Graphene thickness measurements: a comparison of the methods

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Introduction

Graphene, a single layer of graphite, is often poorly distinguishable from more graphite layers. A small change in colour with a number of graphite layers is the first hint for finding graphene flakes in an optical microscope. The common methods for a more detailed graphene investigation and characterization are Raman spectroscopy [1], AFM [2] and surprisingly rarely optical reflectometry [3]. These methods have been mostly applied separately and, when compared their results, significant differences in graphene thicknesses have been found among them. To investigate this problem in a more detail these three different characterization methods have been used simultaneously in our work.

Graphene preparation

The graphene flakes were prepared by mechanical exfoliation of natural graphite (NGS Naturgraphit GmbH). These flakes were transferred onto a Si wafer with a 290 nm-thick thermally grown SiO_2 layer using a blue sticky tape. The SiO_2 layer of this thickness enabled us to localize very thin graphite sheets (including single graphene layer) under an optical microscope.

The Nikon Eclipse L150 optical microscope was used to localize the thinnest flakes in the white light and by means of a green filter with maximum transparency at 547 nm for a better contrast as well (Fig. 1). Afterwards, these graphene- and thin graphite flakes were investigated by several microscopic methods for determining the number of graphene layers of the flakes and their thickness.
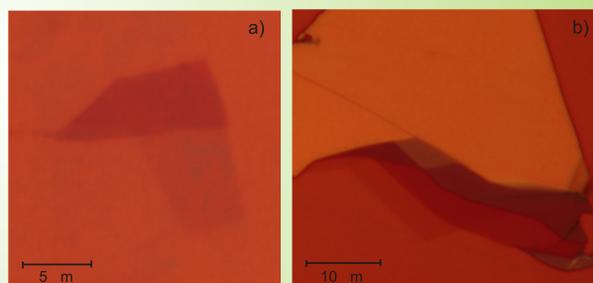

Fig. 1. Graphene flakes observed by optical microscopy (white light). Graphene monolayer - lighter part (a) and graphite flake with various thickness (b).

AFM measurements

AFM topography was measured using the SPM microscope NTEGRA Prima (NT-MDT) in the contact mode. The measured thickness of the four-layer flake (Fig. 2) was 1.2 nm as shown in the detailed scan (Fig. 4 a, c), but the value is very similar to that one obtained for graphene in the bottom part of the flake (the real thickness of graphene is 0.34 nm).

The AFM method is very sensitive to graphene contamination by ambient species and to microscope adjustment and tip parameters. Hence, this method is not so suitable for a precise thickness determination as the optical reflectometry where these influences are not so critical.
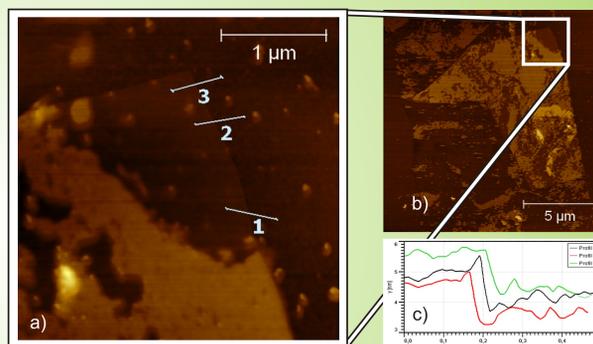

Fig. 4. AFM measurement of the graphene flake from the Fig. 2 (b): a detail of the four layer part of the flake, (a) and the corresponding profiles (c).

Microreflectometry

Optical reflectometry is a method based on the comparison of light reflection spectra taken from a measured unknown sample and a standard sample with the known absolute reflectance (i.e. the ratio of intensities of the reflected and incoming light beam). The relative reflectance, the ratio of these measured spectra, can be used for the calculation of the layer thickness. In this case the thickness of a graphite flake can be calculated from reflected intensity of the flake and SiO_2 layer on Si.

Earlier measurements with optical fibre reflectometry using the optical microscope specified above showed that was possible to fit the experimental reflection spectra with the theoretical ones calculated for a model graphene layer of the constant complex index of refraction (n = 2.6 - 1.3i [4]). The calculated thickness for a graphene layer was 0.22 nm. A significant disadvantage of the configuration based upon an optical microscope is a narrow spectral range of the probing light covering optical wavelengths (400-800 nm) only (Fig. 5).

