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Abstract: This application note reports on true colocalized AFM-Raman measurements of exfoliated graphene on SiO₂/Si. Topographic, contact potential difference, and Raman data are generated on the same location with the same tip using a fully integrated AFM-Raman microscope, the new SignatureSPM. The true colocalization of chemical, electronic, and physical information within reach using the SignatureSPM significantly boosts confidence in the data it provides. In addition to its integration level and user-friendliness, this makes SignatureSPM an essential tool for researchers developing graphene-based nanodevices.

Keywords: Graphene, 2D materials, AFM, Colocalized AFM-Raman, Correlative data, Raman spectroscopy

Introduction

Graphene, the two-dimensional wonder material composed of a single layer of carbon atoms, has captivated the scientific community with its incredible strength, flexibility, and exceptional electrical and thermal conductivity, opening up a world of possibilities for transformative advancements in electronics, energy storage, and composite materials. Graphene is currently used in aircraft and battery industries. Nanocomposite coatings made up of a resin reinforced with graphene replace metal coatings and enable the dissipation of high-energy current present in high-altitude lightning strikes. Thanks to their low density, they allow for reducing the mass of the aircraft and decreasing fuel consumption. Graphene is also used in batteries for energy storage. Its strong mechanical and chemical resistance, along with the thinness of its sheets and good conductivity, make it a valuable asset.

As for electronics applications, while graphene has shown great potential due to its unique properties, there are still obstacles to its widespread use, including difficulties in scaling up production of high-quality and defect-free monolayer material, integrating it into existing manufacturing processes, and achieving economic viability.

Characterization techniques play a crucial role in understanding and deploying graphene for practical applications. Advanced characterization methods, such as atomic force microscopy, scanning tunneling microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy provide valuable insights into

graphene's structure, quality, and electronic properties. By employing these techniques, researchers can assess the number of layers, identify defects, measure carrier mobility, and study the interactions with substrates or other materials in heterostructures. This comprehensive characterization helps optimize graphene synthesis, guide device fabrication, and ensure the desired properties are achieved, facilitating the successful integration of graphene into a wide range of technologies.

Combining information from two different characterization techniques provides valuable additional insights into the properties of graphene. For example, correlating atomic force microscopy (AFM) and Raman spectroscopy data can offer a more comprehensive understanding. AFM can provide topographic information, revealing the surface morphology, layer thickness, and potential defects, while Raman spectroscopy offers complementary data on crystalline quality, strain, and doping levels. By overlaying these two datasets, researchers can precisely correlate structural features with specific spectral signatures, aiding in the identification and interpretation of defects, strain distributions, or local variations in electronic properties. This colocalized information enhances the understanding of graphene's structure-property relationships, guides material optimization, and supports the development of high-performance graphene-based devices.

In this application note, results from the analysis of exfoliated graphene flakes using an **AFM-Raman SignatureSPM** microscope will be reported.

Experimental and Results

The graphene sample was examined with the AFM-Raman SignatureSPM system (HORIBA, France), which combines an atomic force microscope (SmartSPM) with a Raman microscope. The SignatureSPM instrument is shown in Fig. 1.



Figure 1: Picture of the SignatureSPM instrument: a compact multimodal AFM-Raman characterization platform.

The sample was shined with a 532 nm *p*-polarized laser directed at a perpendicular angle via a 100× magnification lens with a 0.7 numerical aperture. After collection through the same route, the resulting Raman signals were sent to a three-grating (150 gr/mm, 600 gr/mm, 1800 gr/mm) spectrometer through optical fiber coupling. ACCESS-NC silicon tips (AppNano, USA) were utilized as their geometrical design are well suited for enabling easy visual Raman laser-tip apex alignment and minimized laser shadowing. To locate the area of interest on the sample,

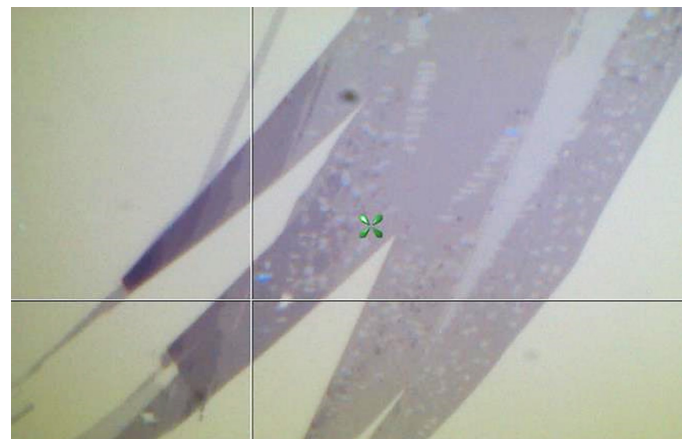


Figure 2 Optical image from the top camera of the SignatureSPM with 100× objective.

navigation was accomplished using imagery provided by an optical top camera. The laser beam is focused onto the ACCESS-NC tip. The “ACCESS” design allows a direct optical view of the AFM tip apex for applications that require seeing the tip as it engages the surface. All “ACCESS” type tips are best suited for colocalized measurements as they ensure easy Raman laser-tip visual alignment. The optical image in Fig. 2 displays a region featuring a large flake. The tip apex-Raman laser spot alignment is performed visually by looking at the top optical camera image. The laser focus is adjusted using the knob moving in the z direction of the 100× objective and eventually maximized the sample signal. An 80 μm × 40 μm AFM scan was acquired at 0.5 Hz with a resolution of 300 lines. A 90 μm × 90 μm Raman map (150 px × 150 px) was collected with a laser power of 70 mW, a 600 gr/mm grating, an acquisition time/px of 2 ms, and a pixel size of 200 nm. The AFM topographic image (a) and Raman map (b) are displayed in Fig. 3.

