Raman Imaging enables the identification of molecules, their allotropes and polymorphs, the determination of their orientation, purity and crystallinity, and the detection of strain states.

SEM/EDX allows for the identification of atoms and chemical compounds and the imaging of surface structures.

RISE combines the advantages of both, thus facilitating the most in-depth characterization of the sample.

RISE analysis of polymorphs:
correlating structure with chemical phases

With SEM it is possible to identify materials consisting of different atoms using EDX (energy-dispersive X-ray spectroscopy). It cannot however distinguish between different modifications of chemically identical materials (polymorphs). As the manner of atomic bonding greatly influences the structure and properties of a material, visualizing not only morphology but also identifying its molecular architecture is important. RISE microscopy accomplishes both of these tasks as demonstrated with the analysis of TiO₂ polymorphs (fig. 1). TiO₂ is studied intensively because of its interesting chemical and optical properties and is widely employed in photocatalysis, electrochemistry, photovoltaics and chemical catalysis. It is also used as white pigment in tooth paste, sun screen and wall paint and as anode material for lithium-ion batteries. Depending on the application, one crystalline form or the other gains in importance. TiO₂ occurs in eight modifications, two of which – anatase and rutile – were examined. For RISE microscopy an SEM image taken of a 1:1 anatase/rutile powder mixture was merged with the corresponding confocal Raman image (fig. 1 a, c). It was demonstrated that though the elemental compositions of the modifications anatase and rutile are identical, they can be distinguished from one another by their characteristic Raman spectra at wave numbers between 300 and 800 rel. 1/cm (fig. 1b). Both phases were combined in agglomerates, in which rutile accumulated in larger particles than anatase. To our knowledge this is the first direct visualization of the spatial distribution of anatase and rutile phases of TiO₂ in a mixture of both.

**Fig. 1: RISE microscopy of TiO₂ polymorphs**

Two modifications of TiO₂, anatase and rutile, were mixed 1:1, ground, dissolved in water and imaged with an SEM (a) and a confocal Raman microscope. Both images were then overlaid (c). In the Raman spectrum (b) anatase (blue) can be easily distinguished from rutile (red).

Image parameters: 12 x 12 µm² scan range, 150 x 150 pixels = 22,500 spectra, integration time: 0.037 s/spectrum.
RISE analysis of allotropes: Single-wall carbon nanotubes

Carbon nanotubes are cylindrical allotrope modifications of carbon. Their special properties such as high thermal conductivity make them interesting for applications in electronics, nanotechnology, optics and materials science.

Single-wall carbon nanotubes (SWCNTs) consist of a single atom thick, curved sheet of carbon. Their unique electronic and mechanical properties make them attractive for electronics fabrication.

The Raman spectrum identifies SWCNTs as single-walled by the presence of their characteristic RBM (radial breathing mode) bands at low wave numbers (fig. 2a). The RISE image of SWCNTs embedded in polyethylene (PE) (fig. 2c) was generated by merging the Raman image (fig 2b) with the SEM image.

To explore the 3D structure of the material, 16 Raman images were taken in the z-direction intervals of 1 µm (fig. 3a). From these data a 3D image was compiled. It illustrates that the SWCNTs lie on top of the PE matrix (fig. 3b).

Fig 2: RISE imaging of SWCNTs on a PE filter
Characteristic Raman spectra of SWCNTs and PE (a), color-coded Raman image (b) and RISE image (c).
Image Parameters: 150 x 150 µm² scan range, 80 x 80 pixels = 6,400 spectra, integration time: 60 ms/spectrum.
PE (red), SWCNTs (green), SEM image (grey).

Fig 3: Three-dimensional RISE imaging of SWCNTs on a PE filter
The confocal setup of the Raman microscope allows the acquisition of 3D Raman images by moving the focus of the objective through the sample. For this picture (b) 16 equidistant Raman images were taken while the focus was shifted by 1 µm for each image. The individual images are displayed as RISE images in (a). The compiled 3D Raman image of the analyzed sample area shows the SWCNTs located on the top of the PE filter (b).

Image parameters: 200 x 200 µm² scan range, 70 x 70 pixels = 4,900 spectra, integration time: 0.037 s/spectrum.
PE (red), SWCNTs (green), SEM images (grey).
RISE microscopy of 2D materials

Thin-layered or single layer materials, defined as 2D materials, have recently attracted enormous research interest due to their special electronic and optical properties which differ significantly from that of their bulk precursors. Inspired by progress in graphene research, other mono-layered materials such as hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMDs) have also received widespread attention. Recent work has shown that exfoliated monolayer molybdenium disulfide (MoS$_2$) is a 2D direct bandgap semiconductor indicating that the material is suitable for optoelectronics and energy harvesting. Bulk MoS$_2$ however is an indirect bandgap semiconductor. Thus detailed knowledge of the structures and features of grains and grain boundaries are essential for understanding and exploring the materials’ properties and its further applications. Here we present with MoS$_2$ and tungsten disulfide (WS$_2$) that RISE microscopy reveals structure as well as crystalline and exciton dynamics of thin-layered TMDs.

MoS$_2$ twin crystals

CVD grown monolayers of TMDs form triangular two-dimensional crystals. Twin crystals of MoS$_2$ on SiO$_2$/Si appear in the SEM image as star-shaped forms (fig. 4a). The Raman spectra of these 2D crystals show the characteristic E$_{2g}$ and A$_{1g}$ Raman band modes of MoS$_2$ (fig. 4b). With an increasing number of layers the two Raman bands drift apart due to inter-layer and in-plane vibrations.

At the grain boundaries the Raman bands not only show shifts, but additional bands also appear, indicating defects or misaligned 2D crystals. They probably result from adjacent crystals colliding out at their boundaries. The overlapping boundaries identified by Raman Imaging correlate perfectly with the dark edges visible in the SEM image.

In situ modification of WS$_2$

In addition to characteristic Raman spectra TMDs show strong photoluminescence (PL) in the visible range making them promising materials for optoelectronics. PL emission is attributed to excitation recombination. The PL - therefore the optical properties - of WS$_2$ can be modified using the electron beam of the SEM.

A monolayer WS$_2$ triangular island shows photoluminescence at roughly 640 nm wavelength (fig. 5a, b). Defined 2x2 $\mu$m$^2$ areas of this WS$_2$ crystal were then scanned at increasing electron acceleration voltages in the SEM. PL was then measured again (fig. 5b, d). Surprisingly PL changed as a function of the previously applied electron acceleration voltage. The most distinct change in PL was seen at 1.2 kV, most likely because at higher kV electrons were being absorbed while at lower kV they were totally reflected. As PL is a measure of optoelectronic properties of TMDs, RISE microscopy enables their modification and analysis in situ. After releasing the sample from vacuum this effect may disappear.