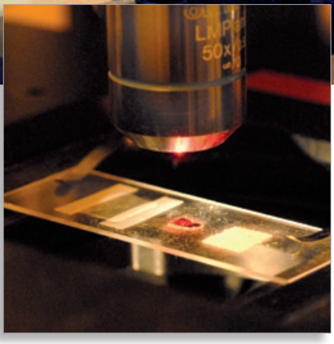


Raman Spectroscopy

- confocal microscopy
- fingerprinting
- bond information
- analysis in devices
- depth and spatial profiling
- on-line analysis

Materials analysis in complete devices can be difficult to perform, as direct contact with the material of interest may not be possible. In such a situation, Raman spectroscopy is a realistic option. This technique is based on the fact that energy lost during the scattering of laser light contains chemical information about the irradiated material. Because water and glass result in little inelastic scatter, analysis can be performed in aqueous solutions or through glass windows. The latter characteristic makes the technique very suitable for on-line, non-destructive analysis.

Confocal Raman microscopy is a specific form of Raman spectroscopy that can be applied to analytical problems that require a high spatial resolution. It allows mapping of surfaces and non-destructive depth profiling with a resolution of 1-2 micrometer.

Philips Innovation labs

PHILIPS

Principle of Raman spectroscopy

When a material is illuminated, light will be scattered, reflected or transmitted. A very small part (1 in every 10^7 photons) is scattered inelastically and the resulting radiation is called Raman scatter. The inefficiency of the process means that in practice only a laser can be used for Raman spectroscopy.

The theoretical background of Raman scattering is shown in fig. 1. A laser photon excites the material to a state with a very limited lifetime (virtual state). When the material returns to its ground state, it loses a well-defined amount of energy to a vibration in the material. The remaining energy, i.e. the difference between the energy of the laser light and the energy involved in the vibration, is released in the form of a Raman photon.

Specific bonds can be identified in both organic and inorganic materials, as they result in typical Raman signals. The intensity distribution of the Raman scatter over the energy spectrum from 20-4000 cm^{-1} (= shift with respect to the excitation wavelength) forms a clear fingerprint of the irradiated material.

Raman versus infrared spectroscopy

Raman and infrared (IR) spectroscopy are complementary analytical tools. In IR spectroscopy, a material is exposed to a spectrum of IR radiation from which it absorbs only specific energies. In Raman spectroscopy excitation is performed at a single wavelength. The energy difference between the excitation radiation (green arrow in fig. 1) and the Raman radiation (black arrows in fig. 1) is in the same range as the energies absorbed in IR spectroscopy (red arrow in fig. 1). However, different bonds are visible for the two techniques. In general, IR spectroscopy is especially suitable for characterizing materials that contain polar bonds, whereas Raman spectroscopy is more suited for studying apolar bonds.
Fig. 2 shows the complementary IR transmission and Raman spectrum for the same polymer. It clearly shows the selective sensitivity of Raman for apolar bonds such as the triple C-C bond at 2200 cm^{-1}. No corresponding IR absorption band is visible.

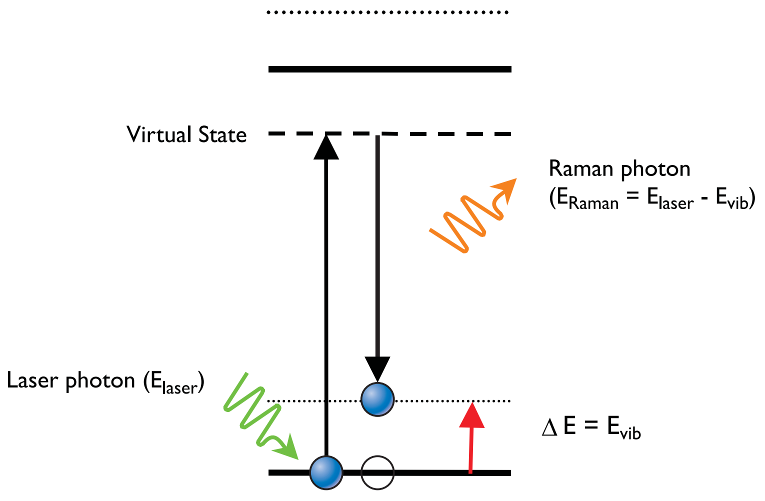


Fig. 1: Energy diagram showing the basis of IR (red arrow) and Raman (other arrows) spectroscopy.

