

## Application Note AN # 523

# Combining Atomic Force Microscopy with Polarized Raman Microscopy

### Introduction

Atomic force microscopy is a powerful tool for the characterisation of surfaces down to the molecular and even atomic level. It is based on a microscopically small tip which is fixed to an oscillating cantilever. The tip is moved across the sample to obtain topographical information.

Since the invention of atomic force microscopy (AFM) by Gerd Binnig et al. in 1986 [1], this imaging technique has developed from the area of fundamental research into a routine tool for the investigation of surface structures. Raman microspectroscopy is recognized as a versatile tool for molecular structure analysis in many fields including materials science. More recently AFM and Raman microscopy were combined to allow morphological/topographical as well as chemical mapping of the same sample area. Raman microscopy ideally complements AFM imaging since it is adding molecular spectroscopic information.

For example Raman microspectroscopy and AFM can provide better understanding of the interaction between epoxy polymer films on a metal substrate. The adhesive interaction between the epoxy polymer and the metallic substrate depends on the molecular structures formed within the

nanoscale interphase region between polymer and metal substrate. Epoxy-based polymers are often applied onto metallic substrates and cured to obtain bonded joint components or painted surfaces.

### Experimental

The integration of an AFM into the framework of a Raman spectrometer which itself is coupled to an optical microscope provided some interesting challenges. In order to maintain the excellent noise level of better than 0.1 nm in z-direction of the AFM the rigidity and physical size of the optical Raman microscope was of crucial importance.

Bruker has developed a compact Raman microscope/AFM system which is based on the Raman microscope SENTERRA and the platform of the N8 NEOS, a benchtop AFM system for use with optical microscopes [2]. Optimum stability was achieved by mounting the Raman microscope SENTERRA on the N8 NEOS granite base (Figure 1). The entire system is placed on an actively damped tabletop with noise isolating enclosure (not shown).

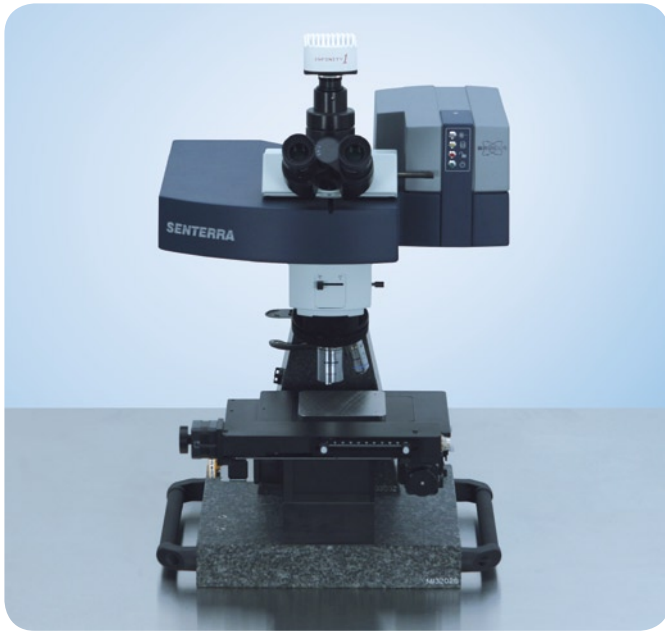


Figure 1: SENTERRA Raman Microscope with AFM N8 NEOS.

Whilst Raman mapping and optical visualisation is realised using the included confocal optical microscope and integrated Raman spectrometer, topographical images are obtained on the identical sample site by the AFM N8 NEOS without sample translation. Sample analysis is further facilitated by software controlled switching between AFM and Raman mode as well as by fast change of the AFM tip in case of necessity (see Figure 2).

The N8 NEOS AFM/SPM uses fiber-optic interferometry for the detection of the cantilever deflection. A cantilever exchange is easily done without alignment or manual adjustment.

