

Characterization of Materials with a Combined AFM/Raman Microscope

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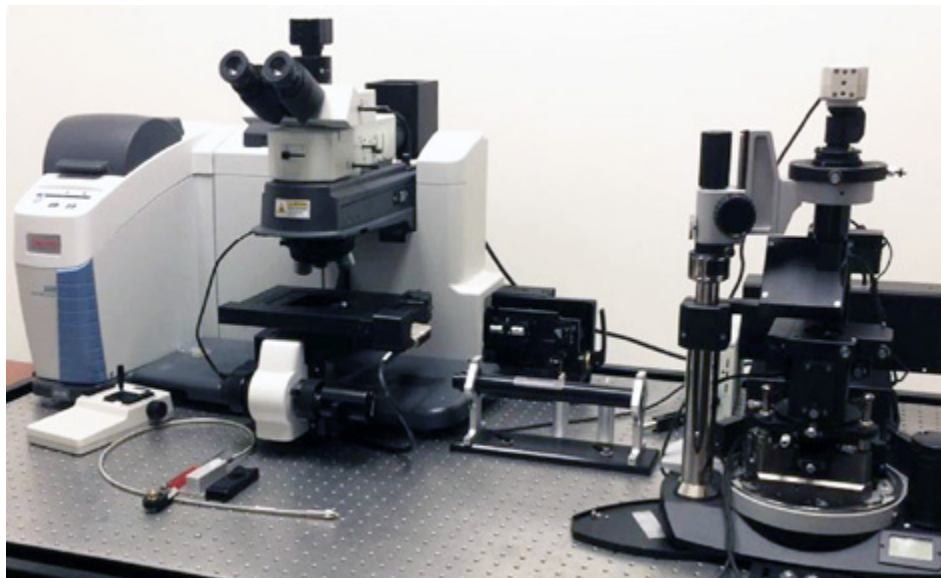


Fig. 1. Photograph of DXR microscope (Thermo Fisher Scientific) with NTEGRA Spectra Scanning Probe Unit (NT-MDT).

INTRODUCTION

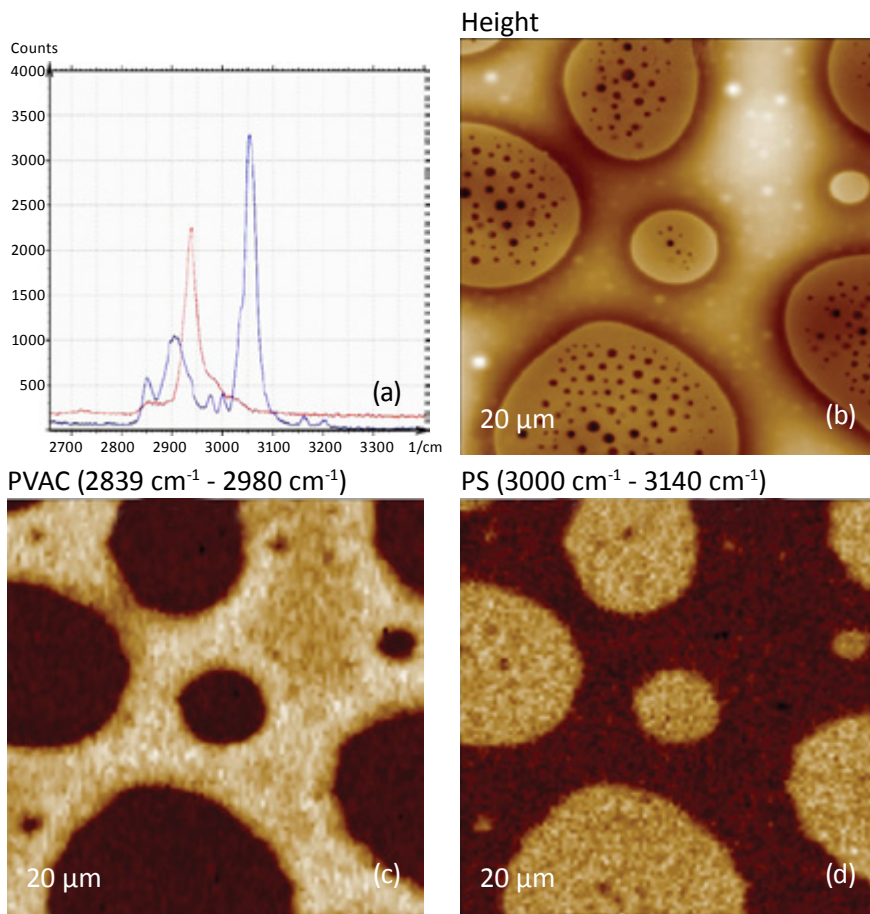
Comprehensive materials characterization relies on studies of samples by complementary techniques. A need for chemical recognition of compounds at the microscopic scale led to the development of IR and Raman microscopes. The identification of the components of multicomponent materials and mapping their distribution becomes difficult as the size of technologic structures shrinks to the sub-micron and sub-100 nm scales. At these scales, atomic force microscopy (AFM) is used for high-resolution

