application note

Lise-Meitner-Straße 6, D-89081 Ulm, Germany
Tel. +49 (0) 731 140 700, Fax. +49 (0) 731 140 70200
www.witec.de, info@witec.de

WITec
focus innovations

Imaging of a Diamond Film, Carbon Nanotubes and Graphene with Confocal Raman and Atomic Force Microscopy

CVD Diamond

Raman Imaging of Diamond Film deposited on Silicon

In the following study, a polycrystalline diamond film deposited on Silicon was investigated. A 50 µm x 50 µm area using 256 x 256 pixels (= 65 536 spectra) with an integration time of 50 ms per Raman spectrum was analyzed. For excitation and detection a 100X objective with a 0.9 numerical aperture (diffraction-limited spot size 360 nm, pixel size 195 nm) and 10 mW of power from a frequency-doubled NdYag laser operating at 532 nm was used. A 300 mm imaging spectrometer equipped with a 1800 lines/mm grating and a back-illuminated CCD camera captured the spectra in under an hour. From this multispectrum file, the rest of the images shown in this example were calculated. Each image took only a few seconds to be calculated. Fluorescence due to impurities is present in many parts of the sample, but strongest at the grain boundaries. To generate the image, the marked area from about 1000 1/cm to 1080 1/cm (see figure 1) was integrated. Even if the diamond line is included in the integration area, however, the image looks pretty much the same, because fluorescence dominates the spectrum. The quality of the diamond film can be examined by integrating over the diamond line in each spectrum, corrected for the fluorescence background (see figure 2). As one can see, the Raman intensity (sum of the Raman scattered signal) is relatively homogenous; background subtraction removes the fluorescence signal.The width of the Raman line shows strong local variations (see figure 3). The bright areas correspond to areas with small linewidths, while the dark areas show broadened Raman lines. The color scale is chosen such that areas appear white where the FWHM of the diamond line is below 5 1/cm, while the dark areas correspond to linewidths larger than 15 1/cm. The FWHM in all spectra varies from about 5 1/cm to more than 60 1/cm. As can be seen, there are areas containing very sharp lines indicating pure diamond. The small spot size of the excitation laser allows us to detect these variations; a measurement with a laser having a 50 µm spot would deliver an inhomogeneous broadened spectrum. Stress and strain in the material affects the Raman signal by shifting the peaks to lower wavenumbers (tensile strain) or higher wavenumbers (compressive strain; (see figure 4). The corresponding spectra have been obtained by integrating over all spectra in the red, green, and blue areas, respectively. The blue spectrum shows a shift of 5.4 1/cm to smaller wavenumbers, while the red spectrum is shifted by 4.2 1/cm to larger wavenumbers.

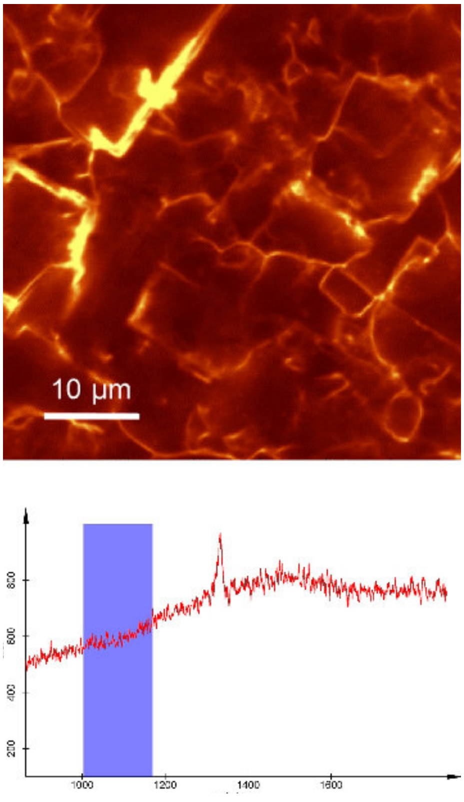


Fig. 1: The fluorescence background in this image is quantified by integrating the signal over the marked area from 1000 to 1080 1/cm; this area does not contain the Raman signal. Note the concentration of fluorescence at the grain boundaries.)

