



Raman imaging of graphene

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Abstract

A Raman spectrum of a solid contains information about its vibrational and electronic properties. Collecting spectral data with spatial resolution and encoding it in a 2D plot generates images with information complementary to optical and scanning force imaging. In the case of few-layer graphene the frequency of the G line and especially the width of the D' line turn out to be sensitive to single layers. The thickness of the few-layer graphene flake is reflected in the intensity of the G line and in the reduced intensity of the dominant peak of the underlying silicon oxide.

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1. Introduction

Combining physical or chemical properties with real space information is the goal of many surface diagnostic methods. Encoding these data in false-colour 2D plots provides high-contrast images different from optical imaging or scanning force microscopy (SFM) due to the inherent sensitivity of the physical or chemical features of the material under study.

Recently it has been shown that few-layer graphene resting on top of an insulating surface is not only mechanically stable but also acts as a true two-dimensional electron/hole gas [1]. A drastic change in the electronic properties is observed when going from few-layer graphene to a single layer: the carrier dispersion can be described by the Dirac equation and mimics massless relativistic Fermions [2,3].

Confocal Raman spectroscopy gives spatially resolved information about the vibrational spectrum and the electronic band structure via the mechanism of double-resonant Raman scattering [4].

Especially the lifting of the band degeneracy from single- to few-layer graphene permits the unambiguous identification

of single layers as opposed to SFM where the step from the substrate to one layer is difficult to distinguish from the step to two layers [5,6].

We present Raman maps for two different few-layer graphene flakes. For the intensity of the graphitic G line and the first-order polysilicon line the contrast is just inverted owing to the proportionality of the G line signal and the absorption of the silicon signal on the thickness of the graphite flake. The peak profiles of the G and D' line are discussed for single- and double-layer graphene and compared to the bulk limit. From that we can interpret the differences in the Raman maps for the intensity of the G line and the full width at half maximum (FWHM) of the D' line. The latter can be used as a single-layer detector. Finally, the peak position of the G line is analysed indicating a shift in frequency for the single-layer graphene section.

2. Experiment

Graphite flakes were deposited by mechanical exfoliation starting from highly orientated pyrolytic graphite (HOPG) of grade ZYH on a highly doped (n^+) silicon wafer with a 300 nm SiO₂ cap layer [1]. On this substrate ultra-thin flakes become visible with the help of a standard optical

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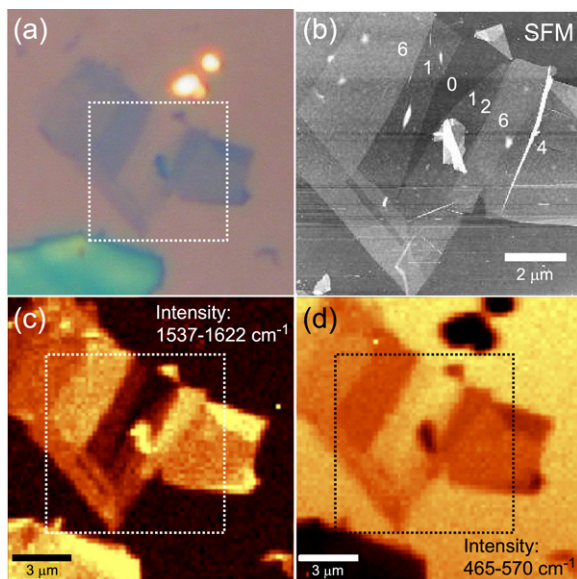


Fig. 1. (a) Optical microscope image of a few-layer graphene flake next to a thicker graphite deposition (lower left) and Cr/Au-markers (upper right) on a $\text{SiO}_2/\text{n}^+\text{-Si}$ substrate. (b) SFM micrograph of the centre part of the few-layer graphene flake (labelled with the number of layers) with an inner V-shaped single-layer section. The scan area is indicated in (a), (c) and (d) with a dotted square. (c) Raman map of the spectrum integrated between 1537 and 1622 cm^{-1} , which can be assigned to the E_{2g} phonon in graphitic material. (d) Raman map of the spectrum integrated between 465 and 570 cm^{-1} , which can be assigned to the first-order polysilicon phonon mode. Notice that the metallic markers also mask the signal from the silicon oxide substrate.

microscope [7]. The Raman spectra were acquired using a laser excitation of 532 nm (2.33 eV) through a numerical aperture of 0.80 operated at the diffraction limit. We obtain a laser spot size of about 400 nm, which determines our lateral resolution. With a very low incident power of 4–7 μW heating effects can be neglected.

