

Spectroscopic Raman Nanometrology of Graphene and Graphene Multilayers on Arbitrary Substrates

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Abstract. Raman spectroscopy is known to be an effective tool for characterization of graphene and graphene multilayers on the standard Si/SiO₂ (300 nm) substrates, which allows one to determine non-destructively the number of the graphene layers and assess their quality. The Raman phonon peaks undergo modification when graphene is placed on other substrates due to changes in the nature and density of the defects, surface charges and different strength of the graphene – substrate bonding. We show that despite the spectrum variations the deconvolution of the double-resonant 2D band allows one to identify the number of graphene layers even on amorphous glass substrates. The results extend the application of Raman spectroscopy as nanometrology tool for graphene and graphene-based devices.

1. Raman spectroscopy as nanometrology tool for graphene layers

The unique properties of graphene have recently attracted major attention of the physics and device research communities [1-2]. Raman spectroscopy has been successfully utilized as a convenient technique for identifying and counting graphene layers on the Si/SiO₂ substrates [3-7]. It was shown that the evolution of the 2D-band Raman signatures with the addition of each extra layer of graphene can be used to accurately count the number of layers [3] together with the position of G peak, which up-shifts with the increasing $1/n$, where n is the number of graphene layers [4].

Most of the Raman spectroscopy studies of graphene were limited to graphene layers on Si/SiO₂ substrates with a carefully selected thickness W of the SiO₂ layer ($W \cdot 300$ nm). The latter is explained by the fact that graphene becomes visible in an optical microscope when placed on top of Si wafer with the 300-nm thick oxide layer due to the light interference. At the same time, it is not obvious that the features of the 2D band and G-peak position will be preserved when graphene is transferred to another substrate due to possible changes in the nature and density of the defects, surface charges and different strength of graphene – substrate bonding.

Here we demonstrate that the sensitivity of the 2D band to the number of graphene layers allows one to count the atomic layers when graphene is transferred to different substrates. As an example, we selected an “inconvenient” substrate of a very different type such as glass. The single-layer graphene

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(SLG) and few-layer graphene (FLG) were obtained by micro-mechanical cleavage of bulk graphite. The same procedure was used to place graphene on reference Si/SiO₂ (300 nm) and glass substrates. The glass substrates were selected as representatives of the unconventional amorphous substrates characterized by many defects. The number of layers was determined from the visual inspection of graphene on the standard Si/SiO₂ substrate (see Figure 1 (a)) and atomic force microscopy (AFM) of the flakes placed on glass. The optical imaging and AFM were followed by Raman spectroscopy. The procedure of separating SLG and FLG on Si/SiO₂ substrates from graphitic flakes is well established [3-6] and relies on differences in the G-peak and 2D-band features (see Figure 1 (b-c)). The AFM inspection of graphene on glass revealed flakes with the thickness below 2 nm, which indicates $n < 4$. This information was used in the analyses of 2D band of FLG on glass substrates (see Figure 1 (d)).