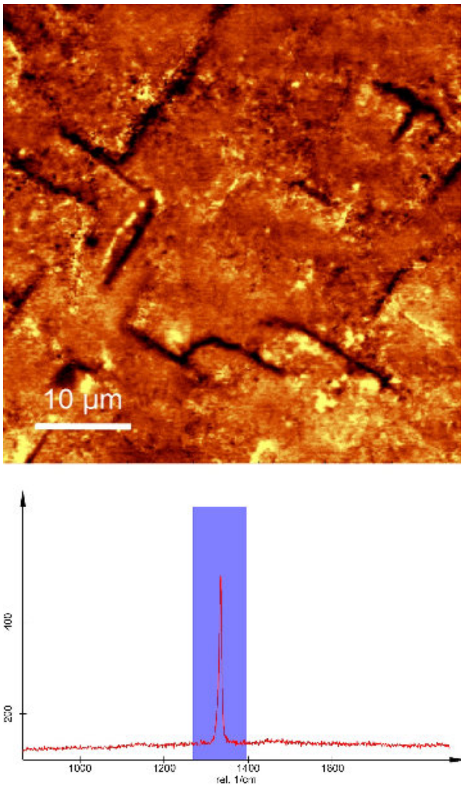
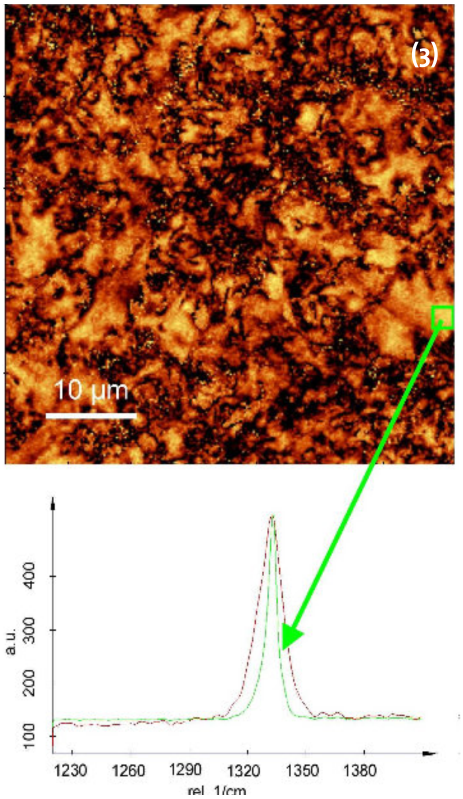


Fig. 2: Raman signal of the diamond line obtained by integrating over the marked area. The fluorescence is not visible because the background was subtracted in each spectrum. Note that not all grain boundaries (dark lines in this image) show a strong fluorescence.



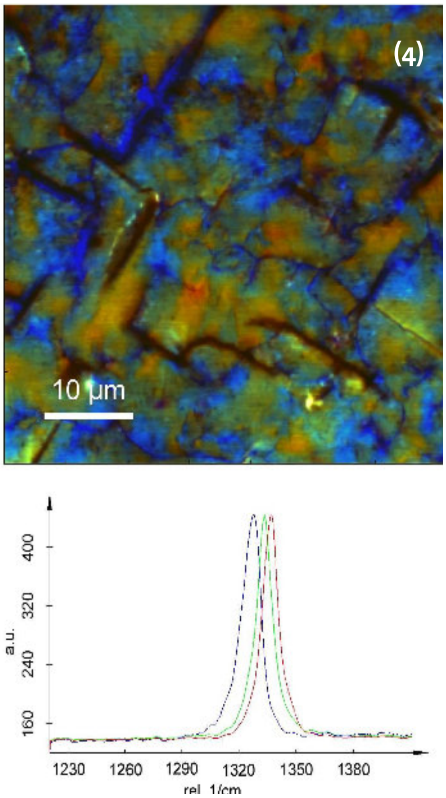


Fig. 3: In this image, areas where the FWHM of the diamond line is below 5 1/cm appear white, while the dark areas correspond to linewidths larger than 15 1/cm. The FWHM in all spectra varies from about 5 1/cm to more than 60 1/cm. The green spectrum has a FWHM of 5.9 1/cm and was obtained by integrating over all spectra in the green box, whereas the red spectrum is the average over all 65 536 spectra and has a FWHM of 15.7 1/cm.

Fig. 4: Stress in the diamond film, color coded from red (compressive strain, peak position above 1333 1/cm) to blue (tensile strain, peak position below 1333 1/cm).