Confocal Raman microscopy

Fig. 3a shows a schematic diagram of a set-up typically used for Raman spectroscopy. The light from the laser is shown in green and the inelastically scattered light is shown in orange. The excitation is performed with laser light that is reflected on a special (notch) filter. This filter only reflects the laser light, while other wavelengths are transmitted. The laser light is then focused on a sample, using a microscope objective. Reflected and scattered light is collected with the same objective and the 'reflection' beam now passes through the notch filter. As only inelastically scattered light can pass this filter, it now functions as a rejection filter for the laser light. The Raman scatter is directed to the monochromator, in which the signal is separated according to wavelength and the spectrum is imaged on a CCD-camera. This simultaneous detection allows time-resolved analysis of processes.

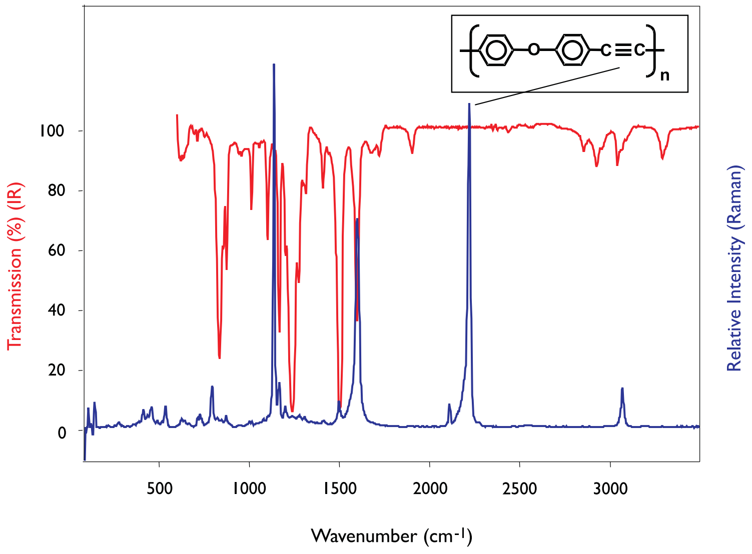
Where IR spectroscopy is limited with regard to spatial resolution of 5 micrometer or more, Raman spectroscopy can be performed with sub-micrometer resolution, using an automated XY-table. For a high-depth resolution, a so-called 'confocal hole' can be introduced in the beam (fig. 3b). In this set-up, the collected inelastic scatter is focused through an aperture. Only light from a specific depth in the sample is transmitted through this small hole. With a piezo-driven Z-stage this makes it possible to obtain depth profiles with a maximum depth resolution of 1-2 micrometer in transparent materials.

Typical applications

Structural studies

Raman spectroscopy is helpful in the structural elucidation of both organic and inorganic compounds. In organic materials, spectra are obtained that contain information about specific functional groups (like –C=O– or –C=C– bonds) and the

Fig. 2: Complementary Raman (blue) and IR (red) spectra for the same polymer.



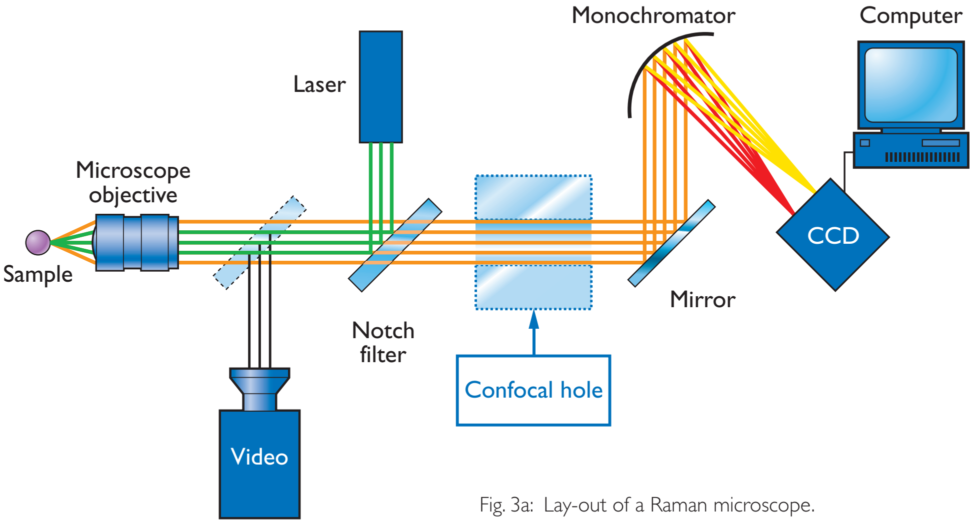


Fig. 3a: Lay-out of a Raman microscope.

total structure of the molecule (fingerprint-like information). In inorganic materials, the information is linked to specific bonds, which helps to identify the material. Raman spectroscopy can also be used to determine structural characteristics such as the crystallinity of silicon or stress in semiconductor structures. Using very short wavelengths, even top layers as thin as 10 nanometer can be studied. One example of structural studies using Raman spectroscopy is the characterization of carbon phases. The technique is able to distinguish the different (semi-)crystalline forms of carbon such as diamond, graphite and carbon nanotubes (fig. 4). For example, the effect of wear on a diamond-like carbon layer (DLC) as used in computer hard disks can be examined as the character of the carbon-carbon bonds in the matrix changes during use.