surface profiling and for quantitative studies of local mechanical and electromagnetic properties. This method is also applied for compositional mapping of complex materials using differences of the shape/dimensions and local properties of the constituents. Yet, the AFM-based identification of the components is indirect. Hence, chemical recognition of the constituents using Raman combined with AFM will advance the materials characterization. In our AFM/Raman studies the intention was to clarify their benefits.

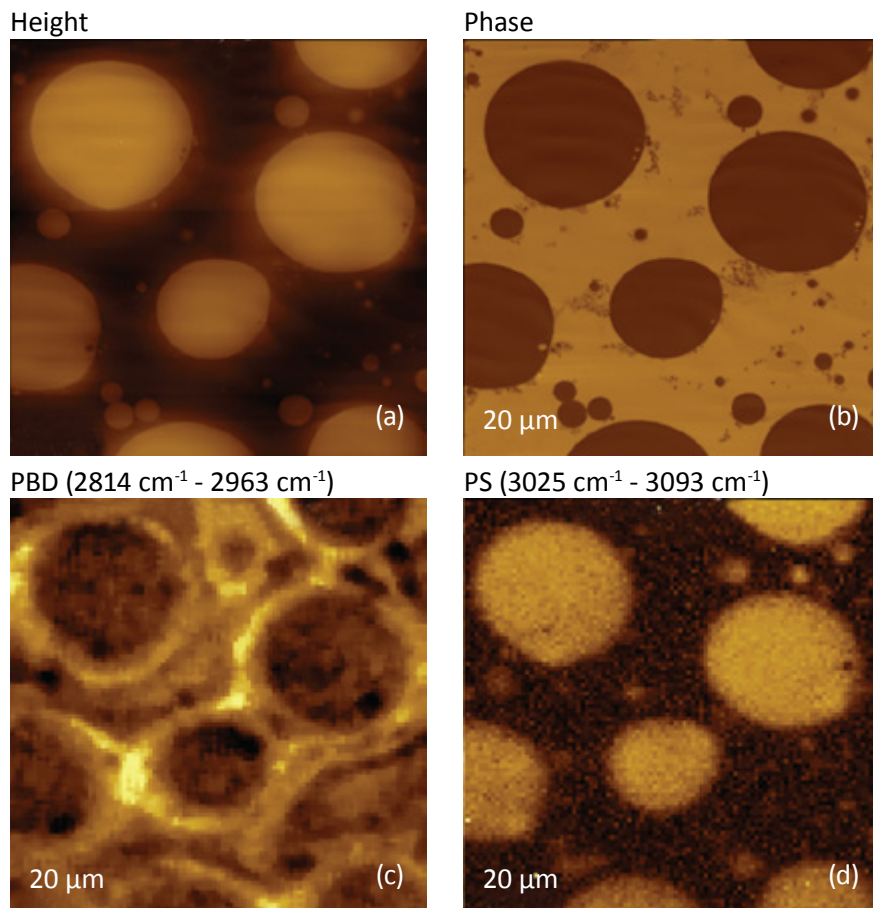
INSTRUMENTATION

In an AFM/Raman study, surface profiling and measurements of local properties are performed simultaneously with the collection of scattering maps at material-specific wavelength bands. We conducted the experiments with a Raman microscope DXR (Thermo Fisher Scientific) integrated with a Scanning Probe Unit NTEGRA Spectra (NT-MDT), Fig. 1. The functionality of this setup is achieved with an expander, which is used for collimation and alignment of the laser beam directed from the DXR microscope to the entrance

