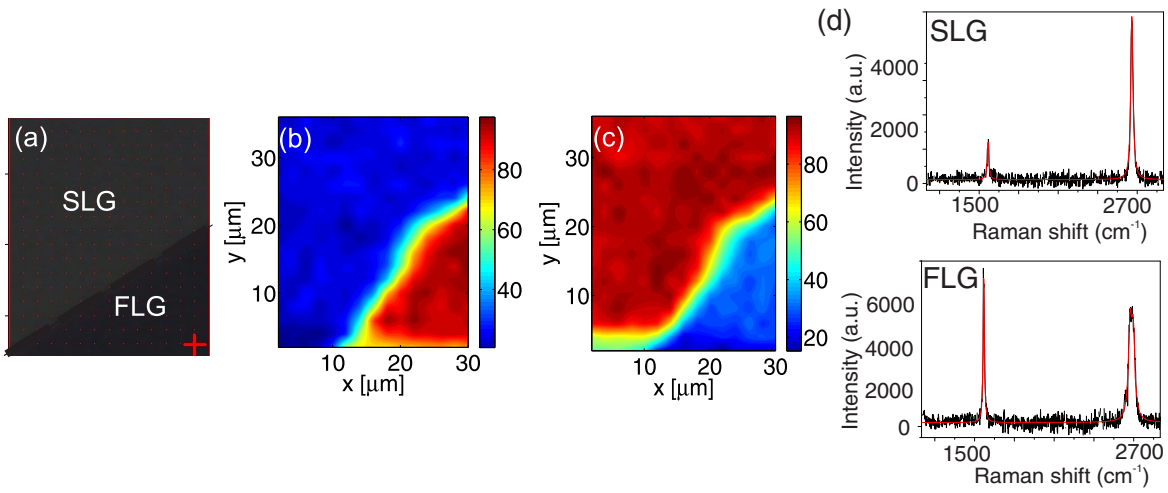

Figure 3. (a) Scheme of the sample with SLG and FLG. Raman maps for (b) the G peak and (c) the 2D peak. (d) Raman spectra of SLG and FLG.

2. Experiment

The preparation of graphene films was similar to that described in [1]. The graphene flakes are placed on Si wafers with 300 and 90 nm thick oxide layers (IDB technologies). Using photolithography, we then made Au electrical contacts, which allowed the application of a gate voltage, between the Si substrate and graphene (figure 1(a)). The atomic force microscopy (AFM) topography image (sample between contacts—position B) as well as the height histogram of graphene and substrate are shown in figures 2(a) and (b). A tapping mode imaging mechanism was used and measurements were done by Ntegra Prima from NT-MDT. The estimated height of graphene, which can be seen from the histogram, is 1.9 nm (figure 2 (b)). The variation in the thickness of the single-layer graphene (SLG) can be attributed to the change in the tip–sample interaction as the tapping tip scans over the surface [12].

We investigated the changes in the Raman spectrum of graphene by applying a gate voltage. The experimental setup is shown in figure 1(c). Raman spectra of graphene samples with applied gate voltage were obtained by the

Table 1. Raman parameters of the SLG sample measured at position A.

	G			2D			
Voltage (V)	Pos (cm^{-1})	I (au)	FWHM (cm^{-1})	Pos (cm^{-1})	I (au)	FWHM (cm^{-1})	I(2D)/I(G)
0	1590.4	552.98	14.04	2691.8	569.52	31.07	1.03
10	1590.4	642.51	12.27	2691.1	515.83	31.74	0.80
18	1591.0	542.49	14.15	2691.3	546.78	31.26	1.00
30	1589.9	561.16	13.09	2691.2	515.27	31.11	0.92

Table 2. Raman parameters of the SLG sample measured at position B.

	G			2D			
Voltage (V)	Pos (cm^{-1})	I (au)	FWHM (cm^{-1})	Pos (cm^{-1})	I (au)	FWHM (cm^{-1})	I(2D)/I(G)
0	1583.8	227.13	13.26	2681.6	210.97	28.28	0.89
9	1583.9	214.82	13.14	2681.6	202.87	30.75	0.94
40	1583.9	186.96	13.31	2681.1	182.01	31.19	0.97