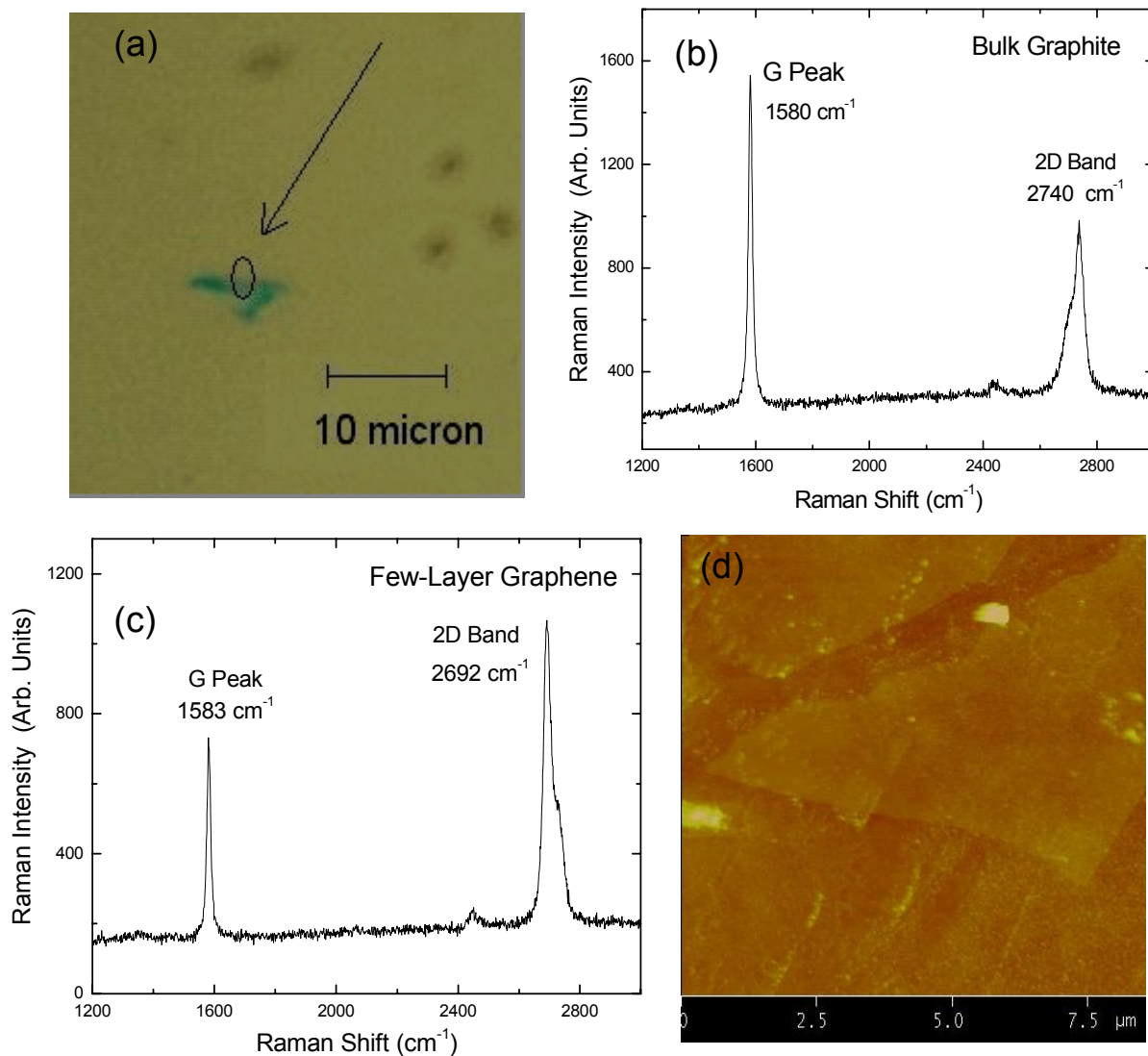


Figure 1: (a) Optical microscopy image of graphene flake on Si/SiO₂ substrate; (b) Raman spectrum of the bulk graphite used to produce graphene and graphene multilayers; (c) Raman spectrum of the few-layer graphene on Si/SiO₂ substrate; (d) atomic force microscopy image of the few-layer graphene (number of layers $n < 4$) on the glass amorphous substrate.

2. Analysis of Raman spectra of graphene on glass substrates

Raman microscopy was carried out under 488-nm excitation at low power levels to avoid the laser heating [8-9]. To separate the effect of the substrate from the spatial variations in the graphene layer properties we accumulated 10-20 spectra in different location for each of the examined samples. First, we have taken a number of Raman scans of graphene layers on a standard Si/SiO₂ substrate and verified the number of layers analyzing the features of the 2D band. Figure 2 shows a typical Raman spectrum from SLG (bottom) and BLG (top). The measured Raman features are consistent with the previous reports [3-6]. The 2D-band sensitivity to the number of layers is explained by the double-resonant model [10] adopted for graphene [3]. The splitting of the electron energy levels in BLG leads to appearance of the four phonon peaks, which make up a broad 2D band for BLG. We have used the spectrum deconvolution procedure to obtain the Lorentzian peaks, which correspond to the four resonant transitions. The wave numbers of the deconvoluted peaks for graphene with $n=1-5$ on the standard substrate under 488-nm excitation are summarized in Table 1. Since 2D band is a resonant band the Lorentzian peak positions depend on the excitation energy.

Table 1: Deconvolution of 2D Band for Few-Layer Graphene on Standard Si/SiO₂ Substrate

Number of Layers	Lorentzian Peak Positions (cm ⁻¹)
n=5	D _{2A} = 2728, D _{2B} = 2762
n=4	D _{2A} = 2702, D _{2B} = 2732
n=3	D _{2A} = 2697, D _{2B} = 2719
n=2	2D _{1B} = 2661, 2D _{1A} = 2688 2D _{2A} = 2706, 2D _{2B} = 2719
n=1	2D = 2691

The measured spectra of graphene on amorphous glass substrates were much noisier and displayed many additional peaks. The 2D-band spectral regions for two typical spots on graphene on glass are presented in Figure 3. A comparison with the spectra in Figure 2 indicates similarities and suggests that the peaks and bulges appearing in the 2D band of BLG on glass correspond to the same resonant transitions determined for BLG on the standard substrate. The extracted peak positions are indicated in Figure 3. Despite some deviations in the Lorentzian peak positions and intensities they can be clearly identified and used to distinguish BLG from SLG or from other graphene multilayers.

