High Resolution Imaging and Chemical Characterization of Heterogeneous Materials

A thorough knowledge of structural and chemical properties is essential for the fields of nanotechnology and materials science, leading to a growing demand for characterization methods for heterogeneous systems on the nanometer scale. However, certain properties are difficult to study with conventional characterization techniques due to either limited resolution or the inability to chemically differentiate materials without inflicting damage or using invasive techniques such as staining. Atomic Force Microscopy (AFM) and Confocal Raman Microscopy (CRM) can effectively overcome these fundamental obstacles. Using AFM, the topography of a sample can be imaged at the highest resolution, revealing details of the surface structure. If combined with Confocal Raman Microscopy, chemical information can be directly linked to this structural AFM information. Both techniques require minimal sample preparation, if any.

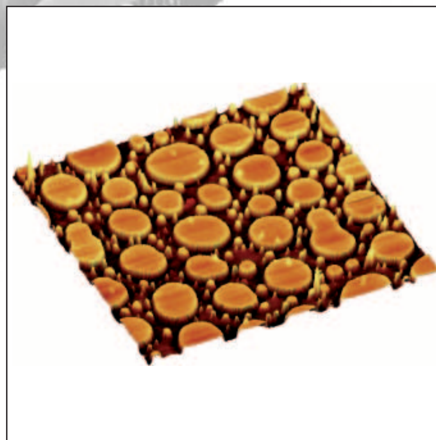

Fig. 1a:
AFM image of a PMMA-SBR polymer blend, spin coated on glass. 20 x 20 µm scan, 30 nm topographic scale.

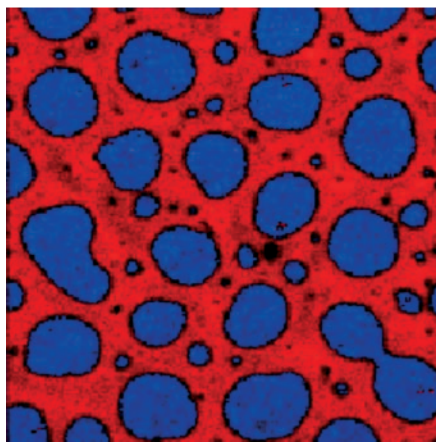

Fig. 1b:
Raman image of the PMMA-SBR polymer blend. The PMMA is color-coded blue, whereas the SBR is shown in red. Imaging parameters: 200 x 200 spectra, 70 ms integration time per spectrum.

Confocal Raman Microscopy

Raman spectroscopy is a well-established, nondestructive analysis technique that provides detailed chemical information about the molecules involved in the scattering process. By integrating a sensitive Raman spectrometer within a state-of-the-art microscope setup, Raman microscopy with a spatial resolution down to 200 nm laterally and 500 nm vertically can be achieved using visible light excitation.

Using the confocal arrangement in which a pinhole is placed in the focal plane of the microscope to reject out-of-focus light, even depth profiling and 3-D imaging is possible if the sample is transparent. With this technique it is not only possible to obtain Raman spectra from extremely small sample volumes (down to 0.02 μm^3), but also to collect high resolution Raman images.

To obtain a Raman image, the CCD camera of the spectrometer is used to acquire a complete Raman spectrum at a user-defined number of image points per line, while the sample is scanned line by line. The number of image points (spectra) is limited only by the memory of the computer. A typical image consists of 10,000 (100 x 100) to 65,536 (256 x 256) spectra. From this multi-spectrum file, an image is computed by e.g. integrating over a certain Raman line in all spectra. The intensity calculated from each spectrum is color-coded and determines the brightness of the appropriate pixel in the image. As all spectra are stored in memory, a large variety of properties such as peak-width, center of mass or peak position of certain Raman lines can be calculated from a single measurement and displayed as images.

To collect a Raman image in a reasonable amount of time, special care must be taken to optimize the optical throughput and sensitivity of the setup. As a Raman image consists of several thousand pixels (spectra), the integration time per pixel (spectrum) must be as short as possible. In an optimized setup, the acquisition time per spectrum is typically less than 100ms for most samples, so that Raman images of 100 x 100 pixels are obtained in little more than 15 min.

Atomic Force Microscopy

By adding Atomic Force Microscopy (AFM) to the imaging capabilities, the optical diffraction limit can be overcome and a new dimension in lateral and topographical resolution is achieved. In AFM, the surface topography of a sample is probed with an extremely sharp tip at the end of a small cantilever, delivering nm precision in the lateral dimension, and sub-nm resolution in the vertical dimension. The topographic structures observed with the AFM can then be linked to and compared with the chemical information obtained by the Confocal Raman Microscope. The advantage of combining these techniques in a single instrument is the possibility of switching between the different observation modes with negligible lateral shift. If two separate instruments have to be used, finding the same sample position again can be very time consuming, if not impossible, without surface markers. In the modular WITec Microscopy Systems, a special objective is available that allows the mounting of a cantilever to perform an AFM measurement with the highest resolution. Switching between Confocal Raman and AFM is possible by simply rotating the objective turret.

