Characterizing Graphene using RISE system

M. Dosbaba[1*]

[1] TESCAN ORSAY HOLDING, Application department, Libusina trida 21, Brno, Czech Republic, marek.dosbaba@tescan.cz

Graphene is considered one of the most promising materials of the future. However, there are still many challenges in terms of both, research and industrial application in different fields such as optoelectronics, photovoltaics and many others [1]. Graphene is commonly combined with many other materials which often require different analytical approaches. Every new complex analytical tool or method can be beneficial under such circumstances. TESCAN ORSAY HOLDING in collaboration with WITec have just recently introduced a system which combines a high resolution scanning electron microscope (SEM) and a Raman imaging system - RISE (Raman Imaging and Scanning Electron microscopy) [2].
Such combination literally opened the eyes of electron microscope allowing for the characterization of even the light elements and especially those carbon rich compounds which were virtually unresolvable using conventional X-ray spectrometry technique RISE has been designed to be compatible with a focused ion beam system resulting in a powerful instrument not only for sample observation but also for sample modification.

While implementing the combination of this system, one of the main aims was to preserve all the imaging capabilities a standalone Raman system can offer, such as high lateral and vertical resolution and confocality, key features which are now fully integrated in the RISE (solution). On the other hand, no compromises were to be accepted that diminished the characteristic and valuable SEM versatility for accommodating different detectors for analysis (EDX, WDX, EBSD, CL, EBIC, AFM). A novel and innovative approach was necessary in order to achieve such a goal. RISE is a unique Raman-SEM system with no parallel. The electron column and the Raman optical microscope have not the same focal point. Instead, they are placed parallel to each other and thus the sample has to be transferred from one to another. The transfer procedure is fully automatic and relies entirely on the precise SEM stage. The Raman optical microscope is equipped with a full-blown optical objective with 100 x magnification and a high numerical aperture. Such a design allows for achieving diffraction limited resolution of 432 nm with a green Nd:YAG laser. The objective is suspended on a 3-axis piezoelectric scanner above the sample. The Raman signal is then measured using a highly sensitive Raman spectrometer allowing for the acquisition of up to 1000 spectra per second. Such a high efficiency makes the spectrometer a suitable tool for Raman (hyperspectral) imaging which enables for collecting the full spectra at each pixel of the selected area. Scanning the sample is less damaging than point spectra measuring for some sensitive specimens. Measuring points spectra and line scans is however still possible.

References

[1] W. Choi, J. Lee Hansma, Graphene – Synthesis and Applications CRC Press, Boca Raton, 2012.

[2] J. Jiruše, M. Haničinec, M. Havelka, O. Hollricher, W. Ibach, P. Spizig, Integrating focused ion beam–scanning electron microscope with confocal Raman microscope into a single instrument (2014) J. Vac. Sci. Technol. B 32.

[3] S. Mou, J. Boeckel, W. Lu, J. H. Park, W.C. Mitchel, S. Tetlak, Imaging of Electron Beam Induced Current in Epitaxial graphene, APS Meeting, 2012.

[4] J. D. Wood, S. W. Schmucker A. S. Lyons, E. Pop, J. W. Lyding. Effects of Polycrystalline Cu Substrate on Graphene Growth by Chemical Vapor Deposition, Nano Lett., 11 (suppl. 11) 4547–4554.

The imaging is performed by the objective movement and not by the underlying SEM stage resulting in far better precision and reproducibility. The scanner allows for 3D imaging of topographic sample surface and even the imaging of subsurface features in the case of transparent samples.

The Raman image is not created directly, it is the result of the raw data processing using in-house software with advanced capabilities such as a cluster analysis and a principle component analysis, fitting tools, filters etc.

The resulting image can bear different sorts of information. The basic result is usually the space distribution of different phases within the sample. The Raman technique is sensitive to the chemical bonds present within the material rather than to elemental composition, feature which allows for distinguishing even structurally different but chemically identical phases e.g. diamond vs. graphite etc. The image can equally contain information on the structural state of the material. The width of the Raman bands corresponds to the crystallinity of the phase whereas relative lateral shifts of the bands can be related either to stress or to a specific chemical substitution changing the energy of the bond. Finally, the images can reflect the intensity of particular bands which could be linked to the quantity of certain phase or its thickness which is typically applied to graphene. The resulting image can be laid over the SEM image creating a correlative microscopy output.

Graphene can be characterized from several points of view using the RISE system. The above mentioned SEM versatility has been further increased by the integration of Raman imaging. It can help to clearly distinguish graphene from any other carbon based impurities on the substrate surface. Subsequent Raman imaging allows for the identification of areas formed by single-, bi- or multi-layer graphene based on the fitting of the G' band (see figure 1). Such observation can be also confirmed by using a built-in AFM. Selected graphene flakes or monolayer areas then can be further modified by using the gas injection system. Both, etching and deposition is possible, allowing for shape modification and contacting. The use of electron beam induced current (EBIC) measurement is also possible in the case of specific graphene structures [3]. EDS or even WDS mapping can be beneficial in the case of samples that combine graphene with different materials. EBSD can help in assessing the substrate structure and its potential influence on the graphene deposition [4].

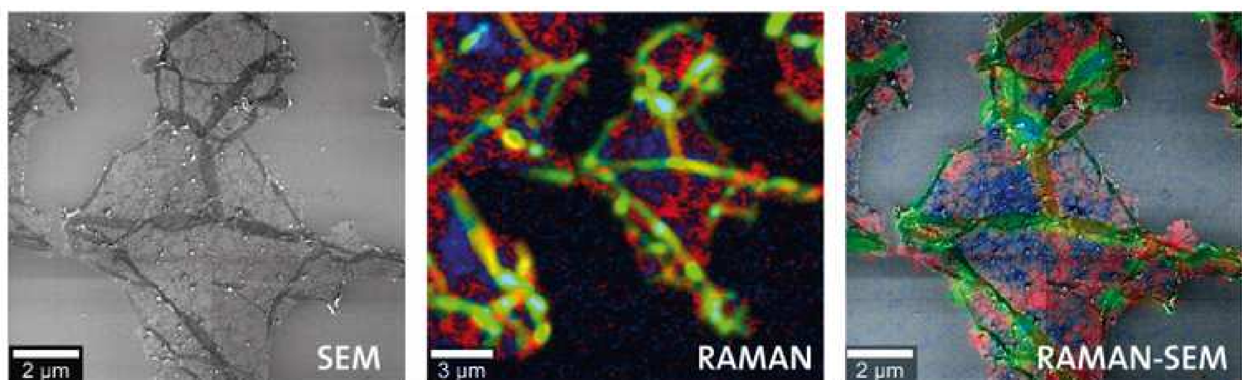

Figure 1: Correlative Raman imaging of a graphene on a silicon substrate (mono-layer red, bi-layer blue, multi-layer green).