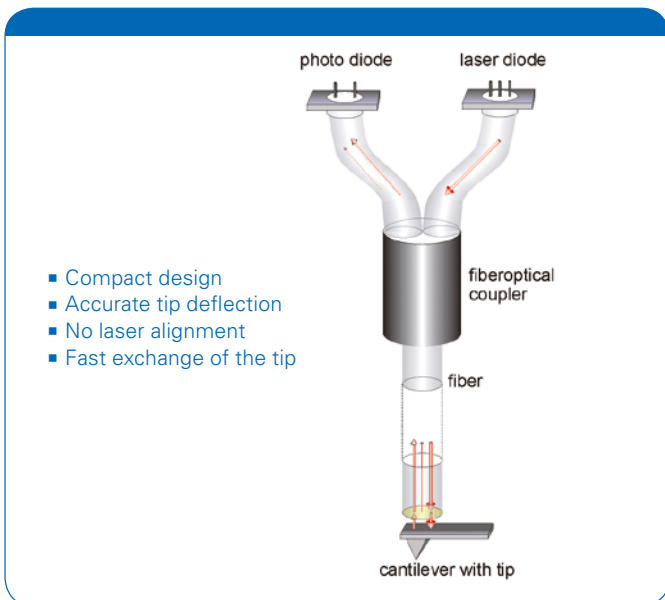


Figure 2: Interferometric detection of cantilever deflection.

## Application example

Applications of the combined AFM/Raman system are ranging from the investigation of semiconductors, composites, defect inspection, nanostructures of various materials including carbon nano tubes and graphene monolayers.

For example AFM/Raman reveals detailed information about the nanostructure of an epoxy polymer which is deposited on a metal substrate. Figure 3 shows the topographical AFM image of a polymer with nanoscale thickness on an aluminium substrate.

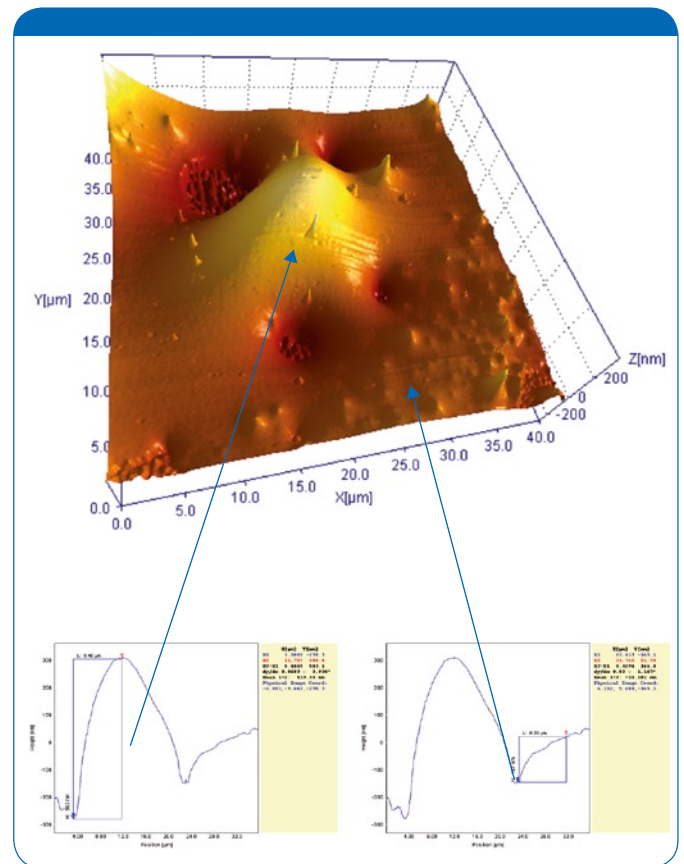


Figure 3: 40  $\mu\text{m}$  x 40  $\mu\text{m}$  topographical AFM image of the epoxy nanostructure on an aluminum substrate with height analysis.

Besides the topographical information AFM can deliver also insight to other properties such as adhesion and viscoelasticity. On the molecular level Raman microscopy can add further valuable information e. g. about the steric orientation or crystallinity.

Figure 4 shows two typical Raman spectra which were recorded at different locations of the 40  $\mu\text{m}$  x 40  $\mu\text{m}$  area of interest. Maximum intensity of the phenyl ring vibration at 1004  $\text{cm}^{-1}$  was found in the flat regions whereas weaker relative intensities to the reference Raman line of the non-aromatic vibration at 1114  $\text{cm}^{-1}$  could be observed in the region of higher thickness.

