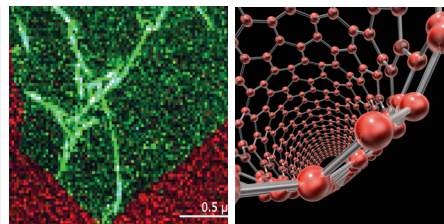


Characterization of Graphene using Tip-Enhanced Raman Spectroscopy (TERS)



Agnès Tempez, Yoshito Okono, Marc Chaigneau
HORIBA Scientific, Avenue de la Vauve, Passage Jobin Yvon, 91120 Palaiseau, France

Keywords

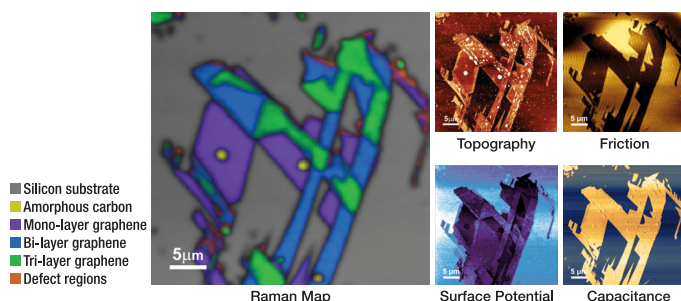
Graphene - 2D materials - Tip-Enhanced Raman Spectroscopy - Tip-Enhanced Photoluminescence

Context and issues

Graphene is a crystalline bi-dimensional material made of an atomically thick layer of sp²-bonded carbon atoms arranged in a honeycomb lattice. It was discovered in 2004 by A. Geim and K. Novoselov who received the Nobel Prize in 2010. Graphene has extraordinary properties, in particular, extremely high electron mobility, which opens up a large variety of applications in nanoelectronics, optoelectronics, and batteries. Strangely, the high electric conductivity of graphene has hindered its integration, but the recent development of semiconductor 2D materials, and their potential combination with graphene, has revived the integration of graphene into nanoelectronics devices. While graphene oxide was primarily considered as an intermediate form for large scale production of graphene due to its easy dispersability in water, graphene oxide is also of interest for a lot of applications as it can be functionalized or used as a non-conductive layer.

Potential / Input from technique

Raman spectroscopy is the characterization of choice for carbon phases in general, and for graphene and graphene oxide in particular, as it is non-destructive and provides a large amount of information such as defects, disorder, edge and grain boundaries, thickness, doping, strain and thermal conductivity. But the ultra high spatial resolution needed for the study of graphene nano-objects cannot be fulfilled using diffraction-limited Raman microscopy. However, tip-enhanced hyphenated techniques based on the amplification of signal from the nano-region under the tip will allow for actual nano-characterization. The recent development of side-illuminated TERS analysis even provides the possibility to investigate the behavior of graphene-based structures under device operation.



Starting point, what is known?

In graphene, there are two main peaks in the Raman spectrum: G (1580 cm⁻¹), a primary in-plane vibrational mode, and 2D (2690 cm⁻¹), a second-order overtone of a different in-plane vibration, D (1350 cm⁻¹) for a 532 nm excitation laser. The position, width and intensity of G, D, and 2D Raman-active modes of graphene are discussed as a function of the incident light polarization and locations on the graphene layer. The number of graphene layers can be measured from the splitting of the 2D peak and a red shift of the G peak. Using the ratio of peak intensities I_D/I_G the level of disorder in graphene can be estimated. The D peak can be used to characterize the edge properties and grain boundaries of graphene crystals.

Description of sample and measurement

A- Co-localized Raman and AFM of Graphene

First, this application note presents co-localized AFM/Raman data obtained on exfoliated graphene deposited on a silicon substrate. A NanoRaman™ system combining an Atomic Force Microscope (SmartSPM, AIST-NT) with a Raman spectrometer (XploRA, HORIBA Scientific) is used in top illumination/collection (objective lens ×100, NA=0.7). The 532 nm laser light is focused onto the apex of the AFM tip in this upright configuration, allowing simultaneous SPM and spectroscopic Raman measurements at the same location of the graphene sample. The 40 μm × 40 μm AFM and Raman images (256 × 256 points) are acquired for a total acquisition time of about ~5 min.