Phase separation

As an example, phase separation of a spin-coated film of a polymer blend PMMA-SBR (poly-methyl-methacrylate – styrol-butadien rubber) on glass is studied with a combination of AFM for ultimate resolution and CRM for chemical information. The topographic image obtained with the AFM (Fig. 1a) reveals round features 20–30 nm in height with diameters varying from 150 nm to 4 µm, surrounded by a network-like structure. From the AFM measurements, the phase separation can be clearly seen, but it can not be determined whether or not the phases are completely separated and which material forms the round features and which the network. A Raman image of the structure (Fig. 1b) clearly reveals the chemical structure of the phases. The Raman image was obtained using a 100x, NA=1,25 oil immersion objective with 532 nm excitation. The image consists of 200 x 200 spectra taken with 70 ms integration time per spectrum. One can clearly see the complete phase separation of the polymers. It is also obvious that the PMMA forms the round, flat structures while the rubber is present in the network structures.

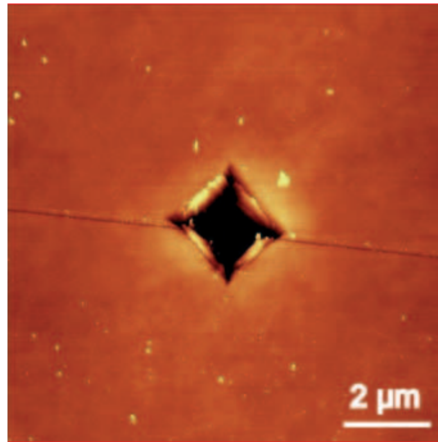

Fig. 2a:
AFM measurement of a Vickers indent into silicon. The indent with 2.75 µm diagonal and 210 nm depth was performed with a force of 50 mN. Scan area: 10 µm x 10 µm. The topographic scale in the image is only 10 nm.

Stress measurements

Fig. 2a shows an AFM measurement of a Vickers indent into Si. A Vickers tip is used for hardness testing. By measuring the diagonal size of the indent applied with a known force, the hardness of the sample can be determined. Usually, the size of the indent is measured with an optical microscope. However, if the hardness of a thin coating has to be measured, the indent should not be deeper than approximately one tenth of the thickness of the coating. Otherwise, the substrate influences the result. For thin coatings, the indent must be extremely shallow and therefore small, which means that size measurements with an optical microscope can be very inaccurate. In this example, the Vickers indent was performed with a force of 50mN and produced an indent with 210 nm depth and 2.75 µm diagonal size as extracted from the AFM measurement. A close inspection also reveals a small anisotropy of the indent, which is due to the limited precision of the shape of the Vickers diamond. The indent produces a stress field that was imaged with Raman spectroscopy. If e.g. a compressive stress is applied to a sample, the binding distance of the atoms is reduced, resulting in a higher vibrational frequency. The Raman line of this vibration is therefore shifted to higher frequencies. Accordingly, a tensile strain shifts the Raman lines to lower wavenumbers. The image shown in Fig. 2b was calculated by determining the peak position of a parabolic fit of the Si-Raman line of each measured spectrum. The scan area is 10 µm x 10 µm and 100 x 100 = 10,000 spectra were taken with an integration time of 70ms per spectrum. For excitation and detection, a 100x, NA=0.9 objective (diffraction-limited spot size 360 nm, pixel size 100 nm) and about 10mW of power from a frequency doubled Nd:YAG laser at 532 nm were used. The complete image aquisition took less than 17 min.

As expected, the stress field as shown in Fig. 2b has the symmetry of the Vickers pyramid. The tensile strain appears along the edges of the pyramid, while the compressive strain appears at the flat sides.

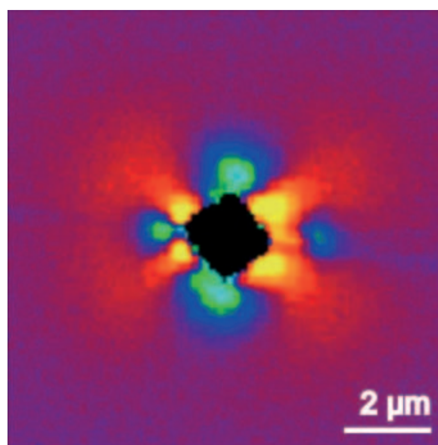

Fig. 2b:
Raman image of the same scan area as in Fig. 2a. The image was calculated by determining the peak position of a parabolic fit of the Si-Raman line of each measured spectrum.
Imaging parameters: 100 x 100 spectra, 70 ms integration time per spectrum. Excitation: 10 mW at 532 nm, objective: 100x, NA=0,9.

Summary

As shown in the examples, Confocal Raman Microscopy is a powerful tool for the analysis of heterogeneous samples on the sub-µm scale.

If the Confocal Raman Microscope is combined with an Atomic Force Microscope, the lateral resolution is extended to the nanometer scale and the ultimate resolution of the AFM can be combined with the chemical information obtained by the CRM. The combination of both methods is an ideal tool for the growing field of nanotechnology and materials research.

Harald Fischer
Witec GmbH
Hörvelsinger Weg 6
89081 Ulm
Germany
Tel. +49 700 94832-366
Fax +49 700 94832-329
harald.fischer@witec.de
www.witec.de

Dr. Olaf Hollricher
Dr. Ute Schmidt