Imaging Carbon materials with correlative Raman-SEM microscopy

Carbon materials are widely used in many industries for their exceptional properties. Electric conductance, light weight, strength, thermal resistance and other attributes are all available in different allotropes of one element - Carbon (diamond, graphite, graphene, etc.). All of these materials consist of pure carbon and have only C-C bonds, which is ideal for Raman spectroscopy. Moreover, Raman spectroscopy has the ability to differentiate small orientation changes in these bonds. Therefore, Raman spectroscopy has the potential not only to discriminate among these allotropes but it can also identify structural damage, or deviations and even different inner stresses.

Introduction

Correlation of this powerful technique with a scanning electron microscope (SEM) is beneficial in many ways. First of all, it achieves the required magnification and resolution for detailed observation of carbon materials such as fullerene clusters, carbon nanotubes (CNT), nanocrystalline diamond (NCD) or graphene. Additional analytical methods such as EDX can be used to obtain elemental mappings of these materials with a focus on impurities or contamination. Moreover, the use of the Focused Ion Beam (FIB) technique has become a standard tool in FIB-SEMs for excavation and 3D reconstruction of defects hidden underneath the sample surface. One of many such examples is the 3D reconstruction of cracks in diamond layers on cutting tools.

Raman, SEM and FIB within one chamber

Mounting a Confocal Raman Microscope (CRM) onto a FIB-SEM chamber allows the transfer of an area of interest from SEM to CRM and back with a single click. It saves a lot of time because the transfer between the two standalone instruments is thus avoided. This in-situ process also avoids the exposure of the sample to the ambient air which prevents it from oxidation.

In the RISE (Raman Integrated Scanning) Electron microscope, an area of interest is chosen through SEM with magnifications ranging from 20x up to 1Mx and, a high resolution image is then captured. Next, with one click the sample is transferred under the optical microscope of the CRM and the sample is imaged with a 100x optical objective. The area of interest is located in the optical image and Raman mapping is performed. That is all – quick and easy.

Diamond

The first of the presented carbon allotropes is diamond. Diamond is transparent over a very wide wavelength range. It is considered to be the hardest, the stiffest (and least compressible) material with the highest thermal conductivity and inert to most chemical reagents. The transference of these outstanding properties onto many tools and materials is possible through the deposition of thin diamond films on many different substrates.
Diamond crystals only consist of tetrahedral sp$^3$ bonds and thus, the Raman spectrum shows only one peak at around 1332 cm$^{-1}$. However, when diamond forms small crystals of surface comparable with their volume (nanocrystalline diamond – NCD), an additional band at around 1620 cm$^{-1}$ appears together with shoulders on both mentioned bands. The band at around 1620 cm$^{-1}$ signifies sp$^2$ bonds from surface defects. A SEM micrograph of nanocrystalline diamond together with Raman spectra are shown in Fig. 1.

### Carbon Nanotubes

Carbon nanotubes (CNTs) have been adopted into a wide range of industries for their chemical, mechanical, optical, magnetic and electric properties. They can be found in super capacitors, fuel cells and hydrogen storages, conductive composites, memory devices, solar cells, displays etc. Carbon nanotubes are cylindrical tubes formed by sp$^2$ bonded carbon atoms. A CNT is basically a roll of graphene planar sheet so-called single-wall CNT (SWCNT). Double-wall (DWCNT) and multi-wall (MWCNT) carbon nanotubes are the SWCNTs wrapped in another graphene sheets of progressively increasing the diameter of the roll. CNTs may be found and imaged by SEM and, an additional Raman microscopy analysis provides the capacity to distinguish between SW, DW and MWCNTs. The quality of CNTs can be also examined (Fig. 2).

The peak at around 1330 cm$^{-1}$ - known as the D band - is important for quality determination. The D band is often called the defect band and it appears when there are some disorders in the structure of the nanotubes. The D band is also present in spectra of DW or MWCNTs. However, these nanotubes do not exhibit a vibration mode at around 190 cm$^{-1}$. This mode is also called radial breathing mode (RBM) and it corresponds to slight, vibrational changes in diameter of the nanotubes. DW and MWCNTs cannot "breathe" because this vibrational mode is restricted by other layers on top of the first one.

![Fig. 1: A SEM image of nanocrystalline diamond and the comparison of Raman spectra of diamond with nanocrystalline diamond. Large diamond crystals have only one peak at around 1332 cm$^{-1}$ due to having only sp$^3$ C-C bonds. In nanocrystalline diamond (on SEM picture) a peak at around 1620 cm$^{-1}$ appears due to the comparable size of the surface with the volume, i.e. more surface defects are visible. Sample courtesy of Marian Varga from Institute of Physics of the ASCR, Prague.](image)

![Fig. 2: A SEM image of carbon nanotubes and Raman spectra of Single-wall carbon nanotubes of different quality. The RBM peak at around 190 cm$^{-1}$ confirms the presence of SWCNTs while the D band at around 1330 cm$^{-1}$ determines the quality. Sample courtesy of Kateřina Dědková from Nanotechnology Centre, VŠB-Technical University of Ostrava.](image)
Combined sample with NCD and SWCNTs

State-of-the-art materials can be comprised of a mixture of different components with unique properties in one advanced material. This is also the case with mixtures of carbon allotropes. When these materials consist of pure carbon it is hard to determine their quality by means of SEM imaging and also to find any damage caused by the preparation process. Here, we show the determination and quality check of a nanocrystalline diamond layer deposited on single-wall carbon nanotubes [1]. The transfer of the sample from SEM to Raman position and visualization of both components (Fig. 3) is done by a single click.

