

Renishaw's structural and chemical analyser (SCA) for scanning electron microscopes



Introduction

The structural and chemical analyser (SCA) enables scanning electron microscopists to benefit from the chemical, structural, and electronic information available from optical spectroscopies, whilst observing the sample using the scanning electron microscope (SEM) or analysing it using energy dispersive spectroscopy (EDS). The SCA can be connected to any of Renishaw's spectrometers, and supports single or multiple techniques. Comprehensive *in situ* sample characterisation is possible using a single instrument. The SEM-SCA system is a unique combination of two mature technologies that results in a techniques tool-set that redefines convenience, efficiency, and productivity.

Optical spectroscopy

The emission, absorption, reflection, or scattering of light by materials forms the basis of a wide range of optical spectroscopies. In general a transition or vibration is induced in the sample and light is emitted or absorbed. The spectrum of the light is normally represented as a plot of light intensity versus light frequency, with peaks or troughs indicating the emission or absorption of light. To study these phenomena requires a spectrometer: Renishaw's spectrometers disperse the light across a sensitive detector so that changes in frequency and intensity can be measured. The range of spectroscopies supported by the SCA, the

excitation mechanisms involved, and the information that they can convey are reviewed below.

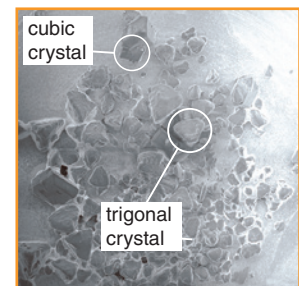
Raman spectroscopy

This is the principal analytical method supported by the structural and chemical analyser. When a sample is illuminated by monochromatic light, a very small proportion of the incident radiation interacts with vibrations in the sample and exchanges energy as a result. The scattered light that has exchanged energy in this way is known as Raman scattered light, with energies lower or higher than those of the incident light by amounts equal to the vibrational energies of the sample. These changes in energy give rise to the peaks in a Raman spectrum, and the amount they are shifted in energy from the incident light is termed the Raman shift. The Raman spectrum represents a fingerprint of a particular sample and the Raman shift of the peaks is affected by chemical composition, crystal orientation and degree of crystallinity, as well as strain in the sample.

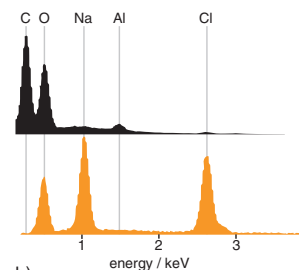
Raman spectroscopy has a spatial resolution comparable to EDS - a micrometre-order sized laser spot can be focused onto or into the sample, and spectra collected from the sampled volume. Provided light can reach the sample, the Raman effect is unaffected by the operating environment, so the technique works equally well under environmental, low, high, or ultra-high vacuum SEM conditions.

Figure 1a shows a crystal mixture on an SEM stub - samples like this might be prepared by forensic scientists attempting to ascertain the nature of suspicious material. It is immediately apparent, given the high depth of field of the SEM image, that there are two classes of crystal present - large predominantly cubic types, and smaller trigonal ones.

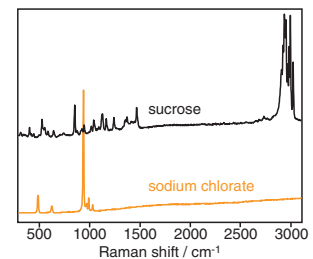
Energy dispersive x-ray analysis (EDS) is available on the majority of SEMs and is the routine choice for analysis of unknown



a)



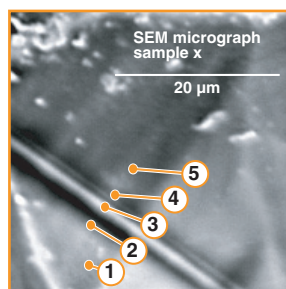
b)



c)

Figure 1

- a) low magnification image of crystals on an SEM stub;
- b) EDS spectra from the cubic- and trigonal-type crystals;
- c) Raman spectra from both types of crystal.



a)

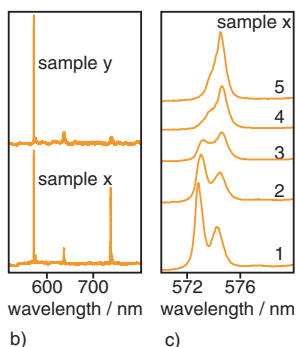


Figure 2

The power of the SEM-SCA combination is illustrated here with the analysis of diamond films prepared by chemical vapour deposition (CVD):

a) SEM micrograph showing a linear feature;
 b) PL spectra collected from two bulk samples ('x' and 'y') at $-172\text{ }^{\circ}\text{C}$; and
 c) CL spectra collected at $-172\text{ }^{\circ}\text{C}$ across the linear feature in sample x.

The SEM micrograph shows the fine structure of sample x, which is not observable with optical microscopy.