Carbon Nanotubes

Wavelength dependent confocal Raman Imaging

Raman signals of Carbon Nanotubes (CNTs) show dependence of the exciting laser wavelength. Raman spectroscopy on Singlewall Carbon Nanotubes (SWNT) is a resonant Raman scattering process of single photons, providing insight into the photonic and electronic structure of one-dimensional carbon molecules in their bonding environment. The radial breathing modes (RBM), can be found at low wavenumbers (120-350/cm) and are the result of coherent vibration of carbon atoms in the radial direction. The position of the RBM provides information on the diameter of the nanotube, the intensity of the peak elucidates the electronic structure of individual tubes, the combination of both parameters then allows the characterization of the structure of SWNTs. Like all resonant processes, the intensity of the Raman scattering from SWNT strongly depends on the wavelength of the excitation laser. This study shows results from one and

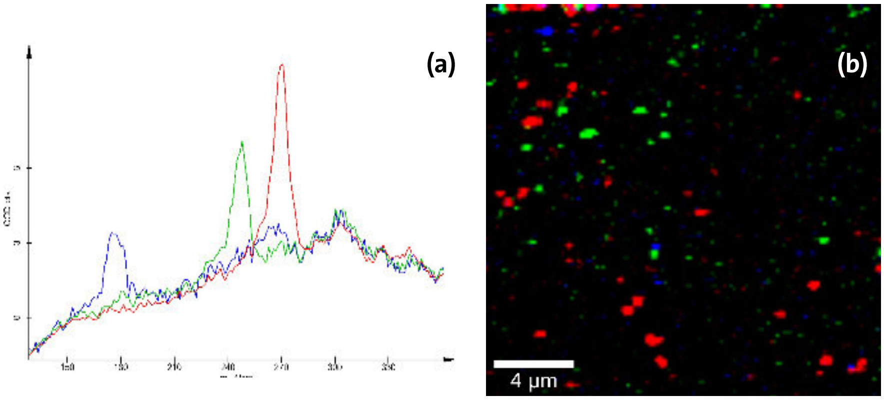


Fig. 5 + 6: Confocal Raman Imaging on Carbon Nanotubes, Scan Range: 20x20µm, 120x120 pixels = 14400 spectra, 92 ms/spectrum, 1800 g/mm grating. **5 a:** Typical spectra @ 514 nm; **5b:** Distribution of corresponding nanotubes on the silicon substrate the same sample area analyzed with 514nm (Fig. 5a and b) and 633 nm (Fig. 6a and b) excitation wavelength,respectively. Using a 514 nm excitation, SWNT with a diameter ranging from 0.9 nm (Fig. 5a red spectrum) to 1.42 nm (Fig. 5a blue spectrum) are detected, their distribution is shown color coded in Fig. 5b. Application of a 633 nm excitation laser, SWNT are detected with structural properties fulfilling the resonance conditions. (Fig. 6a and b)

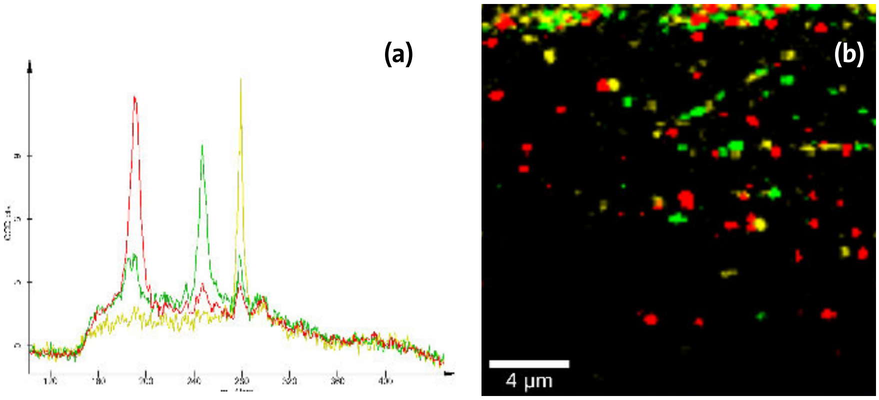
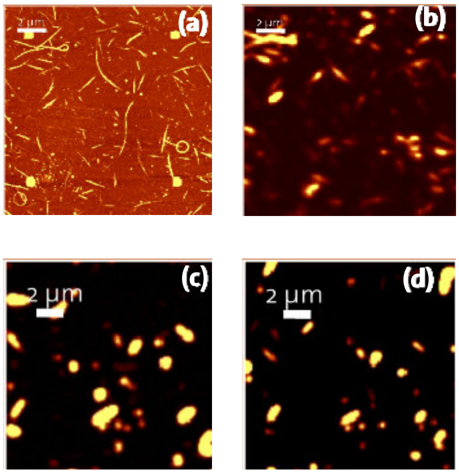


Fig. 6a: Typical spectra @ 633 nm; **6b**: distribution of corresponding nanotubes.