Remote analysis

Raman spectroscopy is well suited for remote analysis and characterization in devices. As water and glass give little Raman scatter, it is possible to perform non-destructive analysis in production processes. Polymerization reactions can be followed, even when these are performed under conditions that do not allow direct physical access to the material. Devices can also be analyzed without destroying their functionality. Polymeric LEDs are tested at high temperature and humidity for long periods of time to determine lifetime-limiting factors. With Raman spectroscopy it is possible to characterize the different organic layers (< 100 nanometer thick) in these devices during such tests.
Obviously, it is not a problem to characterize materials that are sensitive to water or oxygen with Raman analysis either. Such samples can be analyzed in a vacuum chamber or a nitrogen-flushed environment.

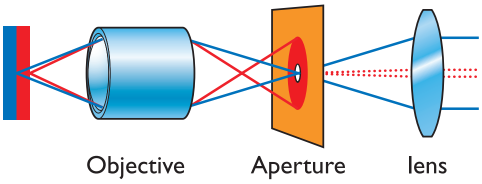
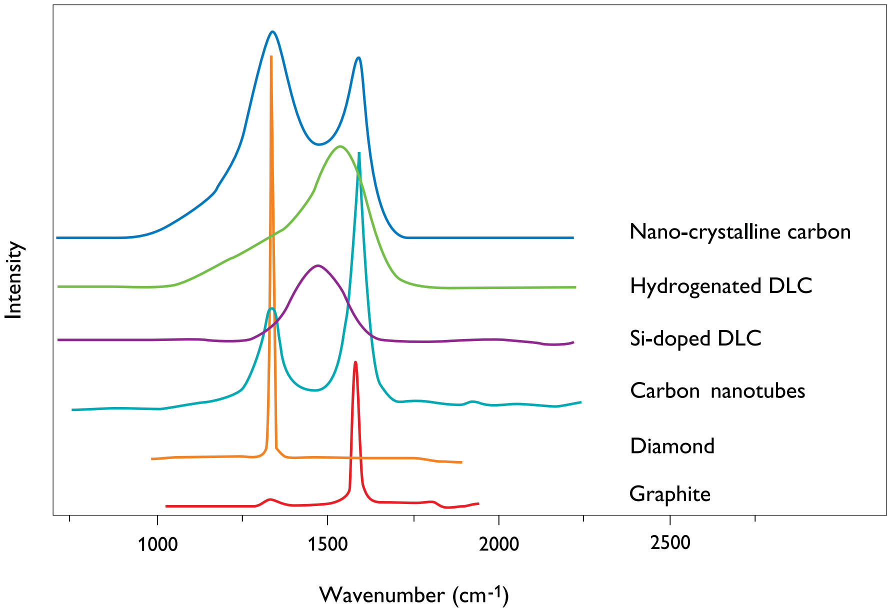
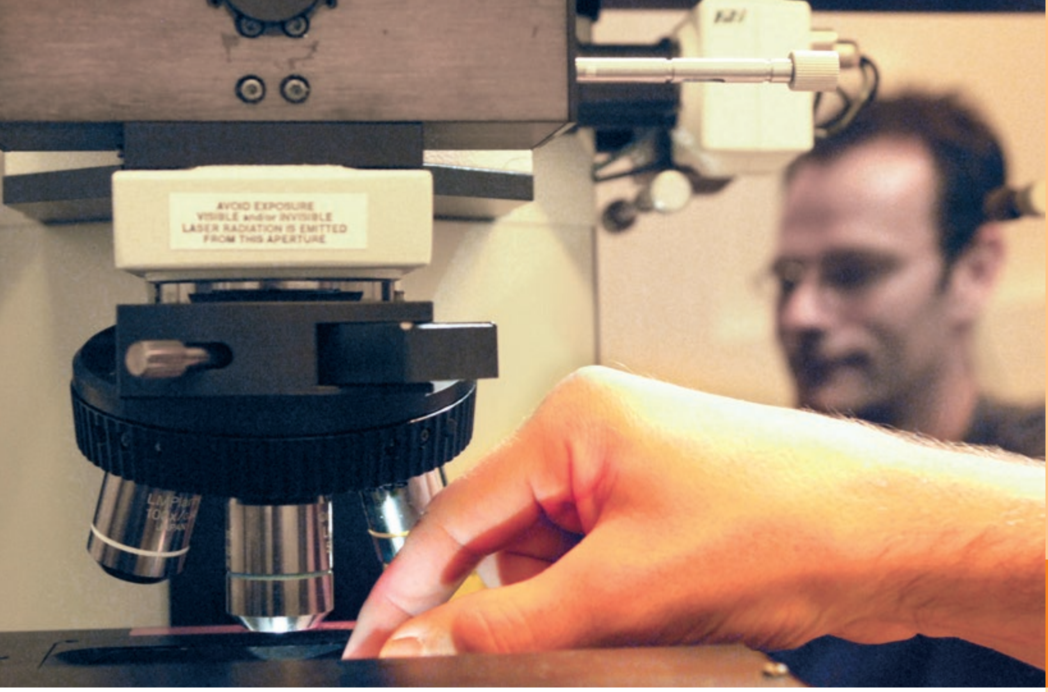


