

Molecular Spectroscopy Workbench Thin-Film Filters for Raman Spectroscopy

Recent advances in thin-film filter technology have enabled dramatic improvements in the performance of filters for laser-based analytical instrumentation.

Turan Erdogan and Victor Mizrahi

Hello again, fellow spectroscopists. I am bringing you another tool for analysis in general, and, considering my interests, a process analytical technology (PAT) to be specific. For some time, molecular spectroscopy has been considered (in this column, for sure) to be mid- and near-infrared. One very important tool that doesn't get enough notice is filter-based Raman spectroscopy.

However, recent advances in thin-film filter technology have made possible dramatic improvements in the performance of filters for laser-based analytical instrumentation, including Raman spectroscopy systems and laser-based fluorescence instruments. These advances add up to exciting, rugged, and accurate tools to add to our PAT toolbox. This month, Turan Erdogan and Victor Mizrahi (Semrock, Inc.) have agreed to submit some interesting information on the subject (based, of course, upon their company's products).

Raman spectroscopy is used widely today for applications ranging from industrial process control to laboratory research to biological and chemical defense measures. Industries that benefit from this highly specific analysis technique include the chemical, polymer, pharmaceutical, semiconductor, gemology, computer hard disk, and medical fields.

In Raman spectroscopy, a laser beam is used to create a small amount of longer-wavelength light through Raman (inelastic) scattering from a sample under test. The Raman spectral "fingerprint," unique to the sample, is measured by a dispersive or Fourier-transform spectrometer.

Fixed optical filters are critical components in Raman spectroscopy systems. These filters are used to prevent undesired laser light from reaching the spectrometer and swamping the relatively weak Raman signal (see Figure 1). Laser-transmitting filters inserted between the laser and the sample block undesired light from the laser (such as broadband spontaneous emission from semiconductor lasers or plasma lines from gas lasers), as well as any Raman scattering and fluorescence generated between the laser and the sample (especially a problem in optical-fiber microprobe systems). Laser-blocking filters inserted between the sample and the spectrometer block the Rayleigh (elastic) scattered light at the laser wavelength, which typically is many orders of magnitude stronger than the desired Raman lines.

Filters and their Functions

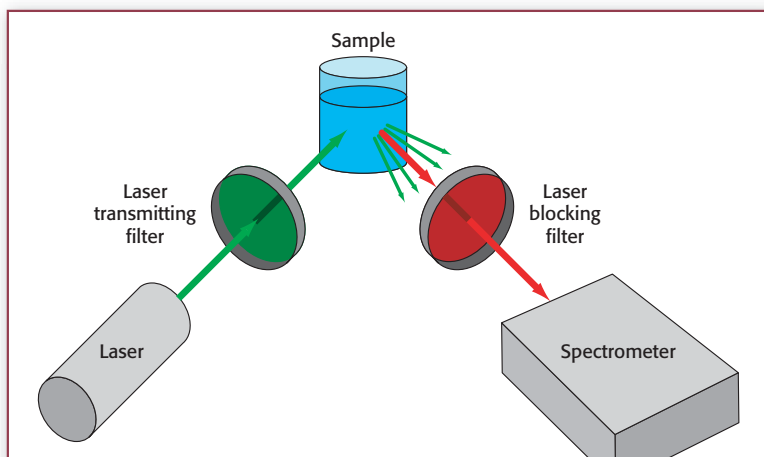
There are three basic types of filters for Raman spectroscopy systems: laser-line filters, edge filters, and notch filters (see Figure 2). Laser-line filters are ideal for use as laser-transmitting filters, and notch filters are the versatile choice for laser-blocking filters. In systems using such a pair of filters, both Stokes (red-shifted) and anti-Stokes (blue-shifted) Raman scattering can be measured simultaneously. However, in many cases edge filters are used for laser blocking due to their superior performance. For example, a modern long-wave-pass (LWP) edge filter placed before the spectrometer can offer higher laser-line blocking than a notch filter, and the steepest possible edge performance, ideal for observing Raman signals that are extremely close to the laser line. Short-wave-pass (SWP) edge filters also can be used as laser-blocking filters for anti-Stokes measurements.

There are various types of optical filters: diffraction gratings, absorption filters, and thin-film interference filters. A number of years ago the state-of-the-art in Raman filters was advanced by the introduction of volume-holographic grating filters. Holographic notch filters accomplish laser-blocking by diffracting a spectral notch around



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files. These filters required hundreds of thin-film layers made with ultra-precise thickness control. Combining modern IBS technology utilizing sophisticated deposition control algorithms, with advanced filter designs that could now be manufactured, has allowed a new standard of performance for spectroscopy filters.

Examples of transmission spectra of these new thin-film interference filters are shown in Figure 3, where the target design and typical measured spectra are overlaid to demonstrate the high degree of accuracy made

