Issue 8
Newsletter from the Spectroscopy Products Division

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Spectroscopy Innovations

Renishaw continues to develop combined techniques

Scanning electron, infrared, scanning probe, and confocal laser scanning microscopies are all available combined with Raman spectroscopy.

These integrated systems enable users to perform two or more analytical techniques on the same sample region, under the same conditions, in a single instrument.

Time and money are saved by eliminating the need to transfer samples between instruments and relocate the same sampling point. One or more of these techniques can be integrated with any Renishaw Raman microscope as the user's requirements change.

Applications are diverse, and include component distribution determination in pharmaceuticals, imaging of biological samples, forensic analyses, nanotechnology research, and also contaminant location and identification in semiconductor failure analysis laboratories.

Structural and chemical analyser for SEM

Renishaw's structural and chemical analyser (SCA) combines the imaging capabilities of scanning electron microscopy (SEM) with the investigative power of Raman, photoluminescence (PL), and cathodoluminescence (CL) spectroscopies, in a single instrument.

The structural and chemical analyser fitted to an SEM column.

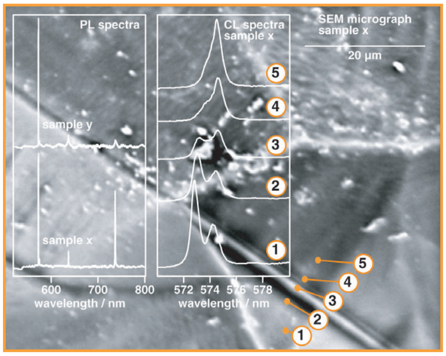
The SCA is fitted to the SEM column and provides the interface between the SEM and spectrometer, enabling secondary electron imaging (the principal SEM imaging mode) and Raman, PL, and CL spectroscopies from the same sample region inside the SEM chamber. Secondary electron imaging provides high spatial resolution, large depth of field, and good contrast, whilst Raman, PL, and CL spectroscopies provide chemical, physical, electronic, and structural information at the micrometre scale.

The power of the SEM-SCA combination is illustrated here with the analysis of diamond films prepared by chemical vapour deposition (CVD). Spectroscopic data were collected at -172 °C, since PL and CL spectra become stronger and better resolved when samples are cooled.

The SEM micrograph shows the fine structure of the sample not observable with optical microscopy. The PL spectra exhibit a peak at 573 nm (1332 cm^{-1} from the laser line), which is the characteristic Raman peak for diamond (changes in its position and shape can be used to evaluate strain in the lattice and crystal quality).

The amount of nitrogen in CVD diamond affects its morphology, mechanical, and electrical properties: intensities, positions, and shapes of peaks in the PL and CL spectra can be used to monitor nitrogen content, crystal lattice strain, and crystal quality. Nitrogen-vacancy defects give rise to the PL peaks at 575 nm ($N\text{-}V^0$), 637 nm ($N\text{-}V^-$) and the CL peaks between 570 nm and 576 nm ($N\text{-}V^-$).

In this case, the PL spectra show comparable intensities for $N\text{-}V^0$ and $N\text{-}V^-$ peaks for sample x and sample y, indicating similar nitrogen contents. However, the N-V peaks are broader for sample y, suggesting a poorer crystal quality than sample x. The Si-vacancy peak (~740 nm) is much less intense in sample y, indicating a lower up-take of silicon (from the chamber windows) during the growth process. The CL spectra illustrate the change in strain in the crystal lattice associated with the feature in sample x. This example illustrates the power of SEM-SCA for the complete characterisation of CVD diamond films.



SEM micrograph, PL and CL spectra of CVD diamond film.

Sample provided by J Butler, Chemistry Division, Naval Research Laboratory, Washington DC, USA.

For more information about the SCA and its applications, please contact your local Renishaw representative.

