



Simultaneous AFM and Raman imaging

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Introduction

Probing simultaneously the surface topography of an object with an Atomic force microscope and its composition with a vibrational technique such as Raman Confocal spectroscopy is of tremendous interest for applications ranging from nano-material and biomaterials to in-vivo biological cell study. Obtaining the vibrational signature with a spatial resolution in the range of 100 nm is of high interest to understand the new properties of nanoscale materials due to possible confinement effects. The correlation of the highly resolved Raman signal with the topographical features can help to localize defect areas or sites of interest that can be stimulated optically (i.e. using the confocal microscope) or mechanically (i.e. using an AFM tip). Surpassing the resolution limit of conventional optical microscopy by a combination of near field techniques with conventional Raman confocal microscopy is a challenge that presents many advantages in terms of spatial resolution and acquisition time resolution.

Experimental set-up

The approach led by Veeco instruments and Horiba Jobin Yvon (HJY) in collaboration with the University of Bordeaux spectroscopy group consists in developing a versatile platform combining state-of-the-art Confocal Raman microscope and Atomic force microscope in a transmission geometry. A sturdy mechanical coupling between the two instruments as well as a communication protocol (Veeco Open Architecture Labview routine and HJY TCP-IP protocol.) allows the control of both instruments in a step-scan AFM/Raman acquisition mode. Once in feedback, the tip is positioned at a given XYZ position and Raman acquisition starts. In each XYZ (or XY Error, XY phase,...) position corresponds a Raman Spectrum recorded over a wide spectral range. The acquisition times as well as the spacing between the XY points are user controlled and depend on the spectral range investigated. This can be repeated on an large array of user-defined points. The sample is then moving in the XY position while the tip and the focal point are aligned. The feedback of the tip authorize movement along the Z direction only.

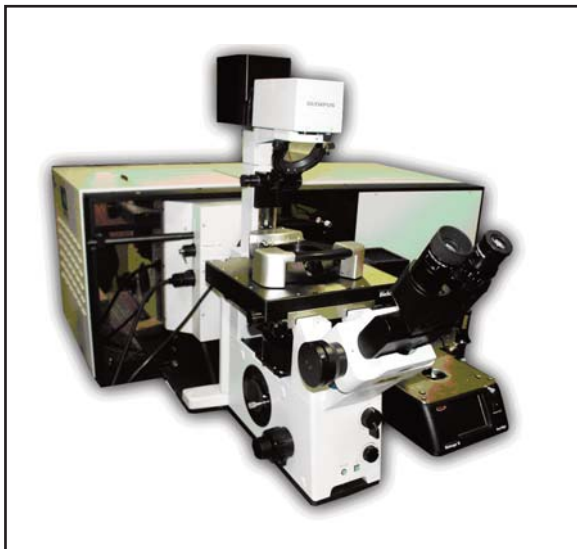


Figure 1. Combination of the Veeco Bioscope II with the Horiba-Jobin Yvon Labram HR spectrometer.

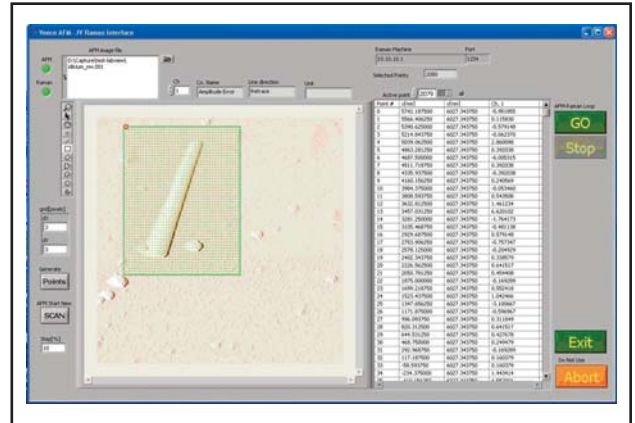


Figure 2. Veeco Open Architecture Labview routine: the initial AFM topography image is divided into discretized points. The AFM tip will be precisely located on each point and the Raman acquisition started in a step-by-step acquisition of both the tip XYZ position and the Raman image.



Application for Nanomaterial Characterization.