Combined Raman and AFM Imaging of individual Bundles of Single-wall Carbon Nanotubes

In this study. Single-wall Carbon Nanotubes (SWNTs) were investigated with Confocal Raman Microscopy and Atomic Force Microscopy using only one single instrument. Laser vaporization-grown SWNTs were deposited on a Si substrate using a spin-coating technique. Fig. 7a shows an AFM measurement of this sample with a scan size of 14 µm x 14 µm and 256 x 256 pixels. Fig. 7b shows the corresponding measurement in the Spectral Imaging Mode of the alpha300 R on the same sample position. In this mode a complete spectrum is obtained at every pixel. Scan range was also 14 µm x 14 µm with 150 x 150 pixels (= 22500 spectra) and an integration time of 50 ms. The image was obtained by integrating over all Raman lines. Using both images the spectral data can be clearly linked to dedicated nanotubes observed in the AFM image. The orientation of the tubes can be determined by measuring the intensity of the Raman spectrum depending on the polarization. The signal is always strongest when the laser light is polarized along the nanotube axis. Therefore two measurements were performed, one initial measurement, and another with the sample rotated by 90 degrees (compare fig. 7c and fig. 7d). Depending on the polarization of the incident light, different carbon nanotubes are visible. A detailed evaluation of the obtained spectral data of one carbon nanotube is shown in Fig. 7e. Different Raman lines are visible. Each part of the spectrum, the radial breathing mode (RBM) at around 180/cm, the D-band at around 1330/cm, the G-band at around 1580/cm, second-order modes and the G`-band can be used to differentiate properties of carbon nanotubes.



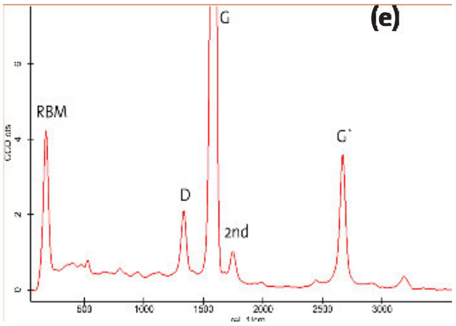


Fig. 7a: AFM measurement of SWNTs deposited on a Sisubstrate, 14 µm x 14 µm; **7b**: Confocal Raman measurement, on the same sample position, 14 µm x 14 µm; **7 c + d**: Different carbon nanotubes are visible, depending on the polarisation of light. Polarisation plain in fig. d is rotatet by 90 degrees; **7e**: Typical Raman spectrum of a carbon nanotube.
Samples courtesy of Dr. D. B.Geohegan, Prof. A. A. Puretzky and Dr. D.W. Austin, Oak Ridge National Laboratory, USA

Graphene

Single and multi-layers investigations of graphene

Graphene is an atomic-scale honeycomb lattice consisting of carbon atoms. For the evaluation of the properties of graphene and the differentiation of single layers from multi layers, confocal Raman Imaging in combination with AFM is an effective tool. In the following study both Raman and AFM are used to investigate a graphene flake. Fig 8a shows the topography image acquired with the AFM option of the alpha300 microscope series. The cross section along the indicated line in the image reveals a single graphene layer with a height of 0.3 nm followed by a bi-layer with a hight of 0.6 nm (Fig. 8c top). On the same sample position, a confocal Raman imaging measurement was performed. The image was generated by evaluating the intensity of the G-band (Fig. 8 b). Along the same line of the cross section in the topography image, the intensity of the G-band signal is represented as shown in Fig 8b (bottom). A clear differentiation between a single graphene layer and a double layer is evident.