of the scanning probe unit. In the unit the beam is focused on the sample from the top with a lens $N/A = 0.7$ and can be positioned on the area of interest or at the tip apex with the piezo-driven mirror. For AFM, the unit incorporates a laser detection of tip-sample interactions by measuring the reflected beam bounced from the probe. The NT-MDT AFM microscope offers a complete set of techniques including HybriD mode (non-resonant oscillatory mode), single-pass electric studies in Amplitude Modulation mode, amongst others.



Figs. 5 a-d. (a) Raman spectra of poly (vinyl acetate) - PVAC and polystyrene - PS. (b) height image of PS/PVAC film. (c)-(d) Raman maps of PVAC and PS bands.



Figs. 6 a-d. (a) - (b) Height and phase images of PS/PBD film. (c) - (d) Raman maps of PS and PBD bands.

COMPOSITIONAL MAPPING OF POLYMER BLENDS

Polymers exhibit Raman scattering bands, which are related to their chemical bonds. Therefore, recognition of individual components of polymer blends using Raman scattering at chemically-specific frequencies in combination with AFM imaging helps to establish the morphology-property relationship for these important industrial materials.

We illustrate AFM/Raman compositional mapping by the study of the polymer blend of polystyrene (PS) and poly(vinyl acetate) (PVAC). Raman bands at 2839 cm^{-1} – 2980 cm^{-1} and at 3000 cm^{-1} – 3140 cm^{-1} , which are specific to PVAC and PS (Fig. 2a), were used for chemical mapping of the film. The height image of the PS/PVAC film on Si (Fig. 2b) shows the perforated protrusions and matrix. This morphology hints to a microphase separation, and the Raman maps in Figs. 2c-d allow the assignment of PS to the protrusions, and the matrix - to PVAC.

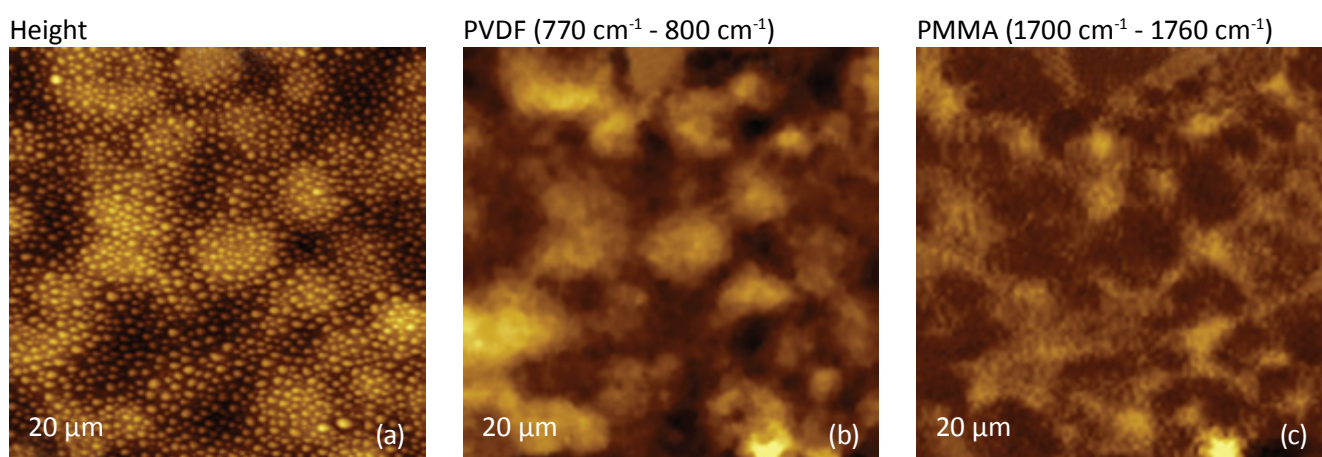
Prior to AFM/Raman microscopes, the AFM phase imaging was used for compositional mapping [1]. The AFM images of PS and polybutadiene (PBD) blend (Figs 3a-b) show a binary contrast of the phase image and, likely, the elevated domains and matrix are enriched in the blend' components. The phase differentiation of the dissimilar components is poorly understood and it is often based on the experimental relation between phase and sample properties. In Raman mapping the constituents are recognized by spectral "finger-prints" as seen in the maps of the PBD (2814 cm^{-1} – 2963 cm^{-1}) and PS (3025 – 2094 cm^{-1}) bands (Figs. 3c-d). Therefore, the matrix is enriched with PBD and the protrusions with PS.