Fig. 3b: Detailed lay-out of a confocal hole as used in a Raman microscope.

Fig. 4: Raman spectra for different forms of carbon.





Philips Innovation labs
Material Analysis lab
offers a full range of analytical methods and expertise to support both research and manufacturing, serving customers by taking an integral, solution-oriented approach.

World-class expertise – working for you

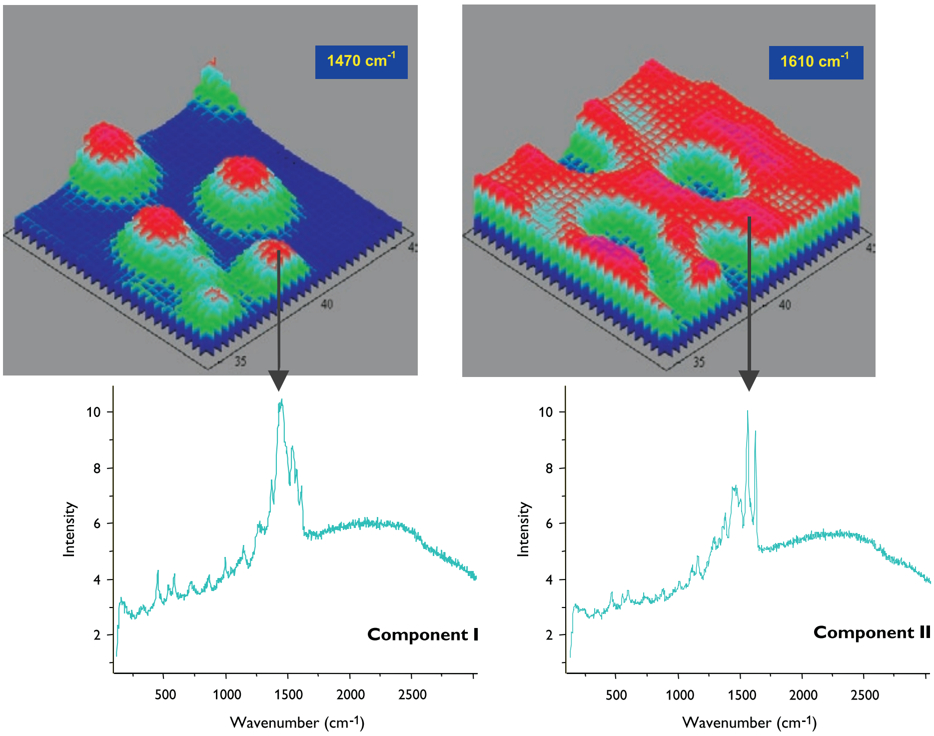
For more information:
Phone: +31 40 27 40455
E-mail: innovationlabs@philips.com
www.innovationlabs.philips.com

Technical Note 10
August 2016

Mapping studies

Mapping studies of inhomogeneous samples, e.g.. polluted surfaces or polymer blends, can be performed with a lateral resolution in the order of 1 micrometer. Fig. 5 shows a mapping of a multi-component polymer layer in which phase separation is visible on a surface area of only 10x10 micrometer.

Fig. 5: Mapping of a polymeric surface (10x10 micrometer); at the top, intensity maps are given for two specific Raman bands, corresponding to two different components on the surface. On the bottom, the complete Raman spectra are shown for two positions.



©2016 Philips Lighting Holding B.V.
All rights reserved.

Characteristics

Obtained information

- structural properties, molecular composition, crystallinity
- qualitative and semi-quantitative

Sample type

- solids, liquids, gases
- bulk materials and thin films
- both organic and inorganic materials

Sample requirements

- no or little sample preparation required
- no size requirements

Lateral and depth resolution

- 1-2 µm resolution (in X-, Y- and Z-direction)

Detection limit

- strongly dependent on material (100 ppm to 1%)

Accuracy

- semi-quantitative; 1-5 % relative if standards are available

Analytical range

- traces to main components

Routine analyses

- yes, in combination with IR analysis as well as in on-line applications

Philips Innovation labs