Raman Update

HORIBA JOBIN YVON

Summer 2006

Welcome to the Raman Update, produced by HORIBA Jobin Yvon's Raman Team, to provide our customers, colleagues & friends with up-to-date information in the field of Raman Instrumentation and Application.

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Tip-enhanced Raman spectroscopy

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Tip-enhanced Raman spectroscopy (TERS) holds great promises for addressing the challenging task of characterizing the physical and chemical properties of nanoscale structures and devices designed in today's and tomorrow's semiconductor and communication industries. Current technology for silicon transistors has already achieved structures 65 nm in size and the drive for ever higher density of microelectronic components will continue to motivate the development of still smaller structures. Unfortunately, the characterization of key properties of such structures remains very challenging and, in many cases, is not at all possible with current spectroscopic techniques.

Raman spectroscopy has been extensively used to map and understand crystal orientation and stress in silicon structures with micron lateral resolution. There is currently a strong demand for Raman spectroscopy techniques that can map stress in semiconductor structures with nanoscale spatial resolution. However, to use Raman spectroscopy for nanoscale analysis, two challenges must be overcome. First, the desired spatial resolution necessitates overcoming the diffraction limitation of light. Second, the Raman signal, which is inherently weak even for macroscopic scattering volumes, is dramatically reduced due to the drastic reduction in the characterization volume when going to the nanoscale.

One route for possibly overcoming the first problem, the diffraction limit, that has already been extensively investigated, is the use of aperture-limited near-field optics.

The spatial resolution is limited by the aperture size to ~100-200 nm. However, the poor optical transmission of the fibers and the tapered aperture leads to a strong decrease of the signal.

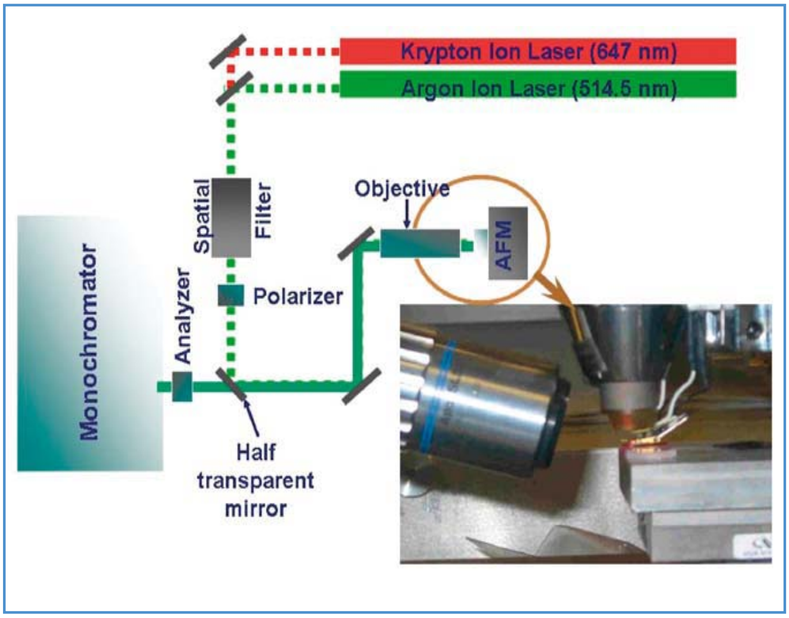

Figure 1: Schematic of a scanning nano-Raman spectroscopy system with side-illumination optics with the inset photograph showing a specific configuration of the AFM head with the objective.[1]

Thus, although the aperture-limited near-field optics helps to improve the resolution, they exacerbate the second problem - the weak signal coming from the small volume of interest.

An alternative approach that addresses both problems is apertureless near-field optics. This approach is based on the use of metal or metal-coated tips with a plasmon resonance at the apex that provides a strongly enhanced and localized signal. The technique of enhancing a local Raman signal using apertureless optics is most widely known by the name "tip-enhanced Raman spectroscopy" (TERS).

One of the simplest approaches in tip-enhanced Raman spectroscopy is to employ bottom-illumination optics. An inverted microscope is used to illuminate the sample and the Raman signal is collected using the same optics. However, the bottom-illumination approach is limited to transparent samples placed on a transparent substrate. So, it cannot be used for analysis of semiconducting materials. In order to overcome this problem, another approach, side-illumination optics, has been proposed and used by several groups. In this geometry the objective of the optical system is placed above the sample surface at some angle with respect to the surface (Fig. 1). The objective illuminates a µm-scale spot on the sample surface and collects the scattered light. A modified scanning probe microscopy (SPM) tip brought into this spot provides a locally enhanced signal. This geometry enables the characterization of non-transparent samples and samples on non-transparent substrates.