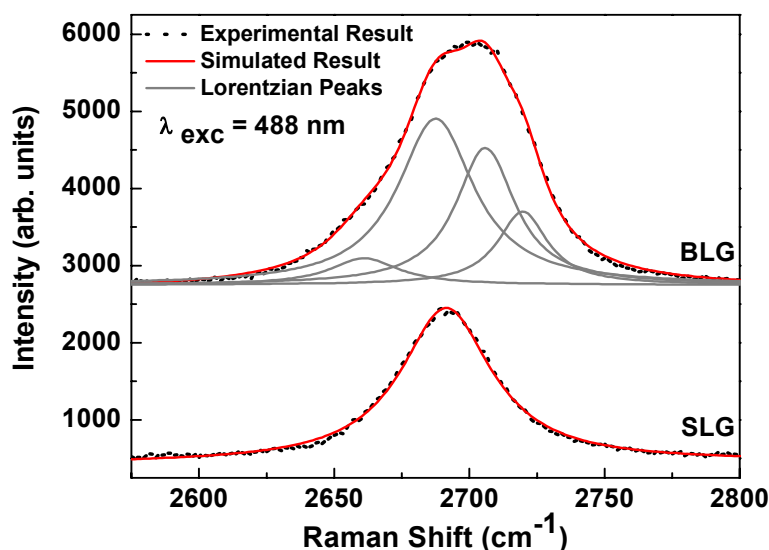


Figure 2: 2D band for SLG and BLG on a Si/SiO₂ substrate. The spectra are taken in the backscattering configuration under the 488 nm excitation. The number of Lorentzian elemental peaks in the deconvolution of BLG spectrum is determined by the double-resonance model. The extracted peak positions are used for comparison with the spectra from graphene on glass substrates.

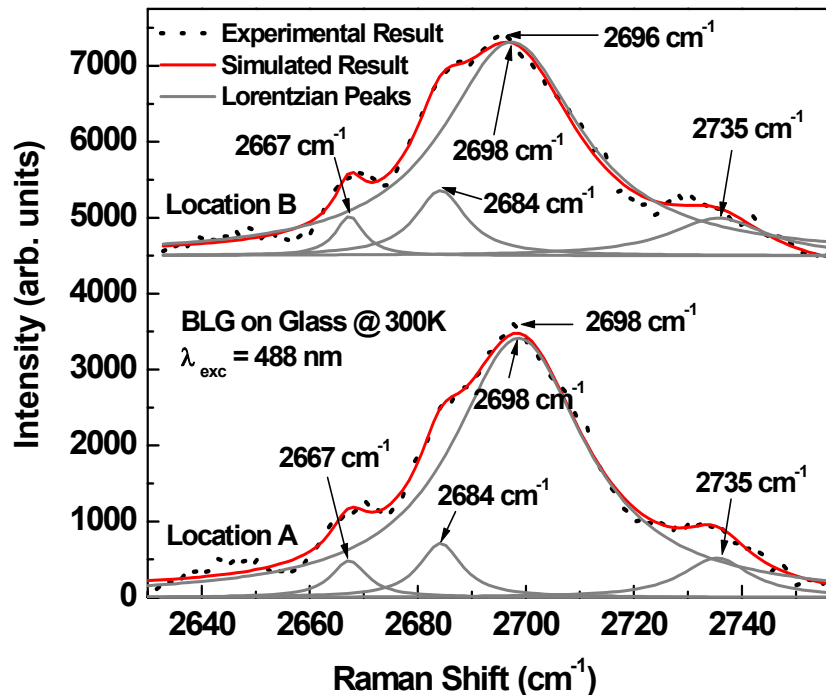


Figure 3: 2D band for graphene layers on glass substrate. The analysis of the spectra, based on the 2D-band deconvolution and its comparison with the peaks in Figure 2, indicates that the examined graphene sample is BLG. The extracted peak positions are marked on the plots. The spectra are taken under the same conditions as those in Figure 2.

3. Conclusions

We demonstrated that despite the changes in the Raman spectrum of graphene when it is placed on different substrates, the deconvolution of the double-resonant 2D band allows one to identify the number of graphene layers. The procedure was tested on the example of amorphous glass substrates. The results are important for extending the application of Raman spectroscopy for nanometrology of graphene and graphene-based devices.

Acknowledgements

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