application note

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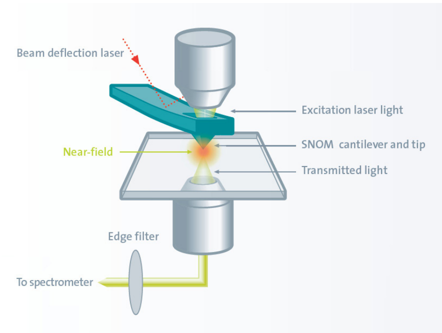
Near-field Raman: Imaging Beyond the Diffraction Limit

Introduction

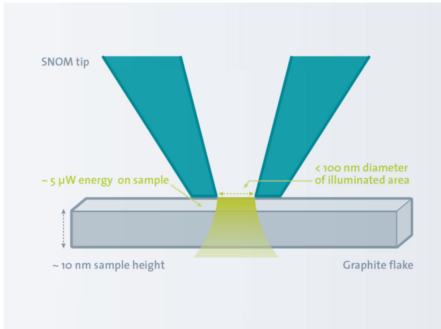
Specialized applications can require Raman imaging capability with a resolution below the diffraction limit of classical optics (< 200 nm). Near-field Raman imaging is a correlative microscopy technique that links chemical Raman information with data acquired through high-resolution Scanning Near-field Optical Microscopy (SNOM). Typically, lateral resolutions of less than 100 nm can be achieved. The combination of a high-throughput spectroscopic system and the cantilever-based SNOM technique provides unrivaled sensitivity and imaging quality in one microscope setup. Microscope systems that combine several measurement techniques offer a more comprehensive characterization and allow the strengths of the individual approaches to complement each other.

Near-field Raman Imaging Principle

The excitation laser light is focused through the SNOM-tip resulting in a "near-field" (evanescent field) on the far side of the aperture. While the sample is moved with a piezo-driven scan stage, the transmitted light is spectroscopically acquired point by point and line by line in order to generate a hyperspectral image. The optical resolution is therefore limited only by the diameter of the aperture (< 100 nm). Using a beam deflection setup, as in AFM contact mode, ensures that the cantilever remains in contact with the sample. Therefore the topography can be recorded simultaneously with the near-field Raman measurement.



Working principle of WITec near-field Raman imaging



Parameters of the near-field Raman measurement

Experimental Results

Raman imaging has been proven useful to study spatially resolved chemical and physical features of graphene. It has been shown that strain variations at the nanoscale effect graphene's quality (1, 2, 3)

Here, an exfoliated graphite flake sample was investigated with near-field Raman microscopy. Fig. 1 shows the sample illuminated by white light. At one point a reference Raman spectrum was acquired through the SNOM tip with 5 sec. integration time per spectrum (Fig. 2). The Raman signal of the graphite flake was analyzed in terms of the integrated intensity of the G-Band (near 1600 rel./cm) along a line depicted in red in Fig. 1. The width of the graphite flake can be determined by plotting the increase in the intensity relative the distance. The complete length of the line trace was 20 µm with 400 measurement points and 1 sec. integration time per spectrum (Fig. 3). Single measurement points can be distinguished through a line-trace zoom-in on the edge of the graphite flake. A lateral resolution of < 100 nm of the near-field Raman technique can thus be established (Fig. 4). Fig. 5 shows the topography image of the exfoliated graphite recorded at the same time as

The WITec alpha 300 RS Microscope

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the near-field Raman measurement. The corresponding topography curve along the blue line shows a height of ~10 nm and the small size of the graphite flake (Fig. 6). With the same scan a near-field Raman image of the G-Band intensity can be acquired (Fig. 7). Due to the extreme sensitivity of the measurement technique, a laser power of approx. 5 µW at the sample and an illuminated area of less than 100 nm was sufficient for image generation. At each image pixel a complete Raman spectrum was acquired with only 0.53 sec. integration time per spectrum. The scan range was 5 µm x 1.7 µm and the image size 100 x 35 pixels. The G-band intensity along the red line reveals the measurable signal variations between the small sample and the substrate (Fig. 6).

Summary and Conclusion

WITec's near-field Raman imaging systems enable the generation of Raman images with an optical resolution below the diffraction limit. The distribution of the chemical and molecular components can be imaged at very high resolution. The throughput and optimized detection setup allow very small sample volumes to be analyzed at excitation energies that avoid sample damage. Topography is also acquired simultaneously with the hyperspectral image. Near-field Raman imaging pairs unrivaled sensitivity with the ease-of-use and reliability of the established cantilever SNOM probe technique within a single microscope system and is suitable for all fields of application in which a detailed sample characterization is required.