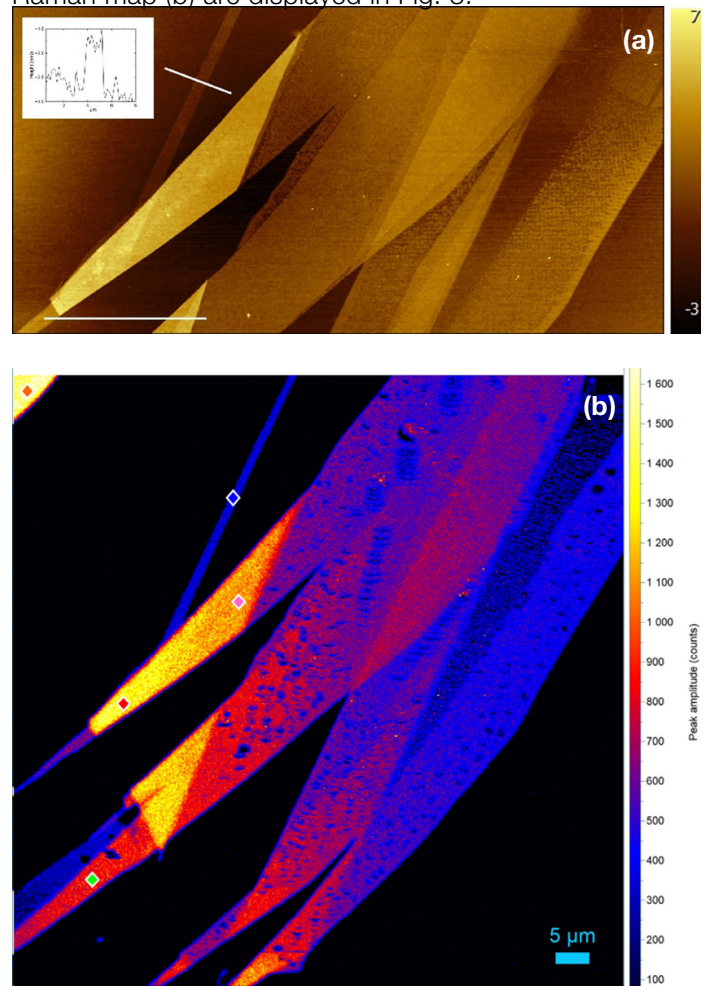


Figure 3: (a) Topographic image, scale bar is 20 μm. The inset shows the height profile across a monolayer graphene stripe. (b) Raman map displaying the G band intensity. Five diamonds are positioned on five areas of linearly increasing intensity: dark blue (monolayer), green (bilayer), pink (three-layer), red (four-layer), orange (five-layer).