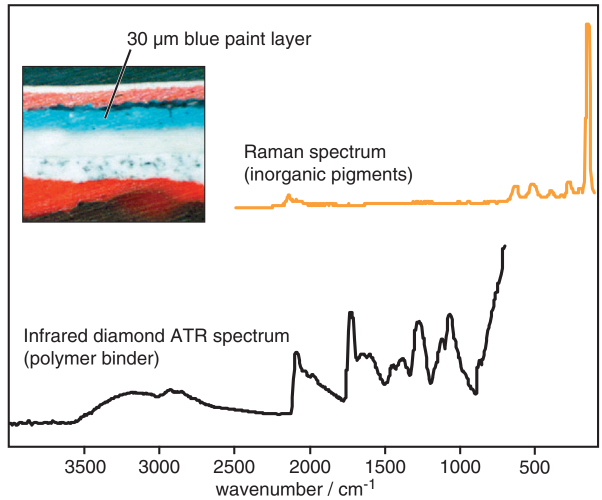
Combined FT-IR microscopy and Raman microscopy

Fourier transform infrared spectroscopy can now be combined with Renishaw's Raman microscopes to offer confocal Raman microscopy and infrared microscopy in a single instrument.

The FT-IR module can be fitted to Renishaw's Raman microscopes at any time: at the time of purchase, or retro-fitted in the field. Space and money are saved by eliminating the need to have two separate instruments, and users save time by performing both techniques on just one instrument.

Example application: paint analysis

Paints comprise several components, including pigments, binders and fillers. Since Raman is more sensitive to the inorganic metal oxides commonly used as pigments, and infrared is better suited for the organic constituents, Raman and infrared microspectroscopies are ideal complements for analysing paints, both old and modern.



In this example, a cross section of an artwork sample with several micrometre-sized layers was analysed with the combined FT-IR/Raman system. Raman spectroscopy of the blue layer yields a strong Raman spectrum indicative of the inorganic pigments, Prussian blue and titanium dioxide, whereas the IR spectrum reveals the protein binder.

Award winning AFM-Raman

The award winning Nanonics NSOM / AFM-100 Confocal™ / Renishaw Raman microscope[†] brings together, in one commercial system, Raman, AFM and NSOM imaging techniques.

The user is able to co-ordinate tip movement with spectrum acquisition, and perform simultaneous and correlated Raman and scanned probe microscopy. All this is carried out without removing the sample from the micro-Raman spectrometer.

For more details, please contact us for **Application note SPD/PN/081, "Combining scanning probe microscopy and Raman microscopy".**

[†]Photonics Circle of Excellence Award 2002.
National Measurement Awards 2003, NPL Materials Award finalist.

Integrated Raman microscopy and confocal laser scanning microscopy

Renishaw's Raman microscope with additional confocal laser scanning microscope (CLSM) offers the imaging, resolution, contrast, and optical sectioning capabilities of CLSM together with the characterisation power of Raman spectroscopy.

The CLSM is coupled to the Raman microscope using Renishaw's RP10 fibre optic probe, which enables Raman spectra to be collected from the same sample position as the CLS data.

For more information about any of the products you see here, please contact your local Renishaw representative.

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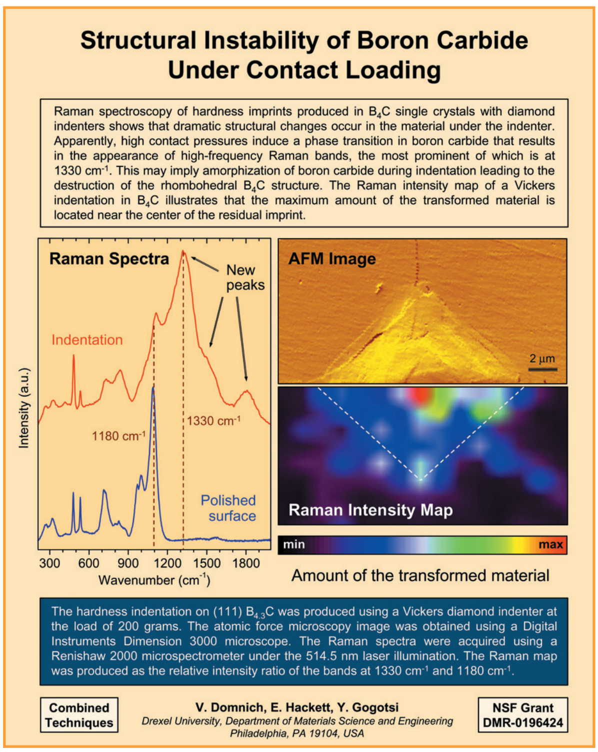
Drexel University wins poster award