The combined setup has been used to investigate single semiconductors nanowires with different sizes and composition and surface modifications. The samples are deposited at the surface of a transparent substrate (glass, fused silica, Petri dish, temperature controlled cell). In the case of nanowires that are deposited onto a surface, atomic layer deposition of Aluminium oxide can help to mechanically stabilize the object at the surface. Here after are shown AFM and Raman image of silicon nanowires deposited on a glass coverslip. The Raman spectra show local broadening and spectral shift that can be correlated with the material properties.

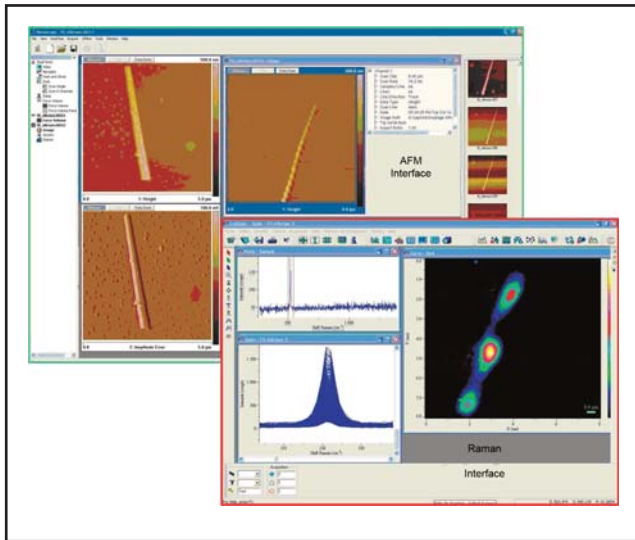


Figure 3. Superimposition of the softwares used to control the AFM and the Raman confocal microscope. The Labview routine interfaces both software through TCP-IP protocol. The AFM image and Raman images are simultaneously recorded

Towards Tip Enhanced Raman Spectroscopy.

In tip enhanced spectroscopy, a metallic coated tip interacts with the object of interest. A focalized laser with the proper polarization interacts with the metallic tip enhancing the EM field through the excitation of the plasmon band of the tip. The metallic tip being close to the sample (in the near-field of the object), the illumination with the proper wavelength can create significant enhancement

of the field leading to larger Raman signal of the sample. The spatial resolution of the optical measurement is also improved since the enhancement is originating from the small tip apex. When the tip is located far from the sample, only the far field signal is collected by the microscope objective. The difference of the two Raman spectra with the AFM tip in close proximity or far from the sample provide the near field contribution and therefore the tip enhanced contribution.

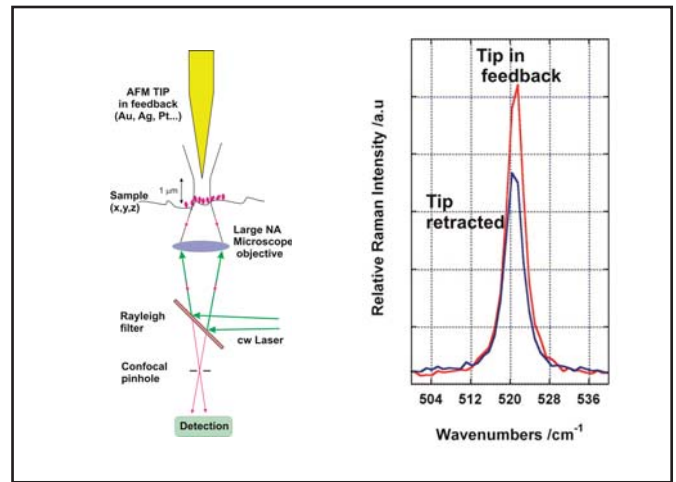


Figure 4. Scheme of the Bioscope II/Labram setup combination . Spectra of Silicon wires

Versatility of the Instruments

The combination of the Veeco Bioscope II and the Horiba-Jobin-Yvon LabRAM HR is certainly one of the most flexible one either used independently or simultaneously. This advanced platform allows the user for the investigation of both morphological and chemical information at the same sample location, while also having the possibility to probe nanostructures with a xxx spatial resolution.

Bioscope II Keypoints

- Mechanical stability
- Independent Z and XY scanner for a higher frequency response.
- Near IR Laser diode



LabRAM HR Keypoints

- High resolution Raman spectrometer, with Multiple choices of gratings and lasers excitations from UV to NIR.
- True confocal microscopy with software adjustment of the confocal aperture
- Possibility of Dual CCD detection and monochannel (InGoRs, PMT...) detection
- Wide range of X47 mapping capabilities & options