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The DXR Raman Microscope for High-Performance Raman Microscopy

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Key Words

- Dispersive Raman spectroscopy
- Confocal Depth Profiling
- Spatial Resolution
- Spectral Libraries

Introduction

One of the key benefits of dispersive Raman microscopy is its excellent spatial resolution. The sampling spot size of a microscope equipped with a 532-nm laser, a 100X objective and a 25-µm spectrograph aperture is just 1 µm in diameter. A well-designed instrument is able to deliver 1-µm x, y spatial resolution. In addition, good confocal Raman microscopes are capable of 2-µm precision depth-profiling. The excellent spatial resolution, combined with the development of extensive spectral libraries and sophisticated search algorithms, makes Raman spectroscopy a powerful tool for the analysis of micron-sized defects in a variety of materials and targets. Typical examples include high tech components, printer heads, polymer films and high-quality papers.

The DXR Raman microscope consists of a high-quality visual microscope equipped with Olympus optics and a high-precision motorized stage that can be controlled in all three dimensions by the OMNIC™ software suite. Accurate analysis of micron-sized features requires precision alignment of the microscope. The DXR Raman microscope employs a patented alignment method to ensure that the visual, excitation laser and Raman scattering light paths are all aligned to the same spot on the sample.[1] OMNIC Atlµs™ software provides sophisticated mapping and data analysis capabilities.

The first part of this application note presents the results of two standardized tests to demonstrate the spatial resolution performance of the DXR Raman Microscope. The second half of the note provides two examples of the benefits of excellent spatial resolution.

Spatial Resolution Performance Tests

Silicon Knife Edge – X, Y Resolution Test

A piece of severed silicon was mounted on a microscope slide. Atlµs software was used to construct a 10-µm line map perpendicular to the cut edge (Figure 1). The map clearly shows the first order silicon 520-cm^{-1} band in its upper portion. For reference, the Raman spectrum of silicon is shown in Figure 2. A correlation profile of the line map against a spectrum of silicon (Figure 3a) shows the quality of the microscope spatial resolution in the sharpness of the boundary between the silicon and the background. The first derivative of this correlation map is shown in Figure 3b. The FWHM of the derivative is 0.47 µm.

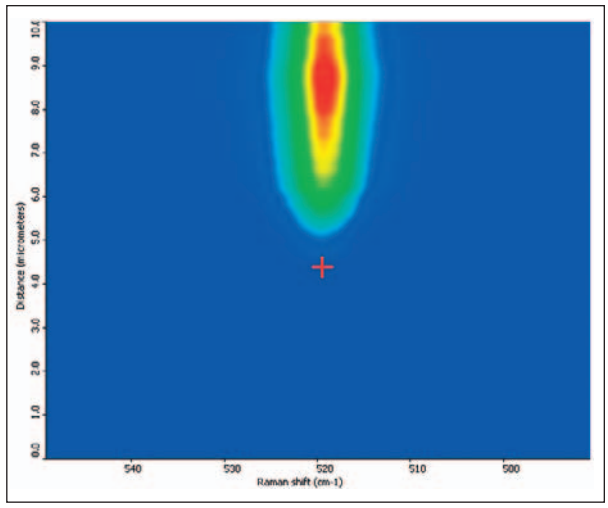

Figure 1: A 10-µm line map with a 0.2-µm step size across the severed edge of a piece of silicon. The y-axis is distance mapped in microns; the x-axis represents the Raman shift in wavenumbers. The map clearly shows the presence of silicon from the 520-cm^{-1} band in the segment of the map from 5 to 10 microns. Data collected using an excitation wavelength of 780 nm and a 25-µm pinhole aperture at the spectrograph.