A new optical instrument for UV microreflectometry has been designed to broaden this range towards shorter wavelengths (250-800 nm) (Fig. 6). Furthermore the beam-spot focused on the sample has been reduced to diameter about 10 micrometers.
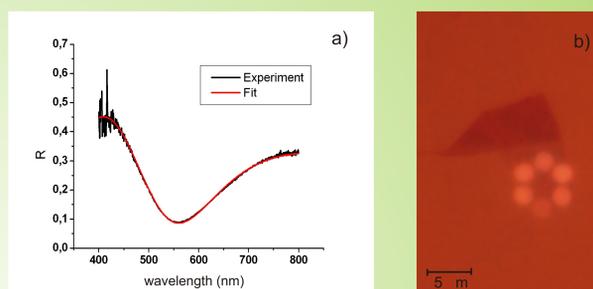
mailto: zuzana-bortlova@post.cz

Fig. 5. Reflection spectra in a wavelength range of 400 - 800 nm (a) and the spot on the sample (b).
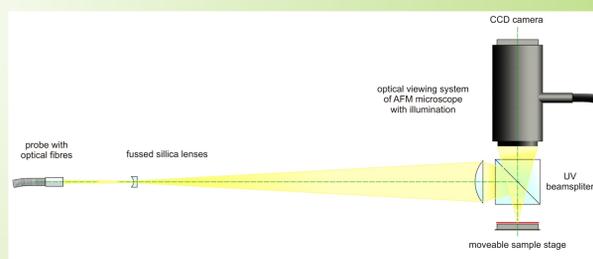

Fig. 6. Scheme of UV microreflectometry setup.

Micro-Raman spectroscopy

Micro-Raman spectra were measured by the inVia Renishaw spectrometer using a laser with a wavelength of 442 nm focused by a microscope optics onto a sample. The beam-spot diameter was 0.5 m and the sample stage enabled scanning the sample across the beam to achieve the maps of spectra (Fig. 2 a).
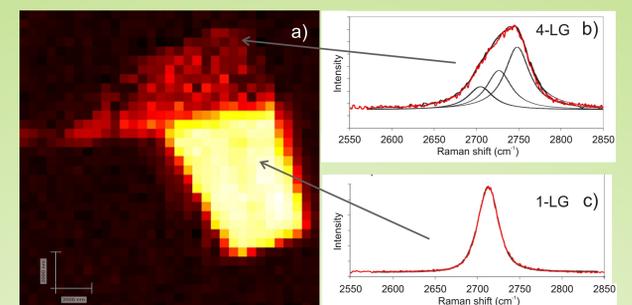

Fig. 2. Raman spectra intensity map taken over a flake (a). The top part of the flake consists of four layers, whereas the bottom part represents a graphene monolayer (b, c). The corresponding Raman spectra were fitted according to Malard [1].

The micro-Raman spectra provided information about the number of graphene layers (LG). The shape of the second order G' band at the wavenumber about 2700 cm^{-1} is important in the layer-number determination. The G' band corresponding to one monolayer of graphene (1-LG) exhibits a single Lorentzian peak with a full width at half maximum (FWHM) of 24 cm^{-1}. The Raman spectra of a bilayer graphene (2-LG) can be fitted with 4 Lorentzian peaks, the trilayer with 6 Lorentzian peaks, the four layers with 3 broader peaks and more layers with 2 complex peaks [1].
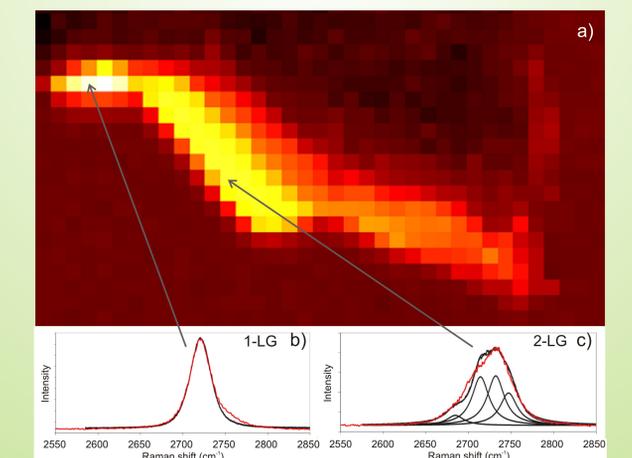

Fig. 3. Raman spectra intensity map of the flake with various thicknesses (a). The spectra of a graphite single layer (graphene) and bilayer (b, c).

Figures 2 and 3 show the maps of micro-Raman spectra on two different flakes. Various colours of map sites express the intensity of signal to baseline between 2660 and 2750 cm^{-1} (the area under the G' peak in the graphene case). The shapes of spectra shown in Figure 2 indicate a flake consisting of two parts - graphene and four-layer graphite (Fig. 2 (b, c)). The second flake depicted in Fig. 3 contains more graphite layers - here the spectra of a graphite single layer (graphene) and bilayer are shown (Fig. 3 (b, c)).

References

[1] L. M. Malard et. al., Physics Reports, 473, 51 (2009).

[2] P. Nemes-Incze et al., Carbon, 46, 1435 (2008).

[3] A. GRAY et al. Journal Of Applied Physics 104, 053109 (2008).

[4] P. BLAKE et. al., Appl. Phys. Lett., 91, 062124 (2007).

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