3. Results and discussion

An optical microscope image allows to locate randomly deposited few-layer graphene flakes on a SiO_2 substrate (Fig. 1(a)). The thickness and the colour of a flake on this particular substrate can be qualitatively correlated: from white to blue and finally to violet for decreasing thickness. The single-layer section in the middle of Fig. 1(a) is almost transparent. With a SFM the number of layers can be determined up to an uncertainty of ± 1 layer, partly because of the surface roughness (0.1–0.2 nm) but also because of the strong height difference between substrate and first layer (between 0.4 and 1 nm). The intensity of the G line signal (Fig. 2(a)) of thin graphite is related to the amount of graphitic material in the focus spot: In Fig. 1(c) thicker sections appear brighter whereas the single-layer part is darker reflecting the smaller peak amplitude. The integrated intensity of the G line increases linearly with the number of layers [6]. For more than five layers the signal starts to saturate and approaches asymptotically the bulk value. The amplitude at the positions of the bare SiO_2 substrate is zero. In addition, we integrate the Stokes spectrum around 500 cm^{-1} , i.e. around the strongest peak

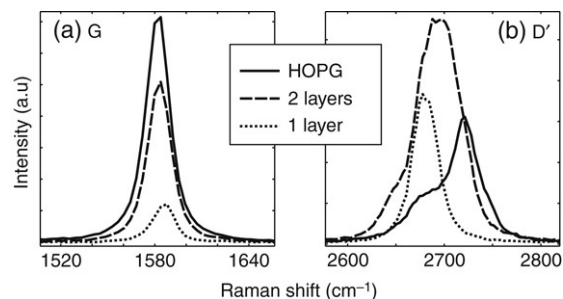


Fig. 2. Raman spectra of the (a) G line and the (b) D' line for HOPG (solid), double-layer (dashed) and single-layer (dotted) graphene. Peak amplitudes are scaled for clarity.

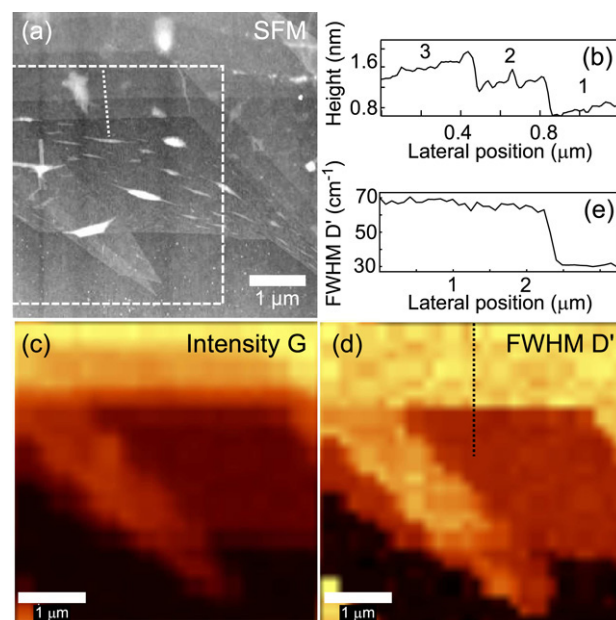


Fig. 3. (a) SFM micrograph of a few-layer graphene flake with rhombohedral single-layer section bordered on the top and on the right by graphene staircases with steps of 1 layer, highlighted in the cross-section (b) along the dotted white line. (c) Raman map of the integrated G line intensity. (d) Raman map of the FWHM of the D' peak and a cross-section (e) along the dotted black line (only lower part of the line lying within the presented Raman map). The Raman map area is indicated in (a) with a dashed square.

of the SiO_2 Raman spectrum. Fig. 1(d) shows that the intensity is reduced by the graphite flakes as a function of their thickness. Fig. 1(c) and (d) thus yield complementary contrast information, analogous to the positive and negative in photography.