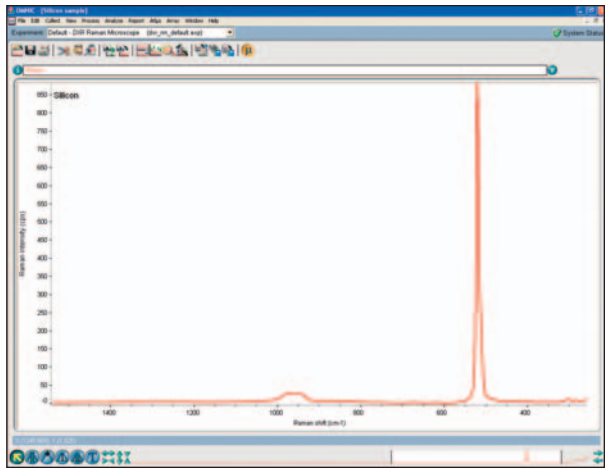

Figure 2: Raman spectrum of silicon collected using a 532-nm excitation laser

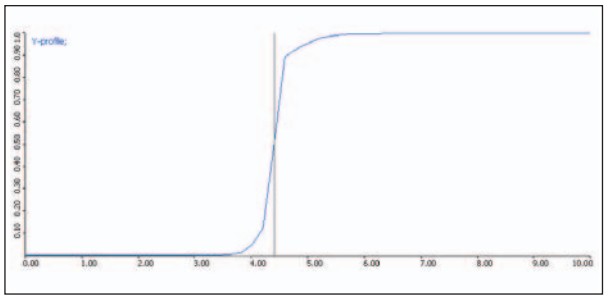

Figure 3a: Correlation profile of the line map in Figure 1 against a spectrum of silicon

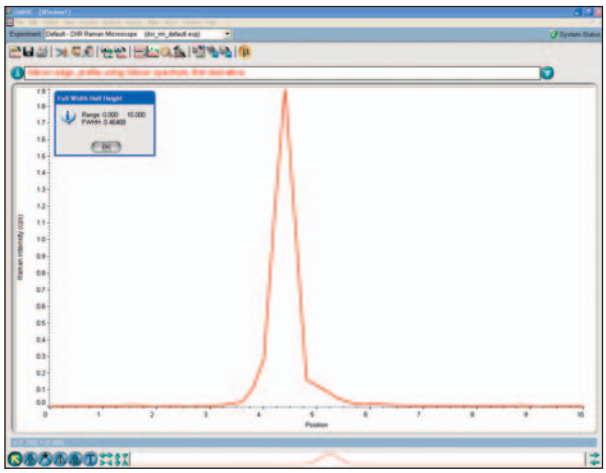

Figure 3b: First derivative of the correlation profile. FWHM is 0.47 µm.

Germanium – Depth Resolution Test

When the 532-nm laser beam is focused using a 100X objective onto the surface of a piece of germanium, the beam penetrates only a very small distance into the pure germanium. As a result, the Raman scatter acts as a small point source. Mapping the laser spot vertically so that the spot passes through the focal plane generates a hyperspectral map of the germanium. The depth of the germanium map is a measure of the spatial resolution of the microscope in the vertical direction. The map is shown in Figure 4. The FWHM of the depth profile generated using the peak at 300 cm^{-1} (Figure 5) is 1.73 µm.

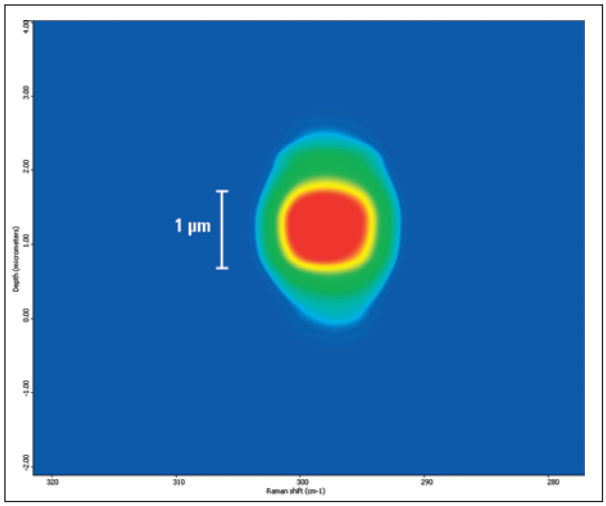

Figure 4: Hyperspectral map of germanium collected in the vertical direction. Data collected using 532-nm excitation, 0.2-µm step size and 25-µm pinhole aperture.

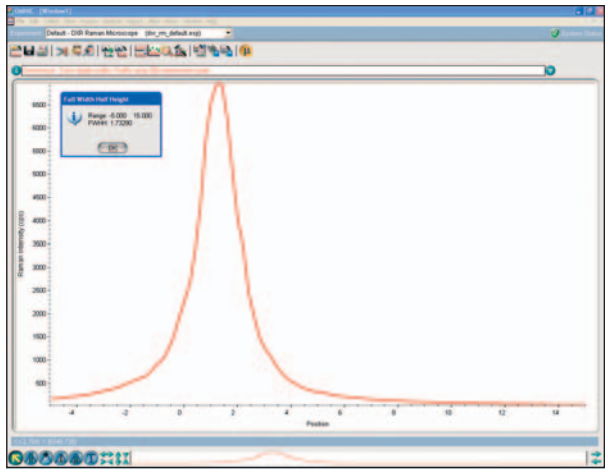

Figure 5: Intensity map at 300 cm^{-1} of the germanium map in Figure 4. FWHM is 1.73 µm.

