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Application note from the Spectroscopy Products Division

RENISHAW
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Combining scanning probe microscopy and Raman microscopy

Figure 1
Nanonics NSOM/AFM mounted on a Renishaw Raman microscope.

Figure 2
Nanonics cantilevered optical fibre tip.

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Introduction

The spatial resolution of Raman systems employing normal optical microscopes is limited to approximately the wavelength of the light (about 0.5 µm), because both the illuminating laser light and the Raman scattered light are collected in the optical far-field (i.e. many wavelengths of light away from the scattering material).

This resolution is sufficient for many users, but some need the higher resolutions attainable by scanning probe microscopies (SPM) such as atomic force microscopy (AFM) and near-field scanning optical microscopy (NSOM). This need can now be fulfiled by the combined Nanonics NSOM/AFM-100 Confocal™/Renishaw Raman microscope.

Previously, investigating a sample with both scanning probe microscopy and Raman microscopy required moving the sample from instrument to instrument. The exact region being analysed by the Raman microscope could not generally be found again for imaging with the chosen scanning probe microscopic technique. Direct correlation of a SPM technique with Raman scattering was a dream…now it is a reality.

The Renishaw/Nanonics combined instrument can operate in two modes:

- **AFM/NSOM with far-field Raman**
  Offers users high spatial resolution scanning probe data, combined with far-field resolution Raman data (typically 0.5 µm resolution). Now Raman data can be recorded and correlated with high spatial resolution topographic, electrical, thermal and near-field optical data.
- **AFM/NSOM with near-field Raman**
  Offers users high spatial resolution data for both scanning probe and Raman.

System integration

The hardware and the software of the Nanonics NSOM/AFM-100 Confocal™ system are integrated with the Renishaw Raman microscope.

The Nanonics NSOM/AFM 100 Confocal™ is mounted on the sample stage of the Renishaw Raman microscope (Fig. 1).

The Nanonics system uses a patented optical fibre probe design. The cantilevered optical fibre (Fig. 2) is held between the objective lens and the sample without obstructing any aspect of the far-field conventional microscope. The tip of the fibre is exposed, allowing direct viewing of the scanned region in the microscope eyepieces or on the video viewer. This is not possible in a standard AFM that uses a silicon micromachined tip, which obscures the scanned region in the standard upright microscope. It is also not possible with straight near-field optical fibre probes.

The Nanonics NSOM/AFM 100 Confocal™, with its cantilevered optical fibres, enables the Renishaw Raman microscope user to record, in parallel with Raman, the wide variety of scanning probe imaging modes. For example, while the silicon Raman peak of a microcircuit is being monitored to detect stress in the silicon, the Raman spectroscopist can simultaneously measure the micro topography with AFM and the micro reflectivity with NSOM.

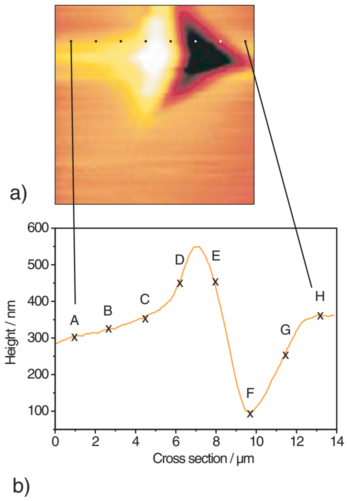

Figure 3
AFM height map (a) and cross section (b) across a nanoindentation in silicon.

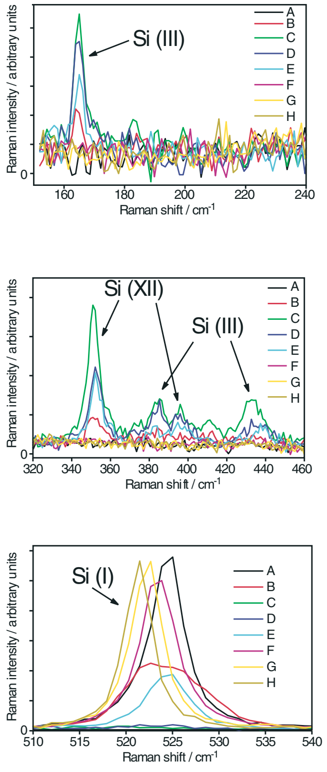

Figure 4
Far field Raman spectra taken from the 8 positions indicated in Figure 3.