A differentiation of the spatial resolution of AFM and conventional Raman mapping is noticed in the

study of a film of poly(vinyl difluoride) - PVDF and poly(methyl methacrylate) – PMMA blend. The AFM/Raman data, which were obtained on the film, are presented in Figs. 4a-c. The height image shows that the film morphology is characterized by a combination of small sub-micron particles, which densely cover a whole area, and the larger round-shaped domains with dimensions in a few microns' range. The Raman maps, which reflect the intensity of PMMA and PVDF bands, distinguish only the round-shaped domains and areas in between.

The domains are enriched in PVDF and their surrounding – in PMMA (Figs. 4b-c). Small particles on the surface are "invisible" in the Raman maps, and the use of tip-enhanced Raman scattering (TERS), which is applied at sub-100 nm scale, is needed. Visualization of different species in composite materials is also enhanced with AFM/Raman mapping [2]. The plant cell is a heterogeneous natural nanocomposite of cellulose, lignin and hemicelluloses. Its structural insights are important to understand the mechanical, chemical and biological performance of plants and plant materials.

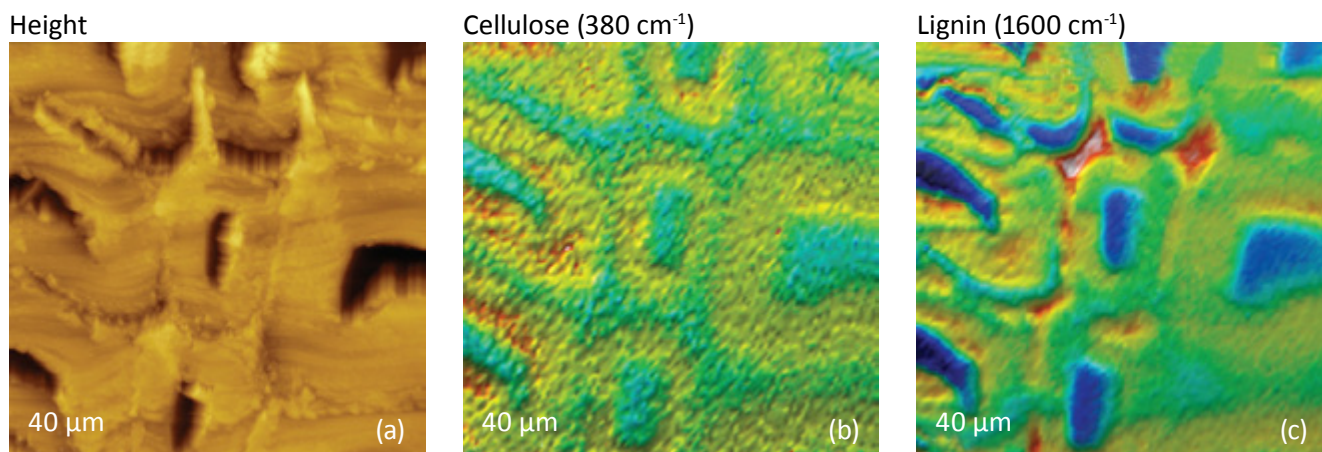
A Raman microscope has been used for studies of a distribution of lignin and cellulose in the cell walls of woody tissue. An example of the combined AFM/Raman study of the wood cells is given in Figs. 5a-c. The height image shows an array of cells with the partially empty cell core, which is surrounded by the multilayer walls (Fig. 5a). Lignin and cellulose are distinguished in the Raman maps (Figs. 5bc) of the cellulose- and lignin-specific bands at 380 cm^{-1} and 1600 cm^{-1} , respectively. In the maps the locations with high/low concentration of cellulose and lignin are shown in red/blue.



