by Willes H. Weber

Raman Scattering Becomes More Accessible

The Raman effect refers to the scattering of light by a medium—a sample of diamond, for example—accompanied by a frequency shift of the light that is associated with an excitation in the same medium. In most Raman studies, the observed frequency shifts correspond to vibrational excitations of the sample under investigation. Moreover, one can also observe electronic and magnetic excitations in certain materials, which provide additional information about samples. The spectrum of frequency-shifted light generally gives a unique fingerprint for the scattering material. This signal can be used to identify sample composition and many other properties important to industrial applications, such as phase state, degree of crystallinity, crystal size and orientation, strain, isotopic composition, and carrier concentration.

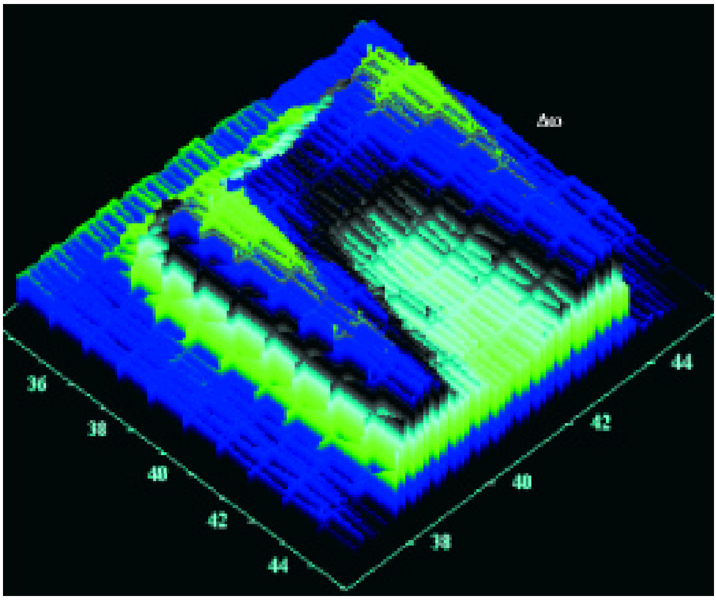

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Figure 1. This image of strain distribution in a 5-μm-wide silicon channel surrounded by oxide was obtained from a two-dimensional, point-by-point Raman scan. Compressive stress is greatest at the edges and corners but decreases in the middle.

The Indian physicist C. V. Raman, for whom the phenomenon is named, received the Nobel Prize in Physics in 1930 for his experimental demonstrations of the effect in liquids, which he did in collaboration with R. S. Krishnan two years earlier. In that same year, 1928, two Russian physicists, G. Landsberg and L. Mandelshtam, independently demonstrated the effect in a crystal. The effect had been predicted on theoretical grounds as early as 1923.

The experimental apparatus required to obtain the Raman spectrum of a material is conceptually quite simple. A monochromatic light source is focused on the sample, and the scattered light is collected and refocused onto the entrance slit of a spectrometer. The spectrometer spatially disperses the light to separate out the different wavelength components, which are measured at the exit of the spectrometer.

Two experimental details complicate this simple picture. First, the Raman effect is extremely weak, which means that it requires a very bright light source. In fact, before the invention of the laser in the 1960s, there was little interest in using Raman scattering as a general spectroscopic tool. Monochromatic light sources were so dim—and the Raman effect so weak—that only ideal samples yielded good spectra. The laser dramatically changed that situation, and today all Raman instruments use laser excitation.

Second, the weak Raman scattering is accompanied by a much stronger elastic scattered component, termed Rayleigh scattering, that can exceed Raman scattering by factors as large as 10^6 to 10^8 for a typical powdered sample. This Rayleigh scattering can lead to background stray light, whose propensity to go in all directions in the spectrometer completely obscures the Raman signal. Until recently, double and even triple spectrometers were absolutely necessary to reduce this stray light to an acceptable level.

During the 1970s and 1980s, the discipline of Raman scattering flourished in many research laboratories worldwide. The typical instruments then included large-frame gas-discharge lasers such as the argon-ion laser, double or triple spectrometers, and photomultiplier detectors with photon-counting electronics. Because of the size, cost, and difficulty of maintaining and operating such instruments, however, industry showed little interest in using Raman scattering for routine sample analyses.

The situation today in Raman instrumentation is very different. During the past decade, remarkable advances have occurred in many technological areas that have made it possible to produce relatively inexpensive, turn-key Raman instruments that have excellent performance and are easy to use and maintain. These instruments are put to such disparate uses as monitoring chemical processes in real time, manufacturing quality control, and monitoring the concentrations of oxygen, carbon dioxide, and anesthesia gases exhaled by patients undergoing surgery. Many of the new instruments can be equipped with fiber-optic probes that allow remote measurements in extreme environments as much as 100 m away.