AFM/NSOM with far-field Raman

The benefit of combining the worlds of AFM and Raman spectroscopy is illustrated in Figures 3 and 4.

A 14 µm × 14 µm AFM image of a nanoindentation in silicon is shown in Figure 3, along with a cross section through the indentation. The lettered points on the AFM cross section represent the points at which Raman spectra were collected.

The AFM image shows that the indentation has caused plastic deformation of the silicon, but does not give any indication whether the deformed regions have undergone any phase changes. However, the Raman spectra (Fig. 4) clearly show the presence of different phases of silicon, along with shifting and broadening of the main silicon(I) 520 cm^{-1} Raman band caused by residual stresses.

Polymer science is another field where the combination of scanning probe and far-field Raman offers great promise. For example, NSOM measurements with linearly polarised light can reveal micro domains and thus the degree of crosslinking in polyethylene and polybutadiene films[1]. Mechanical properties may also be measured. The AFM is able to monitor the elasticity of the polymer film by using the intermittent contact mode of the NSOM/AFM 100 Confocal™. This information can now be directly correlated on-line with the Raman data.

The Nanonics system is also able to operate in intermittent contact mode in liquids. This capability, coupled with Raman spectroscopy's ability to successfully acquire data from samples within aqueous media, opens up the exciting possibilities of imaging biological materials in physiological media.

NSOM Raman

In NSOM Raman, although the Raman scattered light is collected in the far-field, the exciting laser light is delivered through a subwavelength-tipped probe. This results in a spatial resolution far higher than that of a conventional Raman microscope.

The Renishaw/Nanonics system uses an optical fibre that is tapered by glass pulling technology[2] to form a subwavelength aperture. The sample is scanned relative to this aperture in the optical near-field.

The z resolution (i.e. normal to the sample surface) of the near-field optical approach is much better than anything obtained in confocal Raman spectroscopy (typically 1 µm)[3-5]. Thus researchers in biology, for example, can now look at near-membrane Raman scattering to address the critical questions of near membrane molecular changes whilst also using conventional micro Raman to monitor deep alterations within the cell. Additionally, the on-line force sensing capabilities of the cantilevered optical tip enable the near-membrane Raman data to be correlated with the motion of the cell membrane and mechanical or topographical changes.

Surface enhanced NSOM Raman

Surface enhanced near-field Raman combines high spatial resolution with high Raman signal levels.

Over 20 years ago it was discovered that the Raman signal can be magnified by many orders of magnitude when small metal particles are in proximity to molecular species[6]. The exact mechanisms of surface enhanced Raman scattering (SERS) are still hotly debated, but it is now generally accepted that metals (such as silver, gold, copper, and aluminum) which exhibit surface plasmon states that are highly polarisable by the light field can induce this effect.

John Wessel[7] has suggested that this approach can be used to generate near-field Raman scattering. The tip of the scanning probe forms an isolated nanoparticle with surface plasmon states. If the tip is illuminated by an external light field and brought into close proximity with a surface, then Raman signals from the surface could be enhanced by as much as 8 orders of magnitude. Although Wessel's paper was purely theoretical there has been considerable progress in showing this effect experimentally.

There have been many studies of externally illuminating near-field tips to generate fluorescent[8] and other signals[9]. The first attempts to create isolated metallic nanoparticles with surface plasmon states[10] focused on gold and silver nanoparticles, and investigated a variety of non-linear optical generation effects from molecules associated with such isolated nanoparticles. Large enhancements were seen.

Other work[11-17] has shown that it is possible to obtain the surface enhanced Raman spectrum of a single molecule associated with a nanoparticle.