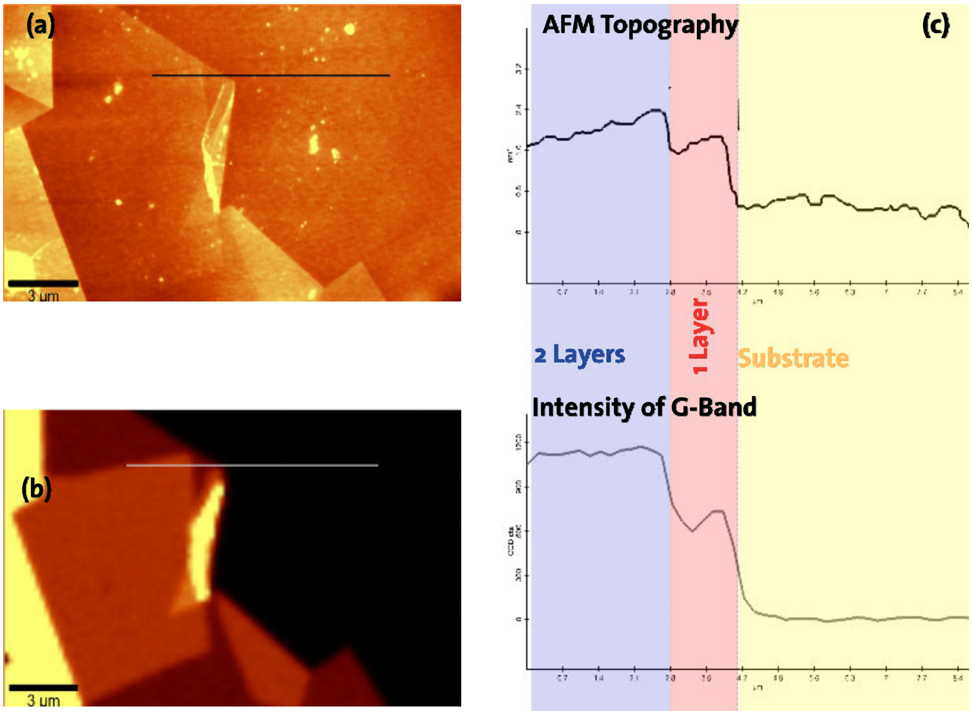


Fig. 8a: AFM Topography image (AC-mode) of graphene, a cross section was plotted at the indicated line; **8b**: Raman image of the same sample area evaluating the intensity of the G-band **8c:** Topography cross section and intensity of G-band along the indicated lines in fig a) and b).

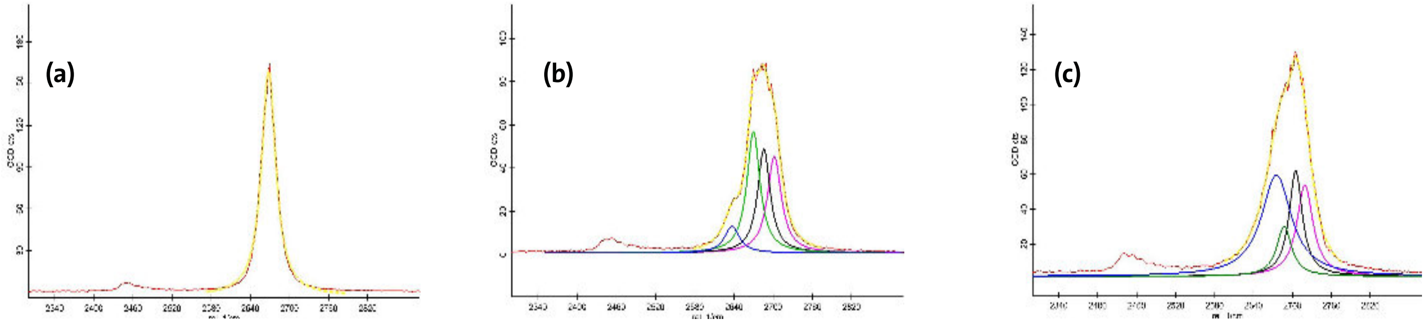


Fig. 9: Line shape of the D-band including fitting results: **a)** Lorenzian curve fits for single layer graphene**, b)** double layer graphene **c:** multi-layer graphene.

Fitting of Multi- and Single Layered Graphene

The shape of the D*-Band in Graphene is strongly influenced by the position of the Raman band. There is a strong change when observing the edge of a flake or a step from one layer height to the next. However, as shown in various publications (i.e. Graf et al* and Hyunseob Lim et al**), the number of layers also has a strong influence on the line shape of the D* band. Fig 9 a, for example, shows the shape for a single layer. Here a single line can easily be seen, with a single, Lorenzian curve fitted to the experimental data. Fig 9b shows the case for a double layer system in which the D*-peak can be fitted well with four Lorenzian shaped curves, which was also shown by Graf et al. Fig 9 c finally shows the case for a multi-layer graphene where again four Lorenzian curves are used to fit the experimental data but with now much different relative intensities than was the case for the two-layer system. Such fits can be performed at each data point using the WITec Project Plus software and the peak properties (i.e. intensity, width, position) can be displayed as images.

References

** D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, and L. Wirtz; "Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene"; Nano Lett., 2007, 7 (2), pp 238–242*

*** Hyunseob Lim, Ji Sook Lee, Hyun-Joon Shin, Hyeon Suk Shin and Hee Cheul Cho; "Spatially Resolved Spontaneous Reactivity of Diazonium Salt on Edge and Basal Plane of Graphene without Surfactant and Its Doping Effect ";Langmuir, 2010, 26 (14), pp 12278–12284*