Mapping and Depth Profile Results

These results from tests using standard targets demonstrate that the spatial resolution of the DXR Raman microscope is excellent in all three dimensions. This is reflected in the excellent results obtained in mapping 1-µm polystyrene beads and in a depth profile of a polymer laminate sample.

Polystyrene Bead

A sample of 1-µm polystyrene beads was prepared by evaporating a suspension onto a quartz surface. The visual image at 100X magnification is shown in Figure 6. A line map (Figure 7) clearly shows the location of the 1-µm bead by the presence of the strong band at approximately 1000 cm^{-1}. The FWHM of an intensity plot using this band is 0.98 µm (Figure 8). Figure 9 shows a two-dimensional map plotted using the relative intensity of the 1000-cm^{-1} band. The map shows the bead dimensions to be 1 x 1 µm. These results show the ability of the DXR Raman microscope to perform precision mapping of 1-micron sample features.

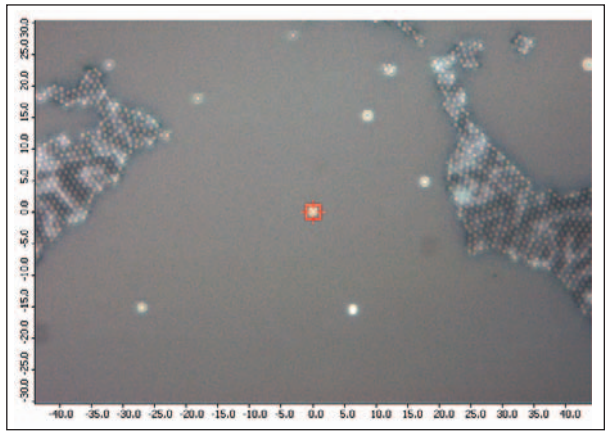

Figure 6: A brightfield image of a 100X magnification of the preparation of 1-µm polystyrene beads

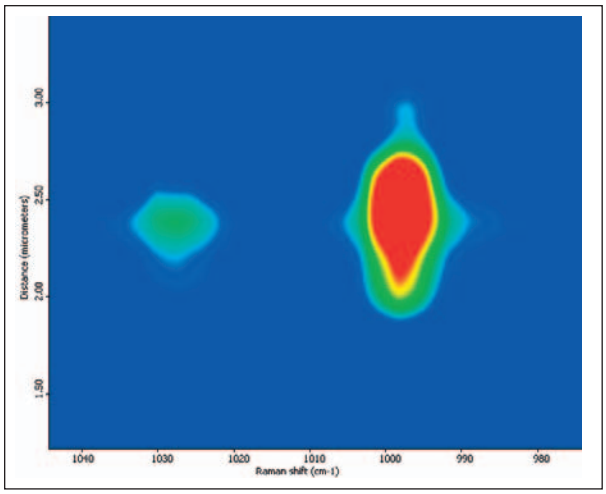

Figure 7: Line map of a single polystyrene bead. The y-axis is distance mapped in microns; the x-axis represents the Raman shift in wavenumbers. The map shows the position of the bead from the presence of the strong polystyrene band at 1000 cm^{-1}. Data collected with an excitation wavelength of 532 nm. Mapping step size was 0.2 µm, 25-µm pinhole aperture at the spectrograph.

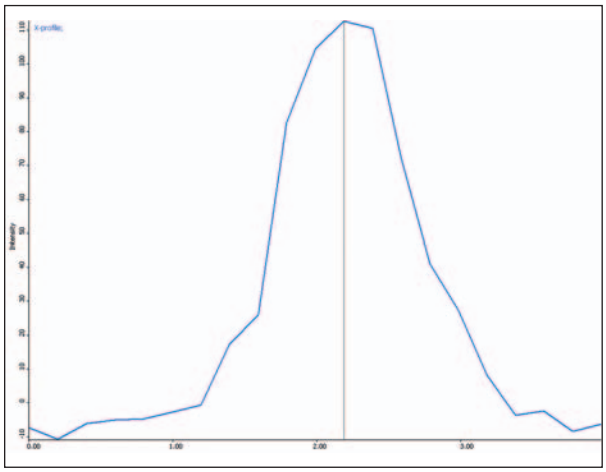

Figure 8: Intensity plot at 1000-cm^{-1} through the polystyrene bead line map in Figure 7: FWHM = 0.98 µm