Sample y has broader peaks in its PL spectrum than sample x, suggesting a poorer crystal quality than x. It also has a much lower intensity Si vacancy peak ($\sim 740\text{ nm}$) than sample x, which indicates a lower silicon up-take by sample y during the growth process.

The CL spectra show the change in strain in the crystal lattice associated with the feature in sample x.

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

samples. For the two crystal types shown, the EDS spectra in Figure 1b show one crystal type contains carbon and oxygen, the other oxygen, sodium, and chlorine - these elemental analyses do not identify the crystals conclusively.

In-SEM Raman analysis using the SCA generates the spectra shown in Figure 1c: these can be matched against Renishaw's Raman spectral databases to show that the crystals are sucrose and sodium chlorate - sugar and weed-killer, common constituents of "home-made" explosives.

Photoluminescence (PL) spectroscopy

This technique, like Raman spectroscopy, illuminates the sample using laser light. Unlike Raman spectroscopy, the resultant spectra represent an emission, rather than scattering, process. The incident laser light can excite the sample. When the system relaxes back to its original state, the excess energy may be dissipated by the emission of a photon of characteristic energy (although other radiative and non-radiative relaxation mechanisms are also possible). For semiconductors, characteristic PL emissions arise across the band gap (between the conduction and valence bands) and from defect states in the band gap.

PL spectroscopy is sensitive to the physical properties of the sample (e.g. strain, degree of crystallinity, lattice defects), its electronic properties (e.g. carrier concentrations), and trace impurities. PL spectroscopy, therefore, provides a sensitive and spatially-resolved means of analysing some of the physical and electronic structure of materials. The band structure within suitable materials is often made more discrete by cooling the sample to liquid nitrogen or liquid helium temperatures. Under these conditions, experiments *in vacuo* (such as in the SEM) are particularly beneficial: the problems associated with ice formation are avoided, and signal collection is better because the absence of a windowed cold-stage means that long working distance optical microscope lenses are not required.

The laser wavelength must be carefully selected so that it excites the transitions of interest. For samples with a large band gap (3 eV to 4 eV) short wavelength lasers (i.e.

UV or blue lasers) must be used to study the transition. An example of PL spectroscopy is shown in Figure 2.

Cathodoluminescence (CL) spectroscopy

In CL spectroscopy an electron beam is the excitation source. Whilst high-energy photons (x-rays) are generated by high-energy primary electrons exciting inner shell electrons (as detected by EDS), interactions between secondary electrons (typically with energy less than 50 eV) and the valence band electrons give rise to CL peaks in the visible and UV regions of the spectrum. The spectral information available from CL (see Fig. 2) is largely analogous to that from PL.

Although the incident electron beam has a characteristic energy, beam-sample interactions result in a continuum of secondary electron energy levels available to excite transitions over an extended energy range.

CL offers a number of additional benefits compared with PL. Varying the accelerating voltage of the electron beam changes the depth from which CL signals are excited within the sample (as much as several micrometres) - so "depth profiles" can be generated for defects, impurities, and carriers (dopants). The CL excitation volume also decreases as the beam voltage is lowered so that sub-micrometre spatial resolution is possible.

Collecting spatially resolved data is easy with CL spectroscopy. When the spectrometer is set to detect a particular wavelength, and a fast auxiliary detector is selected (either a photomultiplier for UV-VIS or an InGaAs photodiode for near infrared), a CL map is constructed synchronously with the beam scanning. Changing the selected CL peak between map acquisitions allows different electrical and compositional properties to be probed at sub-micrometre resolution. Acquisition times for CL maps are similar to those for x-ray maps.

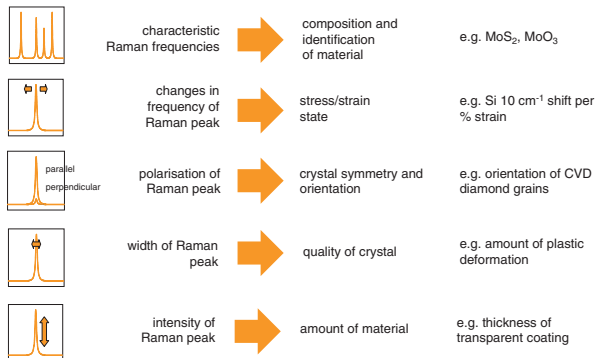
Although the above considers principally the information about electronic properties that a CL spectrum yields, another important characteristic of the technique is its sensitivity to subtle changes in composition. CL mapping

is often used to highlight zoning in mineral crystals, and it can frequently complement the chemical and structural data provided by Raman (and PL) spectroscopy and the elemental data from EDS.

Information available from the SEM-SCA system

When fitted to a SEM with EDS, the structural and chemical analyser provides the means to characterise a sample *in situ* as follows:

- Morphology from the SEM secondary electron image
- Composition information from the SEM (mean atomic number from backscattered electron imaging)
- Elemental composition from EDS
- Chemical composition and identification from Raman spectroscopy
- Electronic structure from CL and PL spectroscopies
- Physical structure and properties (crystallographic and mechanical data) from Raman, CL and PL



Advantages of the SCA

Renishaw introduced its first Raman microscope more than a decade ago, and its revolutionary design made Raman spectroscopy far more accessible and versatile than was previously possible with large, complex, and expensive multi monochromator-based systems.