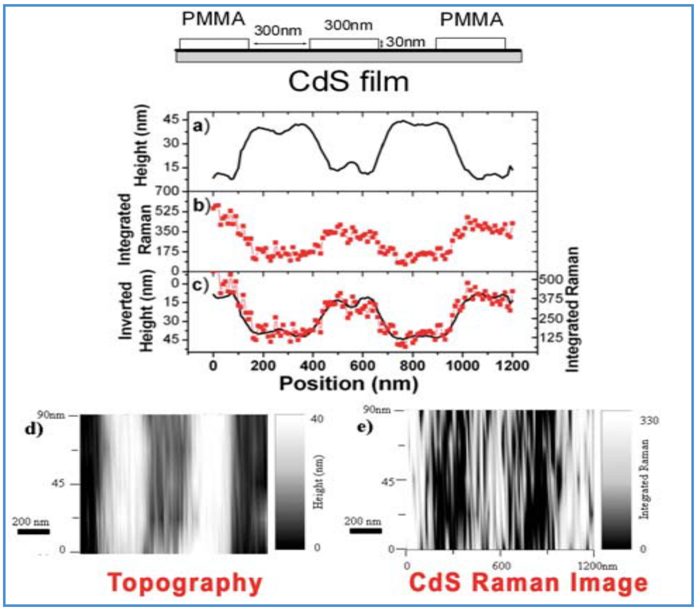

Figure 2: Schematic of the PMMA/CdS structures, correlation between the inverted topography and integrated Raman intensity for a TERS image of PMMA on CdS structure 300 nm in width, and two dimensional AFM image and TERS image of the same structures [2].

Figure 1 shows a schematic of the nano-Raman spectrometer. It includes HORIBA Jobin Yvon LabRAM HR 800 Raman spectrometer optically coupled with a Quesant (QScope 250) AFM using a long-working-distance Mitutoyo (APO SL50) objective (50x, 0.42 NA). The sample is placed on a piezo-controlled XY-stage. The objective is placed at an angle of ~65^{o} (relative to the vertical) and is fixed on an XY-stage controlled by stepper motors to position the objective with respect to the tip. The Raman signal is collected in the back-scattering geometry using the same objective.

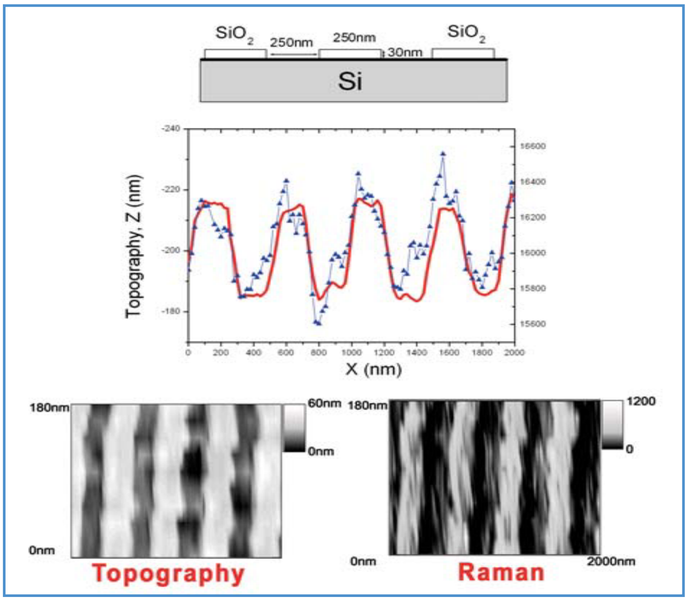

Figure 3: Schematic of the Si/SiOx structures, line scan comparing the integrated Raman intensity of the near-field signal with the topography, and two dimensional AFM image and TERS image of the same structures. [2]

Figures 2 and 3 show two-dimensional topographic (AFM) and chemical (Raman) imaging of periodic nanostructures of poly(methyl methacrylate) (PMMA) on top of a CdS film (Fig. 2) and SiOx lines on Si (Fig.3). Excellent correlation between the inverted topography and the Raman intensity has been observed in both cases. Estimated lateral resolution is ~20 nm.

In conclusion, because the lateral resolution of ~20 nm, unprecedented for optical methods, has already been achieved, TERS becomes the most promising future technology for the chemical and physical analysis of materials at the nanoscale.