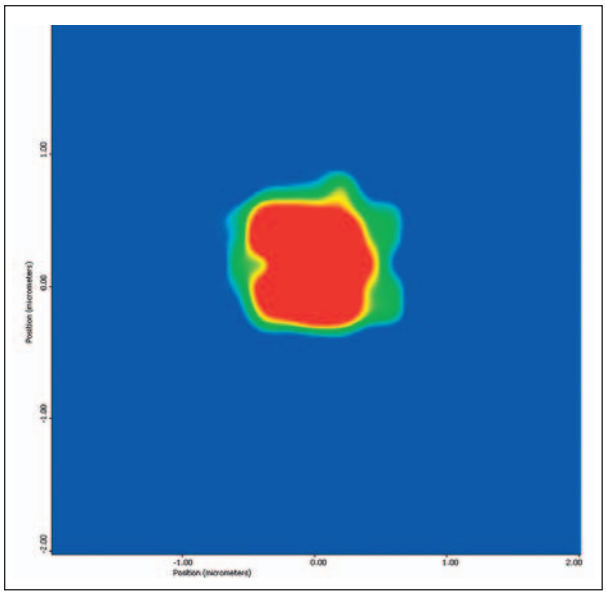

Figure 9: Two-dimensional representation of the polystyrene bead mapped from the relative intensity of the 1000-cm^{-1} band

Depth Profile of a Polymer Laminate

As a demonstration of the benefit of high-resolution depth profile analysis, we examined a sample of a food packaging polymer laminate. The sample was attached to a microscope slide with adhesive. The simplicity of sample preparation is in contrast with other techniques for cross-section analysis which require samples to be embedded in wax and sliced with a microtome. Figure 10 shows two views of a depth profile obtained by mapping a total of 300 microns into the sample using a 532-nm excitation laser and Atlµs software. The depth profiles clearly show three distinct layers. The first and third layers appear to be similar and to be distinct from the second layer. There is some indication that there is also a fourth layer, similar to the second layer.

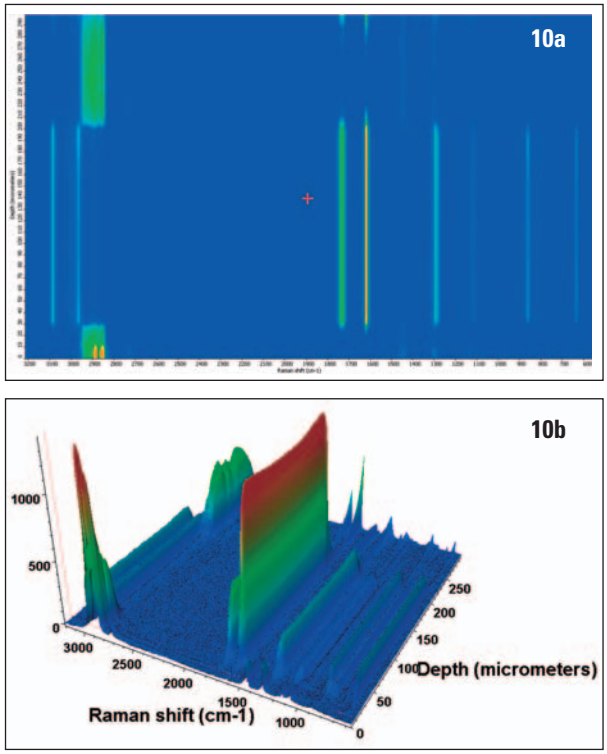

Figure 10: Two versions of a hyperspectral profile of a polymer laminate (food wrapping material) to a depth of 300 microns. Map collected using 532-nm excitation and 2.0-µm step size.

We used OMNIC software to construct correlation profiles using representative spectra (Figure 11) from layers one and two. The results are shown in Figure 12 and confirm that layers one and three are composed of the same material. Calculation of the first derivative of the two correlation profiles permits an estimate of the thickness of the layers; the first is a nominal thickness of 28 µm, and the second is 179 µm.