Comparing the Raman peaks of the G and the D' line at the crossover from bulk to double-layer and finally to single-layer graphene in Fig. 2, it is evident that they are qualitatively different. While the G peak (Fig. 2(a) and with it the integrated intensity) decreases and shifts to higher wave numbers, the D' peak (Fig. 2(b)) drastically changes its shape: For HOPG it is composed of two Lorentzian contributions, for double-layer graphene four subpeaks can be assigned, for the single-layer only one Lorentzian peak is left [6]. This behaviour is qualitatively explained within the double-resonant Raman model [4]: the lifting of the degeneracy around the K point in the electronic band structure allows four phonon transitions

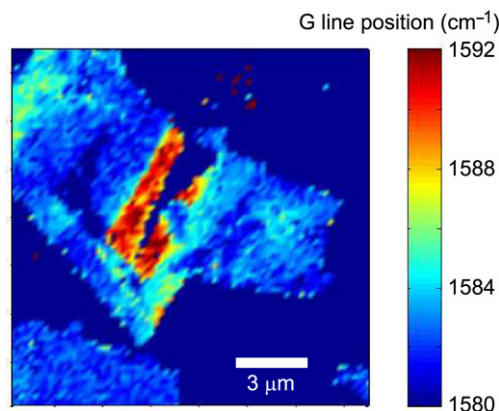


Fig. 4. Raman map of the G line position of the few-layer graphene flake presented in Fig. 1. The bare silicon oxide substrate (homogenous dark blue regions) is excluded from the fitting and set to zero. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in the case of double-layer graphene as opposed to just one possible scattering event for single layer with its cone-like band [5,6].

We expect therefore that the mapping of the FWHM of the D' line indicates the single-layer graphene sections. The rhombohedral-shaped single-layer section shown in Fig. 3(a) is terminated on two sides by graphene staircases of monolayer steps as highlighted in the cross section plot Fig. 3(b). The integrated G line intensity (Fig. 3(c)) gradually changes with the number of layers while the FWHM of the D' line (Fig. 3(d)) marks clearly the transition from the few-layer to the single-layer graphene. The FWHM width is almost constant between 65 and 70 cm^{-1} for several layers and drops to half of its value for the single-layer graphene. Raman spectroscopy provides thus a fast and all-optical nondestructive way to detect atomically thin graphitic planes. Notice that surface irregularities such as up-folded graphene (white spots) do not affect the quality of the G and D' Raman signal.

Another parameter of interest in the Raman spectrum of graphite is the G peak position. In single-wall carbon nanotubes (SWNT) the shift and splitting of the G peak is a measure for the tube diameter [8]. The mapping of the frequency of the E_{2g} phonon mode in Fig. 4 for the few-layer graphene flake shown in Fig. 1 reveals that the variation in the Raman shift is

most important for the single-layer part. A recently published experiment ascribes it to the position of the Fermi level that is to say to the amount of doping [9]. Since the charge transfer is mainly due to adsorbed molecules [10], the sensitivity to donors on the surface decreases for increasing number of layers (considering the very short screening length of the order of the interplane distance).

4. Conclusion

We demonstrate that spatially resolved Raman spectra can be used to differentiate graphite flakes of different thicknesses with up to monolayer accuracy. Especially Raman maps of the width of the D' line and the peak position of the G line clearly highlight the single-layer graphene contribution. The integrated intensity of the G line and the suppression of the Raman signal of the silicon oxide substrate are complementary measures for the thickness of the few-layer graphene flake.

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