Figs. 4 a-c. (a) Height image of PMMA/PVDF film. (b) – (c) Raman maps of the PVDF and PMMA bands.

These components are localized mostly in the cell walls yet their lateral distributions are quite different.

An analysis of the lignin/cellulose ratio in different layers surrounding the cells is given elsewhere [2].

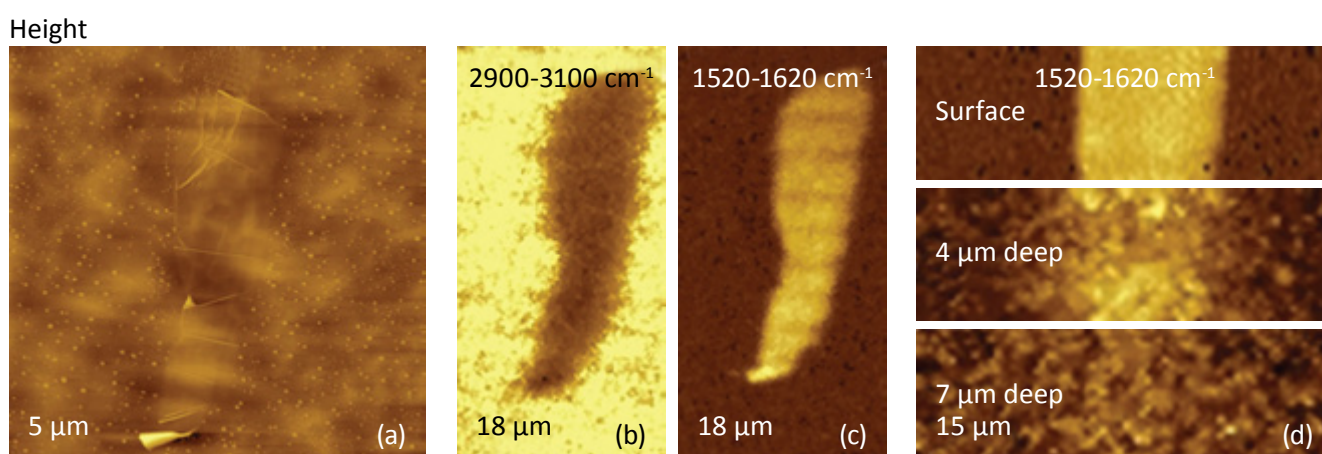


Figs. 5 a-c. (a) Height image of the wood cells. (b)–(c) Raman maps of the cellulose and lignin bands. The red spots correspond to high intensity, the blue spots – to low intensity

COMBINING AFM AND CONFOCAL RAMAN STUDIES

The confocal Raman measurements provide unique in-depth chemical information by placing an aperture at a back focal plane of the microscope [3]. The aperture improves the spatial resolution of the microscope and enables depth profiling by acquiring spectra as the laser focus is moved into a transparent sample. In our AFM/Raman instrument the vertical displacement of the focus is performed with a piezo-scanner and the example of the confocal studies of PVDF film with graphite flakes is illustrated in Figs. 6a-d. Height image shows a polymer surface

area with a flat-lying flake in the center, which is distinguished by few “wrinkles” and by an absence of grainy structures. A clear differentiation between the flake and PVDF is obtained in Raman maps (Figs. 6b-c) for wavelength regions specific for these components: the 2900 cm^{-1} – 3100 cm^{-1} region (C-H) characterizes PVDF and the 1520 cm^{-1} – 1620 cm^{-1} region (G-band) – graphite. The maps of the intensity of the 1520 cm^{-1} – 1620 cm^{-1} band, which were obtained at different depths, point out that thickness of the flake is around $4\text{ }\mu\text{m}$ (Fig. 6d).