References:
[1] D. Mehtani, et al., J. Raman Spectr. 36, 1068 (2005)
[2] D. Mehtani, et al., "Scanning Nano-Raman Spectroscopy of Silicon and Other Semiconducting Materials", In: Tip Enhancements, Eds. S. Kawata and V.M. Shalaev (Elsevier, 2006 in print)

To discover more on TERS applications, please visit our website: www.jobinyvon.com

Raman Spectroscopy Reveals Origins of Ancient Ottoman Pottery

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Leading experts generally base their certification of ancient artefacts on stylistic analysis and on personal sensory perceptions. However, greater objectivity is mandatory for identification and dating purposes. Different manufacturing technologies often result in products of very similar external appearance but which differ completely in their micro or nanostructure. A lot of information about the production process can be gained through Raman analysis to assist in the identification and sometimes dating of ancient artefacts.
As an optical method, Raman (micro)-spectroscopy offers a great advantage over most other techniques in that it can be performed without any contact with the studied artefact, both in the laboratory and on-site.

Figure 1 : Iznik dishes, during analysis with HORIBA Jobin Yvon Raman probe.

Many applications in the science, art and technology of glass, glazes and enamels are based on a controlled modification of the 3D Si-O network. Because a SiO_4 tetrahedron is a solid chemical and vibrational entity, it is well established that the different tetrahedral arrangements have characteristic Raman signatures. Iznik and Kütahya wares and the history of their production remain a source of debate among scholars. The exact origin of "Iznik" products (Iznik, Damascus, Istanbul, Kütahya or elsewhere) is still an open question.
Using a HE532 and Superhead fibre optic probe, a method based on Raman spectra taken from ancient pottery artefacts was proposed (Fig. 2) to identify different types of glassy silicates and to classify them as a function of their composition using two main tools:
i) the spectral decomposition of the Si-O stretching peak into its components associated to the different type of SiO_4 tetrahedra of the silicate polymerised network area and
ii) the polymerisation index calculated as the ratio (A_{500}/A_{1000}) of the Si-O bending (500 cm^{-1}) and stretching (1000 cm^{-1}).

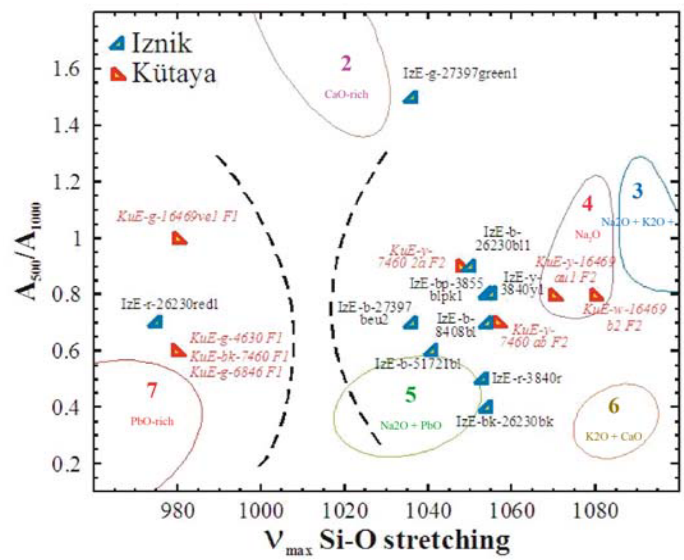

Figure 2: Bi-plot of the polymerisation index (A500/A1000) as a function of the Si-O stretching wavenumber for the series of Iznik and Kütahya fritware glazes.

Most of the Kütayha glazes can be associated to family 7 (PbO-rich glass) but some of them are located in the Iznik group. On the other hand Iznik glazes are all located in between family 5 (Na_2O + PbO) and family 4 (Na_2O-rich silicates) except for two types of glazes.

Differentiation between Kütahya and Iznik Ottoman pottery appears therefore relatively straightforward from the Raman fingerprint. The procedure is also efficient to discriminate between early and late Iznik production.

HORIBA Jobin Yvon HE 532 and SuperHead

For more details see the full application note on our website: www.jobinyvon.com/raman

Sudoku

Don't forget to take your Raman Update produced by HORIBA Jobin Yvon to read on holiday with you. And to let you relax after having read the two articles contained in this edition, we have put together a letter sudoku.

		T					N	S
			U			T	C	
R		S	O					U
	O		A	C	N			
			R	B	U		T	
U					A	S		C
	C	B			O			
S	A					N		

You can fill in the gaps of the following word by using the letters used in the grid, note that the letters can be used more than once. (We have already started you off)

C_ _ _ _ _ N_ _ _ _ _ _ _ _S

For a hint or the solution, go to our website www.jobinyvon.com/ramanupdate/sudoku

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Sudoku rules:
Using as a base the letters already included in the gridyou must complete the grid so that the grid only contains each letter only once in:
- every line
- every column
- every block 3 x 3
A game of logic and patience.

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