The SCA provides a new *in-SEM* analytical technique that both complements light microscope-based Raman spectroscopy, and overcomes some of the limitations of the traditional *in-SEM* analytical technique - EDS.

EDS makes micrometre-scale elemental analysis and mapping a routine operation, but the technique is insensitive to light elements (e.g. B, C, N, O, F), and chemical characterisation of the sample is often a matter of guesswork.

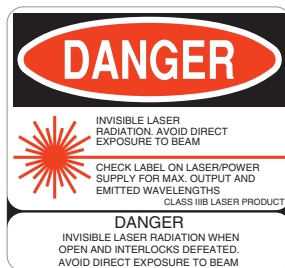
The depth of field and spatial resolution of the SEM are typically orders of magnitude better than that of optical microscopy, and SEMs can image samples using many different contrast mechanisms that arise from both the sample's morphology and its composition. SEMs can rapidly identify regions and features of interest, which can then be characterised using the SCA and EDS.

SEM stages are designed to move samples in 5 axes (x, y, z, tilt, and rotate), and many SEMs are designed to accommodate large and heavy samples. This sample handling capability allows complex and highly topographic objects to be surveyed rapidly.

SEM is a mature technique, and, consequently, there is a wide range of accessories to support experiments in the SEM chamber (e.g. cooling, heating, mechanical-testing, electrical testing). When used in combination with these accessories, Raman, PL, and CL spectroscopies can provide dynamic structural, physical, chemical, and electronic information in combination with SEM observation, e.g. changes in strain in fibres or oxide layers, phase transformations in polymers, and polymerisation reactions can be monitored.

Applications

Nanotechnology	Analysis of self-assembling nanostructures Characterisation of carbon nanotubes	Device failure analysis	Thin film inspection and metrology Lattice, defect, and impurity studies
Materials science	Corrosion and oxidation studies Examination of composite materials	Pharmaceutical	Detection and characterisation of polymorphs Distribution of components within tablets
Electronic materials	Band-gap and free carrier studies Lattice, defect, and impurity studies	Paints/coatings	Distribution of components within paint films Non-destructive studies of "Old Masters"
Polymer science	Characterisation of blends and mixtures Polymerisation and phase transformation studies	Contaminants	Analysis of particles/contaminants on wafers and devices Examination of filtered materials
Mineralogy/gemmology	Characterisation of ores and tailings Identification of thermally treated (HPHT) diamonds	Forensic sciences	Identification of explosives and drugs Characterisation of inks, fibres, and paint chips
Life sciences	Biomedical materials Studies of bone, teeth, and bio-crystals	Environmental	Analysis of airborne contaminants Characterisation of asbestos fibres



Benefits and features

- **No more time is wasted “trying to find the same area” when transferring samples between instruments.**

Secondary electron imaging and EDS analysis are possible with the SCA collection optics inserted.

- **Normal operation of multiple-user SEMs is not compromised in any way.**

The SCA *in-beam* collection optics can be fully-retracted: there's no need for a dedicated SEM.

- **The analysis position is always known.**

The collection optics are positioned with sub-micrometre accuracy, and the laser spot is visible in the white light image.

- **Analytical and observation methods requiring line-of-sight to the sample are unhindered.**

The “standby” mode quickly retracts the SCA collection optics, allowing EDS analysis and BE imaging.

- **“Down time” and servicing costs are minimised.**

The SCA has many safety features, including vacuum interlock, designed to protect itself, the SEM, and your samples against accidental damage. The SCA operates grease-free for cleanliness and low maintenance.

- **Systems can be tailored to meet current and future analytical needs.**

The SCA is fully configurable and can support multiple laser wavelengths and/or techniques. A range of spectrometers from turn-key solutions to full research grade capability are compatible.

- **Minimal training costs.**

The SCA features a high level of automation: SEM operators can be trained quickly to use the system.

Specifications

Spectroscopy

Laser wavelengths	514 nm, 532 nm, 633 nm, 785 nm
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Spot size	< 2 μm FWHM
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Raman shift range	< 150 cm^{-1} to 4000 cm^{-1} (wavelength dependent)
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PL/CL range	< 220 nm to 1000 nm (grating dependent)
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Insertion and retraction mechanism

Insertion/retraction speed	> 20 mm s^{-1}
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Repeatability	< 0.5 μm
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PL/CL range	< 220 nm to 1000 nm (grating dependent)
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Insertion and retraction mechanism

Insertion/retraction speed	> 20 mm s^{-1}
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Repeatability	< 0.5 μm
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White-light imaging

Spatial resolution	2 μm
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Field of view	>25 μm field of view (for 200 mm diameter chamber)
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Spectrometer specifications

All spectrometer specifications are as for Renishaw's *inVia* Raman microscopes. Please see Renishaw's *inVia* Raman microscopes brochure (part no. L-8012-1398) for further details.