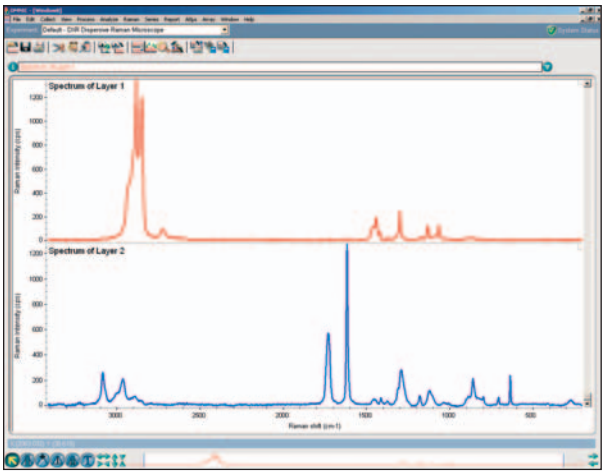

Figure 11: Representative spectra from the first two layers of the polymer laminate in Figure 10

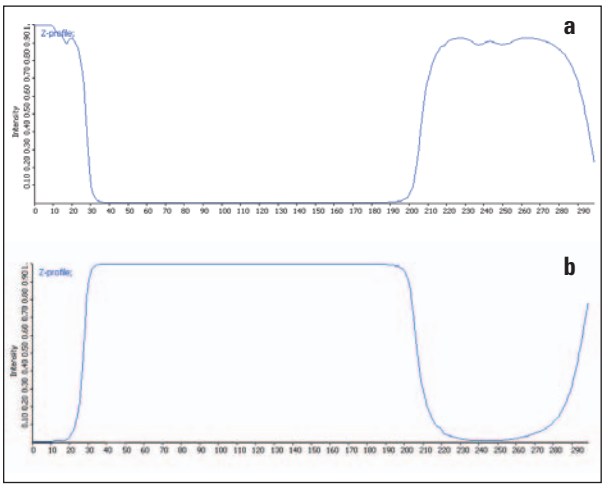

Figure 12: Correlation depth profiles constructed using the spectra in Figure 11. (a) Correlation with the spectrum from the first layer; (b) Correlation with the spectrum from the second layer.

A cross correlation search of a library of Raman spectra of polymers shows a good match between the first layer and ethylene/ethyl acrylate copolymer (Figure 13). The second layer appears to be poly(ethylene terephthalate) (Figure 14). The DXR Raman microscope is able to deliver detailed information about the construction and composition of complex laminates.

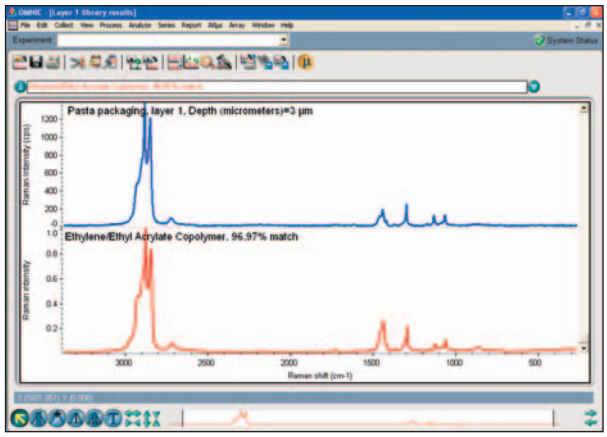

Figure 13: Result of a library search of the first layer shows a good match with ethylene/ethyl acrylate copolymer

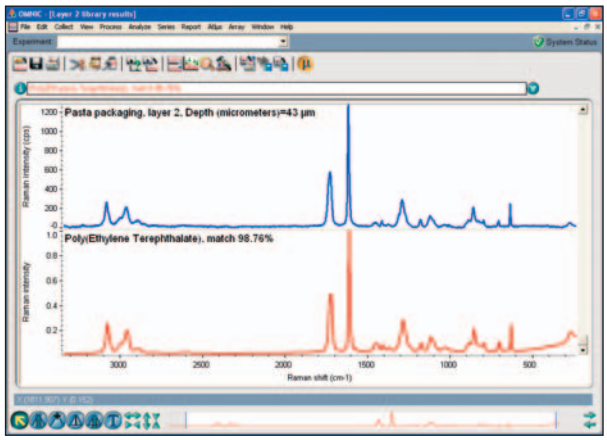

Figure 14: Results of a library search of the second layer gives a good match with poly(ethylene terephthalate)

Conclusion

We have demonstrated that the DXR Raman Microscope delivers excellent spatial resolution in both horizontal and vertical directions. When combined with our patented method for instrument alignment, this microscope becomes a powerful tool for the analysis of micron-sized samples and defects.

References

1. US Patent Number 6,661,509 B2: "Method and Apparatus for Alignment of Multiple Beam Paths in Spectroscopy," Francis J. Deck and Richard C. Wieboldt

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