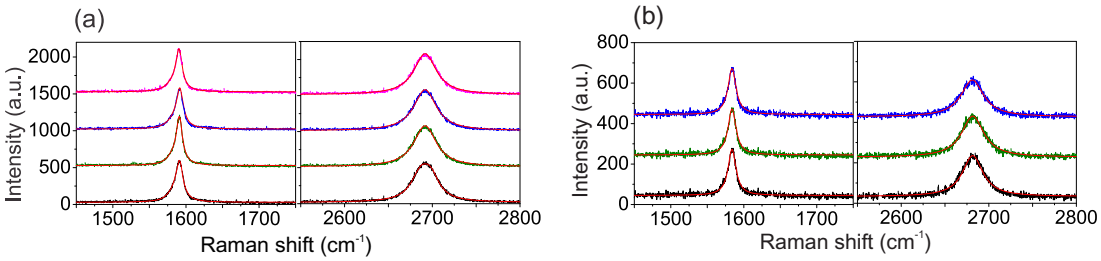

Figure 4. (a) Raman spectra of graphene measured at place A for gate voltages 0, 10, 18 and 30 V. G peak (left) and 2D peak (right). (b) Raman spectra of graphene measured at place B for gate voltages of 0, 9 and 40 V. G peak (left) and 2D peak (right).

TriVista 557 Raman system in micro-Raman configuration with an Ar+/Kr+ laser (514.5 nm). The measurements were obtained in two points, one on the left side of left contact (position A) and the other between two contacts (position B), see figure 1(a). The laser power was 1.5 mW at position A and 0.75 mW at position B (the reduction of the laser spot size—higher magnification). Furthermore, graphene samples were characterized by spatially resolved Raman spectroscopy using a Thermo Scientific DXR Raman microscope (laser line—532 nm). The power on the sample was 4 mW and the sample was measured in 270 points. Also, Raman measurements of SLG and few-layer graphene (FLG) films were done by a Micro Raman Chromex 2000 with a Nd:YAG laser (532 nm). All Raman measurements were performed at room temperature.

3. Results and discussion

Figure 3 shows Raman maps for the G peak at 1580 cm^{-1} (b) and the 2D peak at 2672 cm^{-1} (c) in different regions of the sample and (d) Raman spectra of SLG and FLG. The scheme of the sample with SLG and FLG is presented in figure 3(a). As can be concluded from figure 3, in the case of the monolayer, the intensity of the 2D peak is two times higher than the intensity of the G peak. It was quite the opposite in the case of the G peak and the 2D peak for FLG, where the G peak was of higher intensity and 2D lower. In figure 3(d) there are spectra of SLG (upper) and three-layer graphene (down). The number of graphene layers was concluded from the shape of the 2D peak [13].

At position A, Raman spectra (figure 4(a)) were measured for applied gate voltages of 0, 10, 18 and 30 V. The transport measurements were performed (figure 1(b)) for several voltage values and we obtained the Dirac point at 18 V. The main Raman features are presented in table 1. The frequency and width of the 2D peak were little changed by application of different voltages. It is reported that I(2D)/I(G) is a strong function of gate voltage [7]. Here, we observed the maximum of I(2D)/I(G) at 0 V but a similar value is in the Dirac point, at 18 V. Also, there were some changes in the width of the G peak, which is the highest in the Dirac point (14.15 cm^{-1}).

Figure 4(b) presents Raman spectra of the sample obtained at position B whereas the parameters obtained from the measurements are presented in table 2. Applied gate voltages were 0, 9 and 40 V and the Dirac point was obtained for 9 V. The intensities of the G and 2D peaks decreased, but I(2D)/I(G) increased with the increase of the gate voltage from 9 to 40 V (table 2). As can be seen from tables 1 and 2, the position of the G peak was shifted by 7 cm^{-1} (1583–1590 cm^{-1}) and the frequency of the 2D peak increased by 10 cm^{-1} (2681–2691 cm^{-1}) from position A to position B. Raman spectroscopy investigation of graphene has proved that even graphene samples that are not electrochemically doped are unintentionally doped [1, 11]. This fact explains some variations of the peak positions. Raman studies showed that doping is mainly induced by the interaction of graphene with the underlying substrate rather than with atmospheric particles [11]. The cause for this shift lies in the different values of doping levels in different regions of the graphene samples.

4. Conclusion

In this study, graphene samples were prepared by mechanical exfoliation. We have demonstrated graphene SiO_2 back gating. The results of the Raman measurements for different gate voltages indicated that the G and 2D peaks have different doping dependences. Raman spectroscopy gave information about the number of layers of prepared samples. We carried out Raman mapping which provided information about peak intensities throughout the graphene sample.

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