Application Note

In situ SEM and Raman Investigations on Graphene

Comparison of graphene, graphene oxide and reduced graphene oxide

We make it visible.

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Comparison of graphene, graphene oxide and reduced graphene oxide

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Date: September 2015

Introduction

Graphene is a one atom thick layer of carbon atoms with a thickness of just 335 pm. Graphene can be modified by means of functionalization and oxidization. Graphene gains for example properties like being soluble in water, which is helpful for further processing in devices. Functional groups can also change the interaction with other materials which is necessary for the integration and interfacing in transistors, solar cells, in batteries and so forth. The controlled modification of graphene is still a challenge and needs evaluation with the scanning electron microscope as well as Raman spectroscopy. In situ Raman and scanning electron microscope (SEM) investigations reveal valid complementary information [1]. Raman spectroscopy is the analytical method of choice for the study of functional groups, defects, edge and grain boundaries, strain and thermal conductivity and doping as well as the quality of reduction process. ZEISS SEMs deliver high resolution images, suitable contrasting methods and a high depth of field. They enable quick and easy differentiation between one layer, two-layer and multi-layer graphene as well as the different graphene types especially when using the Inlens EsB detector [2].

Measurements

Two methods, Raman spectroscopy and SEM, were applied to reveal information about mechanical exfoliated graphene, liquid exfoliated graphene oxide and reduced graphene oxide. In the ZEISS FE-SEM the Inlens SE-detector was used. Here the secondary electrons provide a sufficient signal to image the different types of graphene. This imaging was alternated with Raman analysis, using a Renishaw inVia Raman microscope equipped with a 532 nm laser, and coupled to the FE-SEM, using a Renishaw SEM-SCA interface. Thus, repeatedly, an interesting area was defined on the SEM image and a Raman spectrum generated from exactly the same spot. The SEM-SCA interface is positioned below the SEM's pole piece, so a SEM working distance of 14 mm was used. Thus the SEM image is still visible when the SCA interface is inserted, giving a consistent point of analysis in the SEM.

Challenge

The important peaks in the graphene Raman spectrum are D, 2D and G. The number of layers can be derived from the ratio of peak intensities, 2D / G, as well as the position and shape of these peaks. Using the ratio of peak intensities