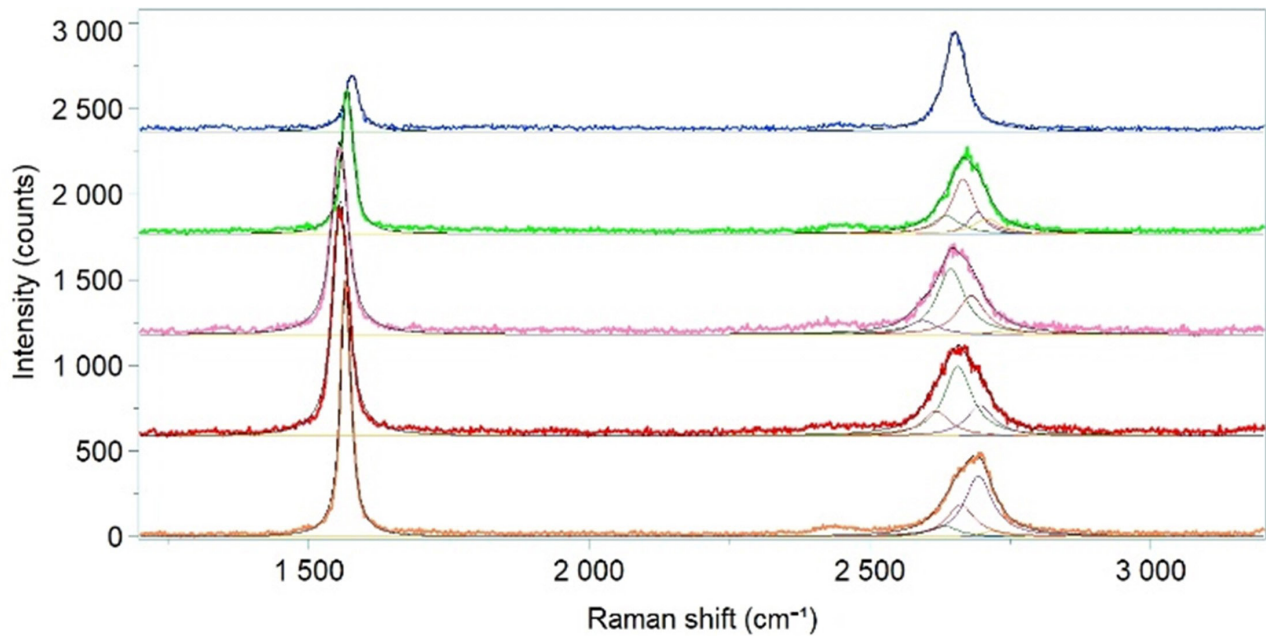


Figure 4: Raman spectra taken from the five characteristic regions identified in Fig. 3b. The results of the deconvolution of the G peak in one symmetric Lorentzian function and of the 2D peak in one symmetric Lorentzian function (for the monolayer) or four symmetric Lorentzian functions are shown.

The Raman map plots the amplitude of the G peak upon fitting to a single symmetric Lorentzian function. Five distinct shades of increasing intensity can be observed on the Raman map. Five spectra extracted from the regions (averaged on 25 pixels) characteristics of these shades are shown in Fig. 4. Fig. 4 also shows the results of the peak fitting of the G peak and 2D peak. On the dark blue spectrum, the 2D peak can be fit in a single symmetric Lorentzian function which indicates a monolayer graphene. This is confirmed by the height profile going across a monolayer “blue” stripe. The 0.9 nm height measured is higher than the actual graphene thickness (0.3 nm) but expected given the presence of adsorbed contaminants and the influence of the substrate surface roughness. The 2D peak of the other four spectra are deconvoluted into four symmetric Lorentzian functions. The G peak intensity as measured upon peak fitting of the five spectra is plotted as a function of graphene thickness (number of layers) in Fig. 5. The linear G intensity vs number of layers variation is in agreement with the one reported in [5] and confirms the presence of the different thickness graphenes. Additional mapping in the amplitude-modulated and frequency-modulated Kelvin modes was acquired and maps are shown in Fig. 6.

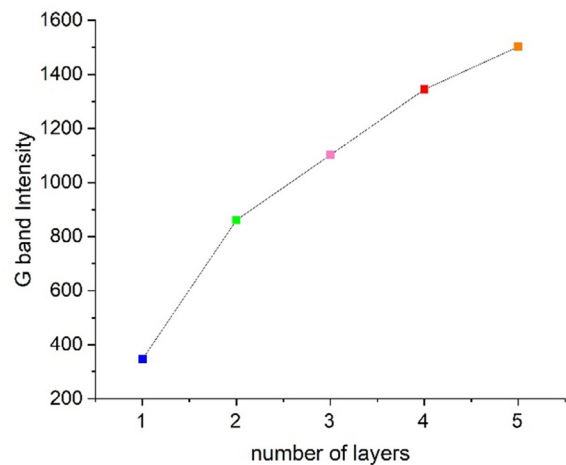


Figure 5: G band intensity upon peak fitting as a function of graphene thickness.

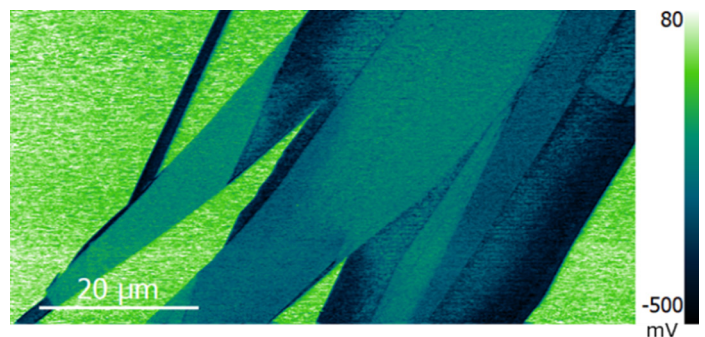


Figure 6: Contact potential difference map from frequency modulated Kelvin mode measurements.

Conclusions and perspectives

Exfoliated graphene flakes transferred onto SiO₂/Si have been characterized using the AFM-Raman SignatureSPM system. Ensuring dependable quality control for graphene is crucial so that it may be effectively integrated in electronic devices. Through colocalized mapping of topography, contact potential difference, and Raman signal, we have successfully determined various characteristics such as layer number, contact potential difference response, and presence of topographical abnormalities, like wrinkles or blisters. By offering detailed correlative morphological, chemical and electrical information, the SignatureSPM promises to serve as a vital resource for scientists dedicated to advancing technology based on two-dimensional materials. It enables trustworthy and exact findings through its capacity for concurrent measurement of multiple characteristics.

Acknowledgments

The authors acknowledge A. Felten, PMR, Université de Namur in the frame of the Graphene Flagship for providing the samples.

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