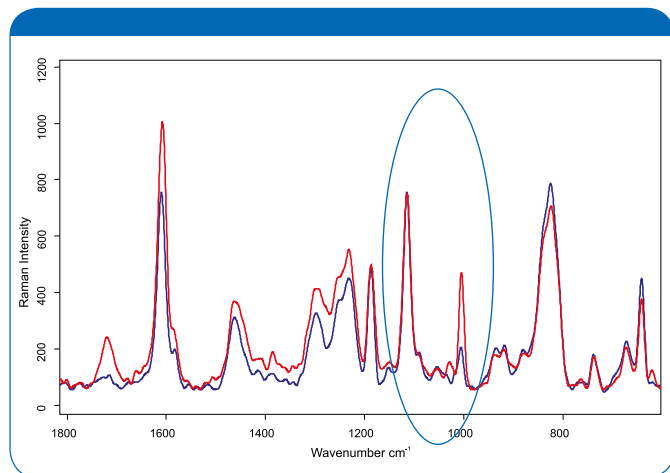


Figure 4: Inside circle: Raman lines (1114  $\text{cm}^{-1}$  and 1004  $\text{cm}^{-1}$ ) used for spectral Raman imaging.

In Figure 5a the Raman intensity distribution of this non-aromatic vibration of the polymer network chains is shown. The Raman intensity corresponds directly to the thickness distribution (ca. 600 nm to 150 nm, see Figure 3) of the sample found in the AFM image. Figure 5b displays the Raman intensity ratio of the phenyl ring breathing vibration at 1004  $\text{cm}^{-1}$  versus the Raman intensity of the non-aromatic vibration (1114  $\text{cm}^{-1}$ ).

Obviously the interaction of the polymer chains with the polarized Raman laser provides information about the steric orientation. It turns out that the intensity ratio is higher in those regions of the sample area with low thickness indicating that the aromatic entities in the network chains tend to orient parallel to the sample surface [3].

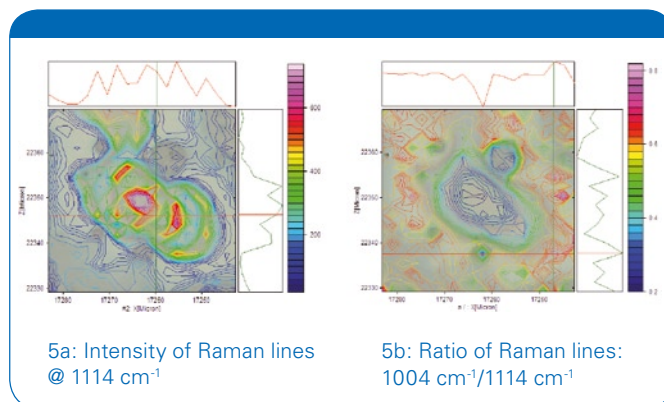


Figure 5: 2D Raman images (40  $\mu\text{m}$  x 40  $\mu\text{m}$ ) of epoxy nanostructure on an aluminium substrate with underlying visual images, figure 5a: Raman intensity distribution of a non-aromatic vibration (1114  $\text{cm}^{-1}$ ) of the network chains, figure 5b: Raman intensity ratio of the phenyl ring breathing vibration (1004  $\text{cm}^{-1}$ ) of the epoxy versus the Raman intensity of the non-aromatic vibration (1114  $\text{cm}^{-1}$ ).

## Summary

In conclusion Raman microscopy and atomic force microscopy integrated in an optical microscope can provide a comprehensive picture for the study of polymer surfaces and thin films providing more insight to the principles of adhesion on a nanometric scale. Topographical information from the AFM such as the thickness of nano layers can be directly related to molecular spectroscopic information in the Raman spectra.

## References

- [1] G. Binning, C. Quate and Ch. Gerber, Phys Rev. Lett. 56 (9), 930 (1986)
- [2] Bruker Nano, company publication "N8 Neos SENTERRA" (2009)
- [3] C. Wehlock, W. Possart et al., publication in preparation

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