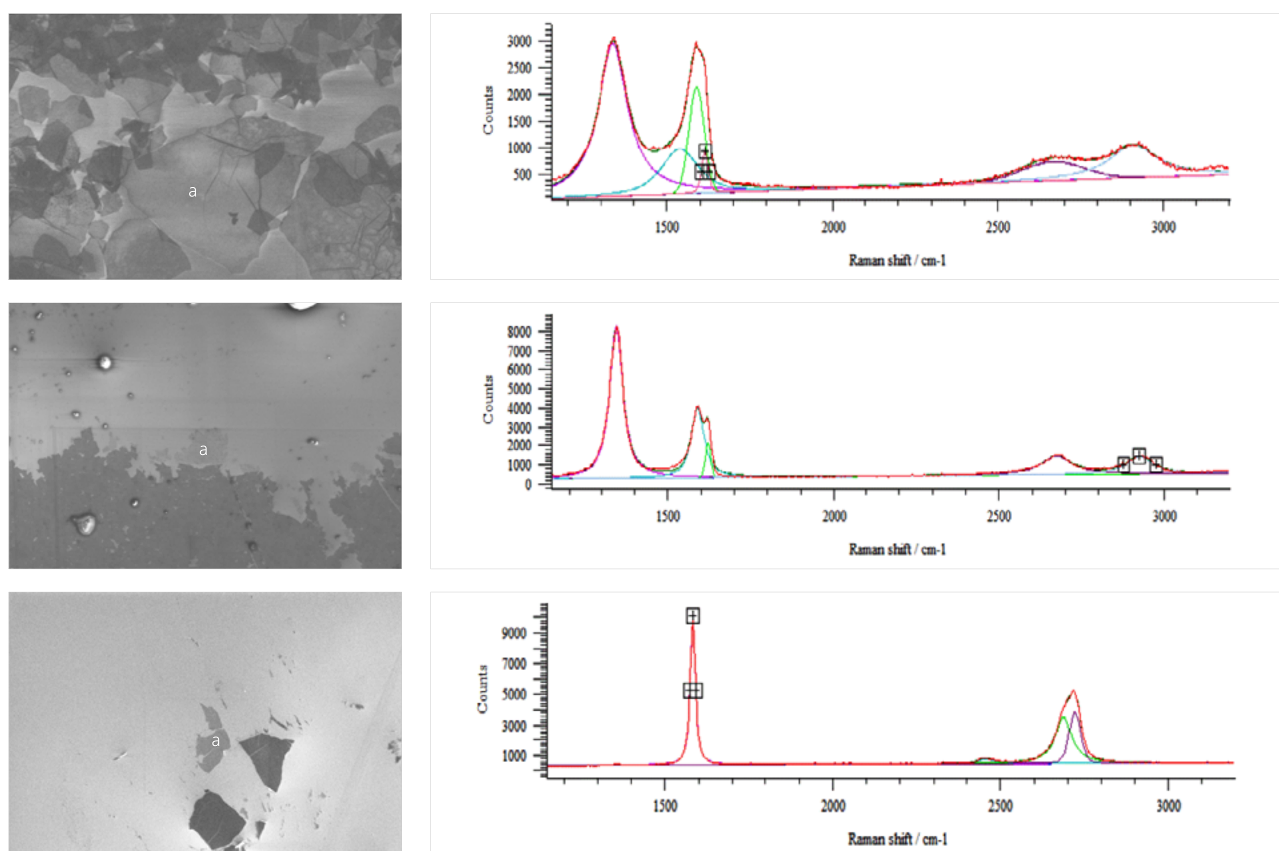

Figure 1 *SEM images and the respective Raman point measurements at point a.*

D / G, one can use Raman spectra to characterize the level of disorder in graphene [3 – 6]. Due to the hexagonal structure of the graphene lattice, ordered crystal edges can have two main structures: zigzag and armchair [7, 8]. Only armchair edges, however, are capable of elastically scattering charge carriers that give rise to the D peak [7, 8]. However, defects cause broadening of these peaks and may cause a decrease of intensity as well as additional peaks in the spectrum, making it challenging to interpret peak positions and ratios [9].

However the Raman I_D / I_G ratio can be used for the estimation of the mean defect distance of densely packed point defects in graphene [10] which was used in this evaluation. The carbon atoms can be sp^3 -hybridized, functionalized, oxidized or missing. The integration of the Raman system into the ZEISS FE-SEM ensured SEM and Raman measurements were co-located, crucial for this work. Prior to the analysis, the electron beam and laser beam of course need to be accurately aligned [1].

Results

Graphene oxide on SiO (Fig. 1, top) shows large flakes up to 30 µm across in the SEM. The GO material consists of randomly aggregated, overlapping, closely associated thin sheets. The layers at the measured spot have a defect density of around 50 %, so every second carbon atom has sp^3 hybridization [10]. The higher the defect density the more sensitive is the material to acceleration voltages. The 3 kV used in this study caused damage of the graphene and probably contributed to the high defect rate. We recommend that a voltage of at least 0.5 kV is used in future.

The reduced graphene oxide (Fig. 1, middle) appears as a nearly closed layer. The Raman spectrum suggests that the rGO has fewer defects. The defect density is around 1 %, so every 100th atom has a defect [11]. Graphene with less defects should be more resistant to electron damage but, as can be seen from the SEM image, again an interaction with the material has probably changed its properties. The me-

chanical exfoliated graphene on silicon oxide (Fig 1., bottom) is basically graphite, not graphene, and does not appear as a continuous layer or overlapping layers but as single flakes. There are at least 10 layers and the defect rate is approximately 0 %.

The SEM image in general exhibit lower resolution and contrast because of the necessary working distance to accommodate the SCA (14 mm) but is easily sufficient for the scientific investigations. Raman bands are not as intense as in a modular Raman spectroscope due to the parabolic mirror and optical fibers. Nevertheless it was easy to interpret the spectra by peak position and peak shape.

Conclusion

The detection of the different graphene states was easily performed using this in situ SEM Raman technique.
The benefit of the integrated system is the combination of high resolution SEM imaging (including alternative detectors), with the chemical analysis provided by Raman spectroscopy. The very accurate co-location of the electron beam and laser spot gives reliable results that are easily interpreted.

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