The different SPM modes allow studying of mechanical (friction) and electrical properties (work function study with the surface potential map and capacitance map) of graphene flakes. Simultaneously, Raman spectroscopy provides information about flake thickness, structural uniformity, presence of defects or impurities with diffraction limited spatial resolution (Figure 1).

Figure 1: 256 x 256 points acquired topography (AFM height), friction (Lateral Force Microscopy LFM), surface potential (Kelvin Probe Force Microscopy KPFM) and capacitance (Capacitance Microscopy SCM) with composite Raman map of graphene. Acquisition time about 5 min.

B-TERS and KPFM on Graphene oxide

Second, carboxylic-graphene oxide (GO-COOH) flakes are measured with the same NanoRaman™ system as described above with the side illumination configuration (using a $\times 100$ objective, NA=0.7), a p -polarized light at 638 nm and a silver AFM-TERS tip.

The objective is to locate chemical groups and evaluate the groups' distribution on GO surface, which cannot be obtained reliably by TEM (destructive method) or XPS (limited spatial resolution to the millimeter scale). In addition, Kelvin probe force measurements are being conducted simultaneously with the aim of correlating the chemical groups distribution to local potentials/electronic properties in nanoscale. Through this study, it has been seen that the Fermi level in an area of GO increases with density of defects: the higher the defect density, the higher the Fermi level.

Figure 2 shows a topographic image of a few-layers GO sample obtained whilst KPFM imaging and TERS imaging; (b) Kelvin potential difference (KPD) image of the sample in (a); (c) TERS image using the I_D/I_G ratio of the D and G peaks; (d) average TERS spectra from region A and B. The nanoscale chemical and electrical imaging of GO-COOH flakes using the NanoRaman™ system that combined TERS and KPFM measurements revealed that not only holes and different chemical groups distribution on GO-COOH surface can be imaged with a resolution down to 15 nm but also the local variation of the Fermi level correlated to the TERS analysis. These results indicate that with a high chemical and electronic sensitivity, nanoscale spatial resolution TERS & KPFM integrated measurement is a powerful tool for mapping low-dimensional electronic devices at the nanometer length-scale.