Renishaw would like to congratulate Vladislav Domnich, Ethan Hackett, and Yury Gogotsi from the Department of Materials Science and Engineering at Drexel University, Philadelphia, USA on their poster award from the American Ceramic society.

The poster, which describes the study of structural changes in boron carbide under high contact pressures using atomic force microscopy and Raman spectroscopy, won first place in the combined techniques category and the "Roland B Snow Best of Show Award" at the ACerS Ceramographic Contest at the American Ceramic Society Meeting, April 2003, Nashville.



Drexel University's award winning poster.

For additional information see
Domnich, V; Gogotsi, Y; Trenary, M; Tanaka, T.
App. Phys. Lett., **2002**, *81 (20)*, 3783.

image courtesy of the Surfers Paradise Marriott Resort

Come and see us at ICORS 2004

The XIXth International Conference on Raman Spectroscopy (ICORS2004) is to be held on the Gold Coast, Queensland, Australia on the 8th to the 13th August 2004.

This international conference brings together scientists and researchers from universities, government, and industry working in all aspects of Raman spectroscopy.

Please come along to an excellent conference and see us at booth number 1. Register before 1st May 2004 to take advantage of the discounted registration fee.

For further information, visit www.icors2004.qut.edu.au, or email icors2004@put.edu.au

You can also see Renishaw at:

- ICNDST-9
  International Conference on New Diamond Science and Technology, 26th to 29st March, Waseda University International Conference Center, Tokyo, Japan.
  www2.convention.co.jp/ICNDST-9
- 2004 MRS Spring Meeting
  Materials Research Society, 12th to 16th April, Moscone West, San Fransisco, CA, USA.
  www.mrs.org
- Microscopy and Microanalysis 2004
  1st to 5th August, 2004, Savannah Convention Center, Georgia, USA.
  mm2004.microscopy.org

Would you like the chance to have your registration fees for ICORS 2004 paid by Renishaw and see your work featured in the next issue?

If your answer is 'yes' and you've got some exciting new results using Renishaw's spectroscopy products, we'd like to hear from you.

For your chance to see your work featured in the next issue of *Spectroscopy Innovations* and enter the free prize draw to have your registration fees for ICORS 2004 paid by Renishaw, simply email, fax, or mail your Renishaw spectroscopy article to your local Renishaw representative.

Please clearly mark all entries 'Spectroscopy Innovations' and include brief details of the Renishaw products used, and how we can contact you. See below for prize draw terms and conditions.

Each article featuring work using Renishaw spectroscopy products submitted by email, fax or mail to your local Renishaw representative will be entered into a free prize draw for ICORS 2004 registration fees. Entry is not dependent upon the article actually being featured in Spectroscopy Innovations nor is the winner's article guaranteed to be featured. The closing date for receipt of entries is 1st June 2004 and the draw will be held on 1st July 2004. The winner will be the person submitting the article that is drawn on the draw date. No cash alternative is available except where the winner has already paid for ICORS registration, when reimbursement will be given. The winner will be notified using the contact information supplied within 2 weeks of the draw date. By submitting your articles to us, you agree that the article may be edited by us and published in full or part by us in Spectroscopy Innovations and other literature produced by the Renishaw Group. For further information, please contact your local Renishaw representative at the address on the back cover.