Graphene

Graphene is widely used because of its electrical and mechanical properties. There are several methods for graphene extraction but all these techniques have one feature in common, they aim to avoid multi-layer carbon sheets. Choosing Raman spectroscopy for the determination of the number of these layers is highly recommended. A single graphene sheet consists of carbon bonded together by means of $sp^2$ bonds. Looking into a number of layers, the most important is the ratio between the G (1600 cm$^{-1}$) and G’ (2700 cm$^{-1}$) bands in the Raman spectrum. We can identify the number of graphene layers and determine the success of making single-layer carbon sheets in both CVD graphene (Fig. 4) and exfoliated graphene (Fig. 5).

**Fig. 4:** An image of exfoliated graphene overlaid with Raman map shows two different areas. The corresponding spectra reveal single-layer (blue) and multi-layer (pink) graphene. In the blue spectrum, the G’ peak is twice as tall as the G peak, which means a successful preparation of single-layer graphene.

**Fig. 3:** The correlation of SEM image and Raman map of a nanocrystalline diamond layer on single-wall carbon nanotubes. Carbon nanotubes were determined by the intensity of the RBM peak at 190 cm$^{-1}$ and the NCD was visualized according to the lack of RBM and the presence of both $sp^2$ and $sp^3$ peaks with their shoulders. Sample courtesy of Marian Varga from Institute of Physics of the ASCR, Prague.
Graphite

Another allotrope of carbon is graphite. Graphite consists of many graphene layers. Basically the Raman spectrum looks like multi-layer graphene. The G band dominates over the G’ band. Moreover the G’ band changes its shape and becomes more complex. Graphite is used in pencils, lubricants, etc., however, more applications of graphite are nowadays being invented. For example, the combination of graphite with ZnO nanoparticles acts as a disinfection medium [2]. These ZnO/graphite microparticles were analysed with SEM, EDX and Raman spectroscopy.

Fig. 5: Overlay of SEM image and Raman map of CVD graphene (5a), Raman map (5b) and spectra (5c). The colors correspond to the number of layers present on the sample. The ratio between G and G’ confirms that red area is composed of bi-layer graphene – G:G’ ~ 1:1. Green and blue areas – G’.

Fig. 6: A SEM micrograph of ZnO on graphite correlated with an optical image and Raman map. The area in the blue frame was imaged with an optical microscope of CRM and overlaid with Raman map of the G peak intensity. The area in the red frame was correlated with another Raman map. On both Raman maps, the ZnO particles are clearly visible due to the enhancement of the signal. Sample courtesy of Kateřina Dědková from the Nanotechnology Centre, VŠB-Technical University of Ostrava.
Fig. 7: EDX analysis on the sample from Fig. 6.

Fullerenes:

Fullerenes or buckyballs are balls made of carbon atoms only. The properties and sizes are different depending on the number of carbon atoms forming the ball. Fullerenes are used, e.g., in medical science as contrast agents for NMR and X-ray imaging, in pharmaceutics as a drug or gene delivery medium. It

Fig. 8: Correlative imaging of C₆₀ fullerene clusters. Raman intensity map of 1462 cm⁻¹ band (8a) with corresponding Raman spectra (8b). Images of fullerene clusters obtained with the STEM detector (8c), the white light image under the CRM (8d) and TEM micrograph (8e).
is possible to visualize fullerenes and their clusters with electron microscopy thanks to their sizes. In the optical microscope fullerenes with diameters of around 1 nm are invisible. Fullerenes can be easily localized with SEM and their structure, quality or mono-dispersion can be checked in a single click using CRM. In Fig. 8, the well-known fullerene $C_{60}$ is shown in a cluster. The Fig. 8b shows the Raman spectrum dominated by a sharp band at around 1462 cm$^{-1}$, which is a pentagonal pinch mode. This peak reflects the sp$^2$ bonded carbon and the sharp shape and high intensity confirms the highly symmetric molecule of $C_{60}$. If there were any other fullerenes present (such as $C_{70}$ etc.), more bands arising from structure defects and inhomogeneity in C-C bonds would be seen. Using a TEM grid as a substrate is an easy way to perform scanning transmission imaging with a retractable STEM detector in order to locate an area for Raman imaging. Afterwards, TEM imaging was performed as well, which confirmed the presence of $C_{60}$ fullerenes.

### Experimental setup

The present analysis was performed on a RISE microscope comprising a GAIA3 FIB-SEM system or MIRA3 SEM combined with an integrated Confocal Raman Microscope (WITec).

The Raman analysis was acquired with a green laser (532 nm). Two gratings were used, one for imaging in the 0-3500 cm$^{-1}$ range and the second one for more detailed particular regions of the spectra. The second grating is suitable for precise determination of peak position, which is needed mainly for observing internal stresses. A 3D piezo scanner with a precision of a few nm allows the targeting of an image area with 100 nm steps in the X and Y direction. It is capable of imaging with a lateral resolution of 360 nm using a 100x objective. Lateral movements cover an area of 250 x 250 µm$^2$ using the piezo scanner. The acquired Raman data were processed and visualized in the Project Four Plus software from WITec.

### References