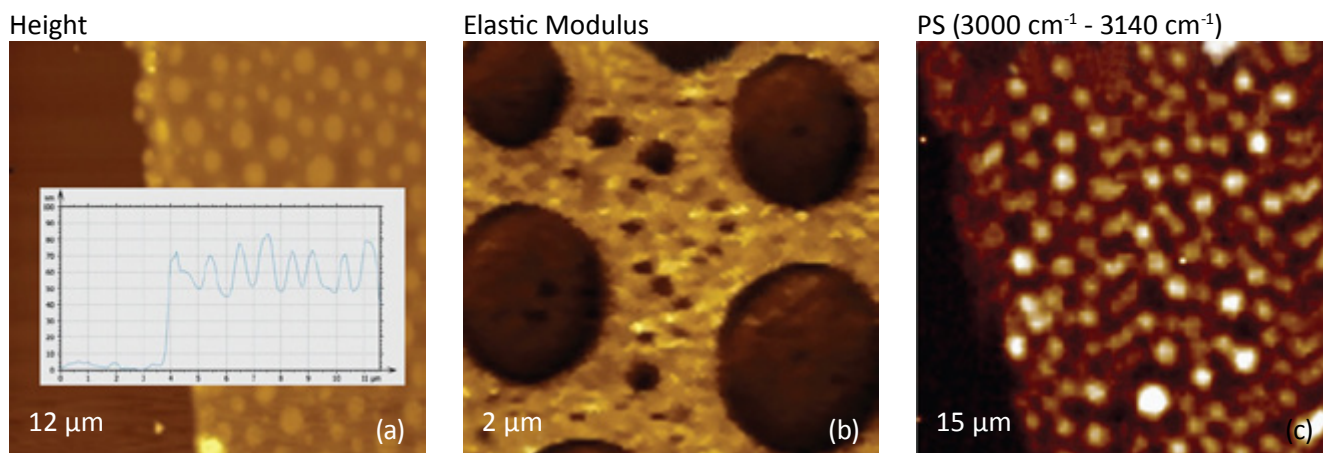
Figs. 6 a-d. (a) Height image of PVDF film with a graphite flake. (b) - (c) Raman maps of PVDF and graphite. (d) The maps of the graphite band at different depths.

INTERPLAY BETWEEN NANOMECHANICAL AND AFM/RAMAN MEASUREMENTS

Advances in non-resonant oscillatory Hybrid mode [4] facilitate the quantitative mapping of elastic modulus.

The modulus of polymers varies from several kPa to 10 GPa, therefore, the modulus maps can be used for

compositional imaging. Yet, in a study of an ultrathin (<100 nm thick) polymer films on rigid substrate the situation is complicated. The height image of ultrathin film of PS/PBD on Si reveals its morphology with a matrix embracing the protrusions: see the right side of Fig. 7a. On the left side is a scratch that opens the



Figs. 7 a-c. (a) Height image of the PS/PBD film on Si. (b) The elastic modulus map with the modulus variations in the 2-3 GPa range. (c) Raman map of PS band.

Si surface. The height profile in the insert shows that the protrusions and matrix are ~ 70 nm and ~ 40 nm in height. The modulus map of the sample (Fig. 7b) made in Hybrid mode indicates that the modulus of the protrusions is lower than that of the matrix, yet they are both close to the modulus of PS (2-3 GPa).

The results are clarified with the Raman map of PS band that helps to assign the elevated domains to PS and the matrix to PBD (Fig. 7c). Therefore, the determined elastic modulus' values are influenced by the substrate that leads to a stronger tip-induced deformation of PS domains compared to the PBD matrix.