All these studies suggest that it is possible to probe, with nanometre precision, the Raman spectra of surfaces. A crucial experimental step to achieve this goal is the appropriate placement of a single metal particle of gold or silver at the tip of a force sensing structure. Nanonics has recently made significant progress toward this goal. Figure 5 shows a probe with a silver particle at the tip. The particle in this scanning electron microscope image is visible as a faint circle. Its presence is confirmed by electron induced x-ray emission, which reveals the presence of the silver, in addition to silicon and aluminum from the glass, and gold from the probe's coating.

An example of an application of such a nanoparticle probe is shown in Figure 6. A Nanonics AFM glass cantilever, tipped with a 100 nm gold nanoparticle, was brought in close proximity to a styryl dye. The tip enhanced the signal of the molecules by at least three orders of magnitude. The high level of enhancement is indicated by the presence of diffraction rings around the gold tip, arising from the intense second harmonic generation that was induced in this particular enhancement experiment.

Nanonics, in partnership with Renishaw, is committed to developing and exploiting such technology to achieve the ultimate resolution in Raman spectroscopy.

Acknowledgments

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The Nanonics/Renishaw system uses additional software from Cavendish Instruments Ltd. that is integrated with Renishaw's WiRE control software.

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Figure 5
Scanning electron micrograph of a Nanonics probe tip for surface enhanced near-field Raman studies.

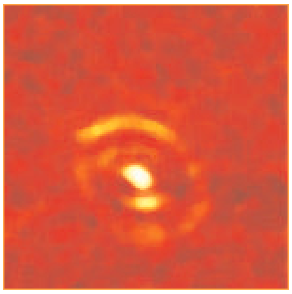

Figure 6
Image of gold-tipped cantilever in close proximity to a styryl dye.

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NSOM detailed specifications

Operating modes

Near-field optical microscopy	Transmission, reflection collection, fluorescence
Atomic force microscopy	Contact, non-contact, intermittent-contact (shear force optional)
Feedback mechanism	Optical beam deflection (shear force optional)
Confocal microscopy	Transmission, reflection, fluorescence

Scanning

Scanner	Piezoelectric flat scanner (thickness 7 mm)
Scan range	70 µm (z), 70 µm (xy) (30 µm and 10 µm on request)
Maximum load	75 g
Spatial resolution	< 1 nm (x,y,z)

Coarse sample positioning

Positioner	Inertial piezo motion
Range	6 mm
Accuracy	1 µm
Maximum sample size	16 mm diameter, custom mounts for larger samples can be provided

Probes

NSOM-probes	Cantilevered or straight, pulled optical fibre probes, apertured silicon cantilevers
AFM-probes	Cantilevered, pulled glass probes, or any commercially available AFM probes
Specialised probes	Cantilevered probes for electrical or thermal measurements, AFM controlled Nanopens for gas and liquid chemical delivery
Custom probes	Available on request

Optics

Accessibility	Free optical access to top and bottom of sample for far-field observation, and for detection of NSOM signals
Detectors	Photomultiplier tube (PMT), avalanche photodiode (APD), InGaAs detector for IR, CCD
Video system	Integral to Renishaw Raman microscope

Imaging

Confocal microscopy	Diffraction limited
Near-field microscopy	From 50 nm upwards, depending on the aperture size of the NSOM probe used
Atomic force microscopy	z resolution < 1 nm x,y resolution dependent on radius of curvature of tip used (carbon nanotube tips have achieved highest x,y resolution of < 1 nm)
Controller	Nanonics/Topaz (Digital Instruments, RHK, Park Scientific and Topometrix controllers can also be used to control the NSOM/SPM 100 microscope)
Software	Quartz software for Nanonics/Topaz controller (Win 95/98 and NT). Real time image display, image acquisition (up to 8 channels) and analysis, 3D rendering of Raman, AFM, and NSOM data.

Options

Low Temperature Module	Room temperature to <10 K, down to 10^{-6} torr
Environmental Chamber	Control humidity, gas composition, gas pressure
Liquid Cell	For NSOM measurements in liquids
Electrical/thermal	Options for resistance and thermal measurements
Nanochemical	Deliver a chemical via the micropipette-AFM tip to your sample surface with on-line Raman and AFM