Literature

1) K. S. Novoselov et al., *Nature* 2012, 490: 192.
2) A. Ferrari et al., *Phys. Rev. Lett.* 2006, 97: 187401
3) C. Neumann et al., *Nature Comm.* 2015, 6: 8429.

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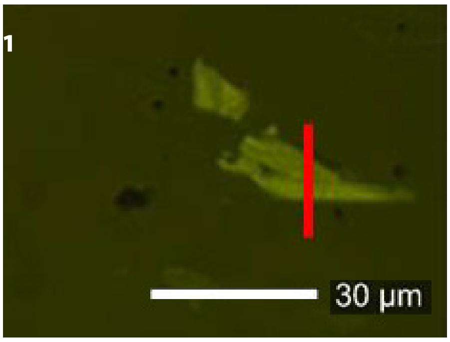

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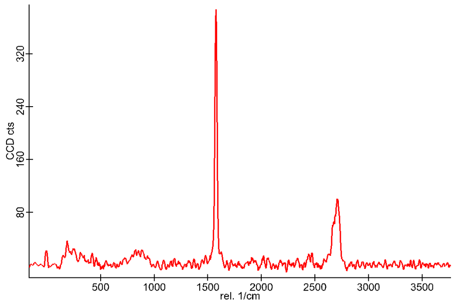

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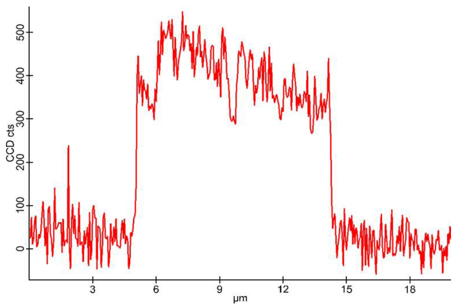

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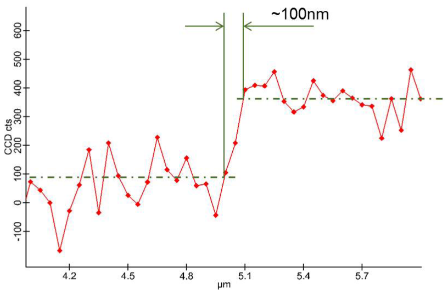

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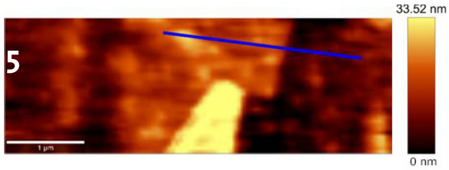

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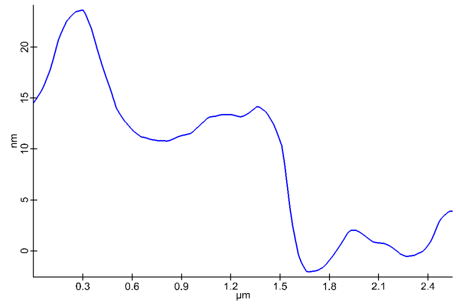

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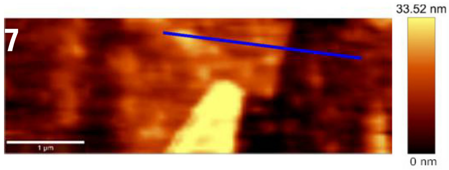

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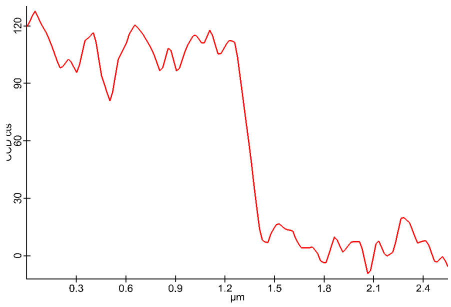

Near-field Raman measurements of exfoliated graphite

1. Video image of an exfoliated graphite flake
2. Raman spectrum acquired though the SNOM-tip
3. Line scan showing integrated intensity of the G-Band
4. Line trace zoom-in
5. Topography image of exfoliated graphite (scale bar = 1 µm)
6. Topography curve
7. Near-field Raman image (scale bar = 1 µm)
8. G-band intensity.