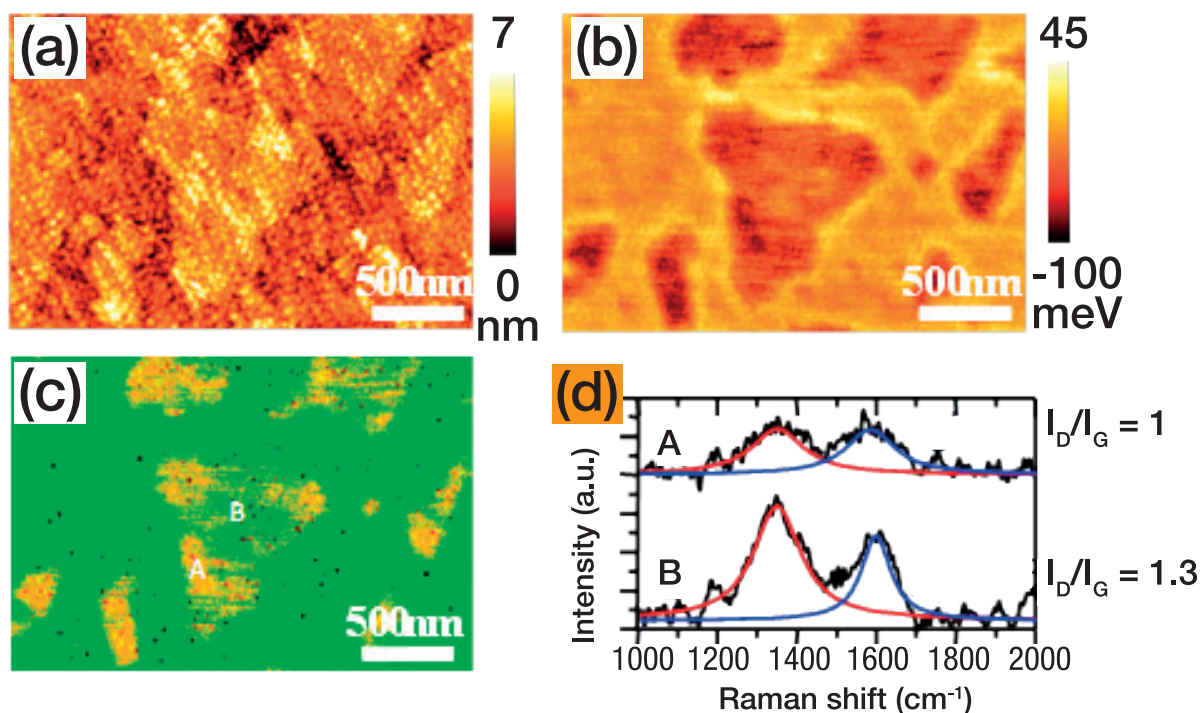


Figure 2: (a) Topographic image of a few-layers GO sample; (b) Kelvin potential difference (KPD), (c) D-to-G band TERS intensities and (d) overlay image of average TERS spectra from region A and B and KPD.

C-TERS exploration of resistance of Graphene nanostructure directly probed on an electronic device

Last, after pointing out the nanoscale chemical sensitivity of TERS on graphene, this final study shows that such analysis can be directly made onto final graphene-based electronic devices. In particular, the effect of applying close-to-breakdown current on CVD graphene/Cu transferred to a structure of 10 μm wide Cr/Pt electrodes on SiO_2/Si has been investigated here by TERS (Figure 3).

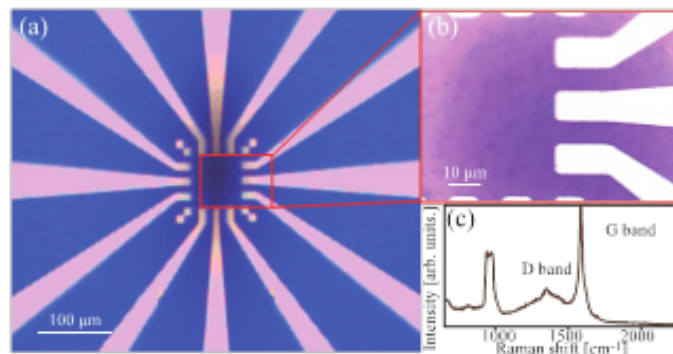


Figure 3: (a) Optical image of graphene and electrodes. (b) Magnified image obtained using the 100 $\times$ objective lens of the NanoRaman™ system, showing islands dispersed on the SiO_2/Si substrate. (c) Raman spectrum measured at a region containing both islands and the surrounding single-layer graphene, showing a sharp G band and a broad D band.

TERS measurements were performed again by a NanoRaman™ system coupling the AFM with a confocal Raman instrument using a $\times 100$ objective tilted by 60° with respect to the sample plane. A 638 nm p -polarized laser is focused onto the Au tip with a 0.10 mW power on the sample. TERS maps are obtained using 1s acquisition per spectrum. The application of a 10 A/cm ($\sim 3.0 \times 10^8$ A/cm²) current under Argon ambient leads to the formation of graphene islands. The TERS results of this study show that this high current density induces Raman bands at 1456 and 1530 cm⁻¹, which were assigned to edge-phonon modes originating from zigzag and armchair edges (Figure 4). This led us to conclude that C–C bonds are cleaved due to the high current density, leaving edge structures behind, which were detected through the observation of localized phonons.

Conclusion and perspectives

In this paper, we have shown that AFM/Raman and TERS analysis combined with the electrical SPM modes, can deliver important insights into the nanoscale properties of graphene and graphene oxide flakes, and into the correlation between topography, chemical and electronics properties.

This becomes essential as the dimensions of graphene devices continue to decrease and as 2D heterostructures emerge with the use of 2D materials such as transition metal dichalcogenides and hexagonal boron nitride.