The problem of reducing, or rejecting, stray light has been solved by the introduction of holographic notch filters, which are basically three-dimensional Bragg gratings imposed by holographic means in a polymeric coating on a glass substrate. They are designed to have low transmission (high reflectivity) at the laser wavelength and high transmission at all other wavelengths. The stray-light rejection ratio for a single filter can be as high as 10^6, which allows a small single-stage spectrometer to be used in

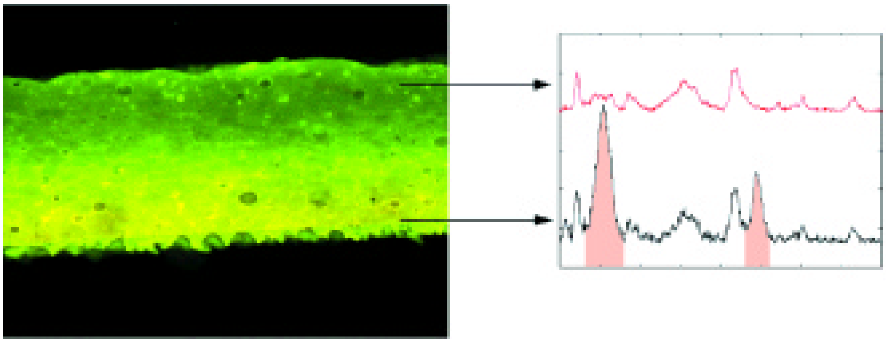

Figure 2. Raman spectra (right) of an aged, 1-mm-thick poly(vinyl chloride) sample show the formation of polyenes (highlighted peaks), the first step in degradation that leads to embrittlement and discoloration.

place of the double- and triple-grating behemoths of a few years ago. Holographic notch filters are probably the first successful example of a commercial photonic-bandgap device.

Silicon-based array detectors have sped up the collection of the weak Raman signal. In older systems, the spectrometer was step-scanned through the spectral region of interest while a photomultiplier sequentially counted the number of scattered photons at each wavelength. In newer instruments, a single-chip array detector placed at the focal plane of the spectrometer measures the Raman signal simultaneously at 500 to more than 2,000 different wavelengths. The number of wavelengths measured depends on the number of pixels in the array, the focal length of the spectrometer, the groove density of the grating, and the wavelength region. The breadth of the spectral region covered can be as large as 3,000 cm^{-1} (in frequency units). This multiplex advantage, coupled with the higher throughput of a single-stage spectrometer, has reduced by a factor of 10^2 to 10^3 the exposure time needed to acquire a typical Raman spectrum. Some sophisticated instruments even combine the multiplex advantage of the array detector with a step-scanning capability to produce continuous spectral scans that are much longer than the spectral coverage of the static array.

Finally, new laser sources have been developed that make virtually any wavelength from near-infrared to ultraviolet (UV) available for Raman studies. This wide choice of excitation wavelengths allows an instrument to be optimized for specific applications. By choosing a wavelength of light near an absorption frequency of the material under study, one can achieve resonance enhancement of the Raman signal. If samples are to be examined at high temperatures, UV excitation is needed to avoid the thermal background. An example that demonstrates both of these features is the use of a UV Raman system operating at 244 nm to monitor the in situ growth of diamond films in a plasma reactor at temperatures as high as 1,000 °C.

Some samples, including many commercial plastics, show a strong fluorescent signal with visible-light excitation, which tends to overwhelm the weak Raman signal. This fluorescence is uncommon with near-infrared light. For example, a fiber-coupled Raman system using a high-power diode laser emitting at 785 nm has been used to sort waste automotive plastics in a recycling plant. Even longer-wavelength excitation sources can be used, in which case the Raman spectrum is extracted with a Fourier-transform spectrometer. This instrument cannot use an array detector, but it has a multiplex advantage nevertheless, because it is capable of measuring all wavelengths simultaneously.

Raman research instruments have incorporated most of the advances discussed here. In addition, these instruments are often coupled to optical microscopes so that Raman spectra can be obtained from objects as small as 1 μm. Two-dimensional Raman maps can be produced using automated scanning of the microscope stage and automated spectral analysis.

Figure 1 shows an example of such a map. Here, a two-dimensional image of the strain distribution in a semiconductor device is obtained from shifts of the silicon Raman line at 521 cm^{-1}, measured at each of about 600 points on the surface of a 5-μm-wide silicon channel surrounded by oxide. A compressive stress ($\Delta\omega > 0$) is measured, which can be seen to be greatest at the edges and corners and decreases in the middle.

Another industrial application of Raman scattering is shown in Figure 2. The picture on the left is a cross-section fluorescence image of an aged, 1-mm-thick, poly(vinyl chloride) (PVC) sample similar to that used in automotive dashboards. The fluorescence intensity measures the degree of degradation. The Raman spectra, on the right, are obtained with a confocal Raman microscope. These spectra show the formation of polyenes, characterized by the two highlighted Raman lines at 1,107 and 1,490 cm^{-1}, occurring preferentially near the lower surface next to the urethane foam backing. Polyene formation is the first step in degradation of PVC, which ultimately leads to embrittlement and discoloration. These results show that in field-aged PVC, a chemical process originating in the urethane backing dominates photo- and thermal-assisted processes in promoting degradation.

With the advent of the laser, Raman scattering became an important tool in research laboratories. Technological innovations during the past decade have revolutionized its use in industrial applications. Further advances will certainly expand the potential benefits of Raman scattering to industry, both in the research laboratory and on the plant floor. Ω

BIOGRAPHY

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