IELECTRIC MEASUREMENTS AND AFM/RAMAN STUDIES

Single-pass Kelvin force microscopy (KFM) is a most sensitive and high-resolution AFM technique for local electric studies. The joint KFM and AFM/Raman experiment was performed on a sample of Si (111) covered with 80-nm polycrystalline Si-C film.

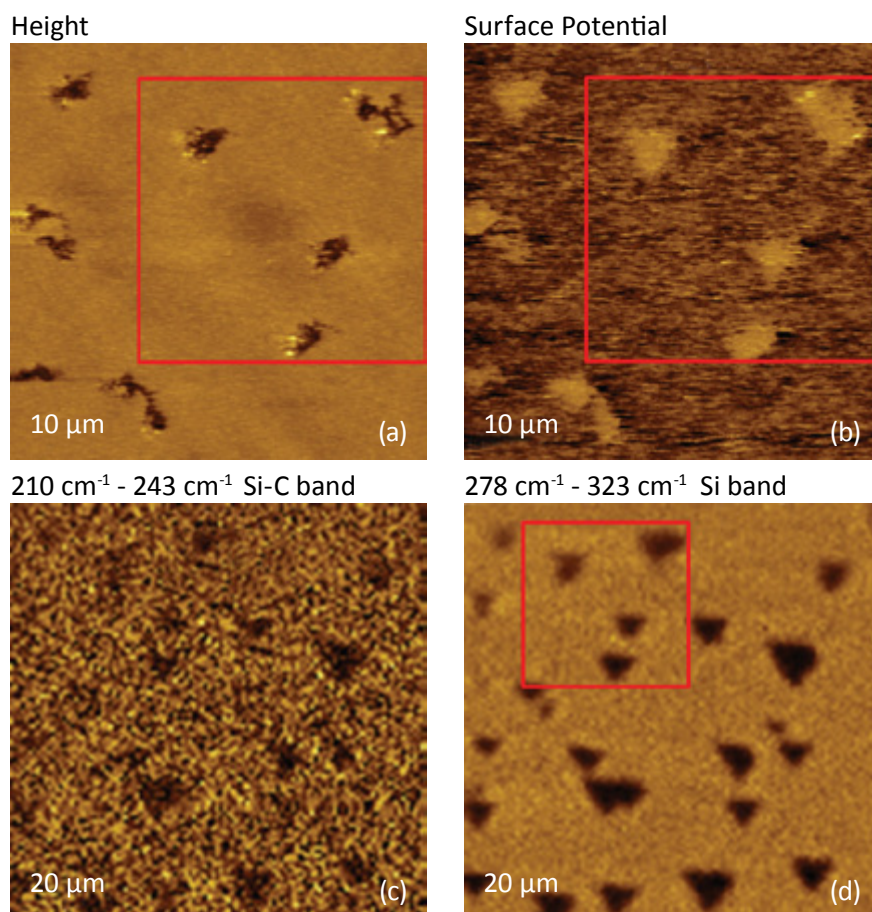
The film surface is characterized by a number of pits of irregular shape (Fig. 8a). The pits' locations exhibit a surface potential, which is ~ 1 V higher than the surrounding area, and the related patterns have a triangular shape (Fig. 8b).

The Raman maps of the Si-C and Si bands (Figs. 8c-d) were collected on the larger area, and a red square marks the same size location in the images.

The contrast of Si-C band, which is weaker than that of the Si band, reflects a small thickness of Si-C film.

The height image displays the top layer topography, whereas the Raman maps refer to a bigger sampling volume, which includes the underlying substrate defects.

The surface potential image also provides some sen-



Figs. 8 a-d. (a) – (b) Height and surface potential images of Si-C/Si sample. (c) – (d) Raman maps of the Si-C and Si bands. A red square shows the same area.

sitivity to the underlying substrate defects due to a long-distant nature of tip-sample electrostatic forces. This example shows a complementary nature of AFM and Raman studies.

CONCLUSIONS

The chemical mapping, which is based on Raman scattering spectroscopy, is an invaluable addition to AFM in combined AFM/Raman devices. The results

demonstrate how this combination enhances the materials characterization. Further advances are coming with broadening of TERS applications.

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