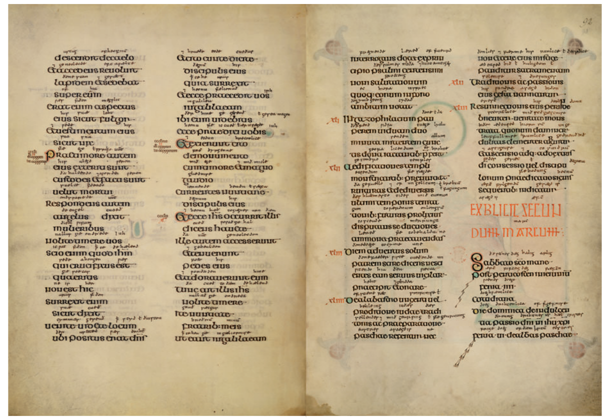
Gospel blues

The Lindisfarne Gospels was written between 715 AD and 721 AD in the Monastery of Lindisfarne, on Holy Island, which is off the coast of Northumberland in the north east of England. The Gospel Book is Britain's most important surviving treasure from early Northumbria, and the majority of the 259 vellum (calf skin) pages are devoted to the Latin texts of the Christian Gospels according to St. Matthew, St. Mark, St Luke, and St. John, with sparse patches of ornamentation. A total of fifteen pages are used to mark the major divisions in the book, consisting of 'title', 'carpet', and 'initial' pages, and these are intricately decorated with a wide range of rich colours.

Carpet page from the Gospel according to St. Mark

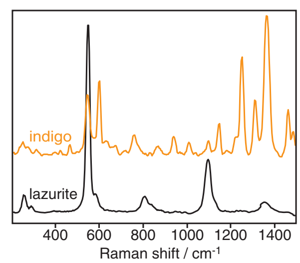
The artistic and historic significance of this early Christian treasure commands much interest in its creation and preservation. Writing and painting sacred texts required great dedication and was considered to be a work of the highest order, the maker's personal 'opus dei' - a work for God. The maker would have been a skilled scribe and artist, mixing the materials to make the extensive colour palette used on the decorated pages, including purples, crimsons, blues, yellow, red/orange, green, white, and black.

Identification of the pigments used in a work of art aids in dating and authentication, and provides valuable insight into how to approach restoration and conservation. Until recent years, non-destructive analysis of pigments has been limited, so identification has largely been done by visual inspection and recipe reconstruction, which can be unreliable. Such an analysis of the Lindisfarne Gospels in 1960 identified the blue pigment as the mineral lazurite. Since the provenance of the Gospels had already been established, the presence of lazurite on it would represent the pigment's earliest use in an English manuscript. This has further historical significance as it suggests, by implication, the existence of a trade route from what is now north-east Afghanistan (the source of most mined lazurite) to Northumbria in the early 8th century.



Spread from the Gospel according to St. Mark

However, a recent analysis of the Gospels by Robin Clark and Katherine Brown[1] of University College London, revealed that the blue pigment was not lazurite, but indigo, probably made locally from the woad plant. The researchers performed the analysis using Renishaw's Raman spectroscopy instrumentation and fibre optic probe, with a book cradle to support the large and heavy manuscript. The use of indigo rather than lazurite on the Gospels is consistent with Raman studies of other manuscripts, which have found the earliest use of lazurite to be around 920 AD, some 200 years later than the original visual analysis of the Gospels in 1960 suggested.



Reference Raman spectra of indigo and lazurite

The Lindisfarne Gospels can be viewed at the British Library Exhibition Galleries in London, UK. See www.bl.uk for further details.

Renishaw gratefully acknowledges Prof RJH Clark, University College London, and Dr L Burgio, Victoria and Albert Museum, London, UK, for supplying the Raman spectra, and Dr M Brown and D Jacobs from the British Library for supplying the images of the Gospels.

[1] Brown, KL; Clark RJH. *J. Raman Spectrosc.*, **2004**, *35*, 4.

If you or any of your colleagues would like to be added to our mailing list, or if you would like further information about our spectroscopy products or applications, please contact us.

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