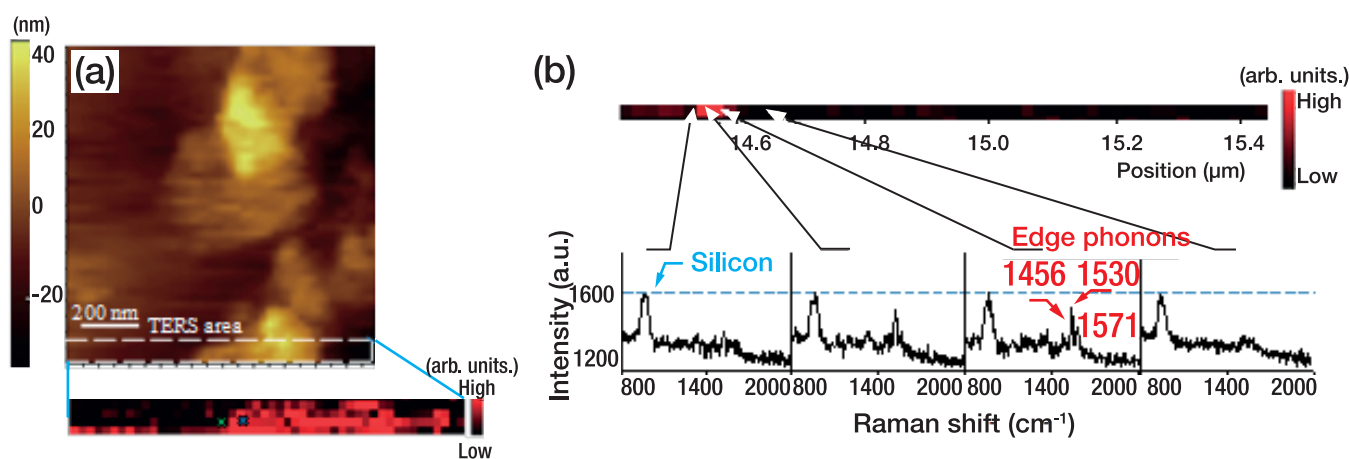


Figure 4: (a) AFM image of graphene between electrodes and corresponding TERS map of the area enclosed by the dashed rectangle, (b) detailed TERS line analysis of graphene by plotting peak intensity at 1530 cm⁻¹. The intensity of the edge phonons varied at the nanometer scale.

Bibliography

«Simultaneous Topographical, Electrical and Chemical Nanoscopy of Carboxyl Graphene Oxide using Combined Tip-enhanced Raman Spectroscopy & Kelvin Probe Force Microscopy» Weitao Su, Andrey Krayev, Naresh Kumar and Marc Chaigneau, submitted (2017).

«Side-illuminated tip-enhanced Raman study of edge phonon in graphene at the electrical breakdown limit» Yoshito Okuno, Sanpon Vantasin, In-Sang Yang, Jangyup Son, Jongill Hong, Yoshito Yannick Tanaka, Yasushi Nakata, Yukihiro Ozaki and Nobuyuki Naka, Appl. Phys. Lett. 108, 163110 (2016); doi: 10.1063/1.4947559

«TERS at work: 2D materials, from graphene to 2D semiconductors» Andrey Krayev, Sergey Bashkurov, Vasily Gavriluk, Vladimir Zhizhimontov, A. Edward Robinson, Proc. SPIE 9925, Nanoimaging and Nanospectroscopy IV, 99250A (2016) doi:10.1117/12.2237678

«Nanoscale imaging and identification of a four-component carbon sample» E. Sheremet, R. D. Rodriguez, A. L. Agapov, A. P. Sokolov, M. Hietschold, D. R.T. Zahn, Carbon 96 (2016) 588-593.

HORIBA
Scientific

info.sci@horiba.com

USA: +1 732 494 8660
UK: +44 (0)20 8204 8142
China: +86 (0)21 6289 6060

France: +33 (0)1 69 74 72 00
Italy: +39 2 5760 3050
Brazil: +55 (0)11 2923 5400

www.horiba.com/scientific

Germany: +49 (0)6251 8475 0
Japan: +81 (0)3 6206 4721
Other: +33 (0)1 69 74 72 00