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Thin While film interference filter technology have made it possible to produce the

ing a large market for extremely reliable filters with complex spectral pro-

table 1 compares the minimum specified performance of a modern

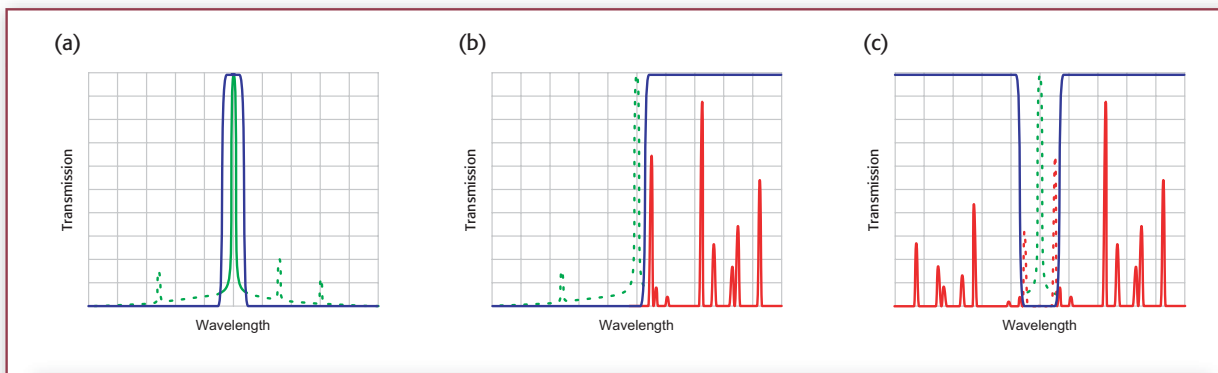


Figure 2. Schematic illustration of typical Raman filters, where blue lines represent the transmission spectra, green lines represent laser spectra, and red lines represent the Raman signal. (a) Laser-transmitting filter for both Stokes and anti-Stokes measurements. (b) Laser-blocking steep edge filter for superior Stokes measurements. (c) Versatile laser-blocking notch filter for both Stokes and anti-Stokes measurements.

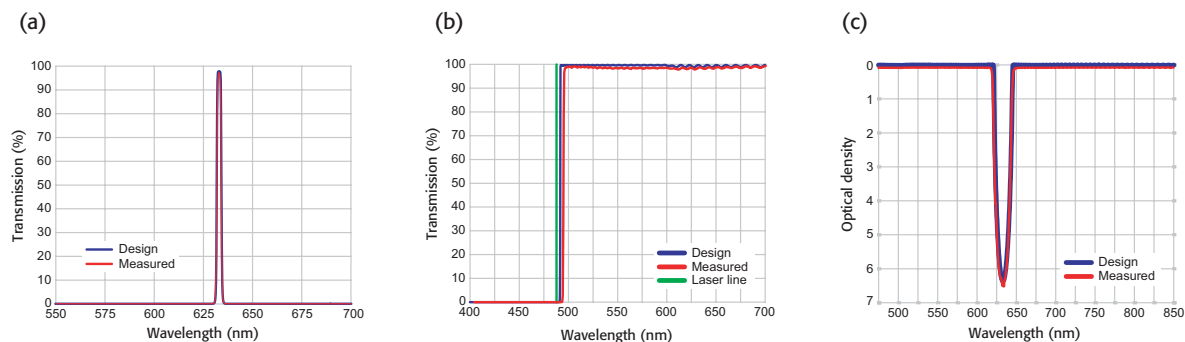


Figure 3. Spectra of modern thin-film filters, showing both target design and typical measured example spectrum: (a) 632.8-nm

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Bandwidth

Modern thin-film notch filters also exhibit excellent spectral performance with steep edges, deep blocking, and very high transmission. A challenge that has always existed for thin-film notch filters is to make the notch bandwidth narrow. Because the bandwidth is approximately inversely proportional to the optical path length of light in the filter, a narrow bandwidth requires a thick filter. Holographic filters achieve narrow bandwidths by taking advantage of a thick layer of photosensitive material (usually dichromated gelatin). Fortunately, with recent advances in IBS coating technology, thin-film filters now can achieve sufficiently thick coatings to enable bandwidths that are compara-

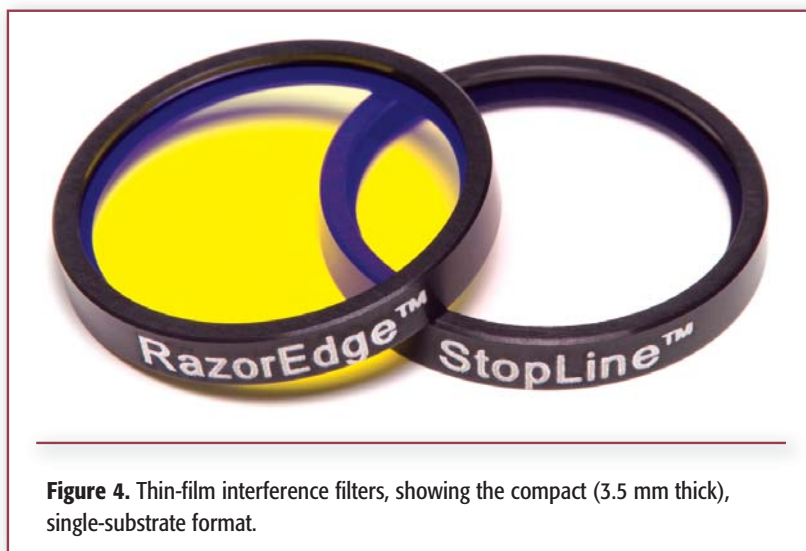


Figure 4. Thin-film interference filters, showing the compact (3.5 mm thick), single-substrate format.

Table II. Comparison of the minimum specified spectral performance of a new thin-film notch filter to that of both performance- and premium-grade holographic notch filters

Property	Performance Holographic Filter	Thin-Film Notch Filter	Premium Performance Holographic Filter
Notch bandwidth – frequency (for 532-nm filter)	< 700 cm ⁻¹	< 670 cm ⁻¹	< 350 cm ⁻¹
Notch bandwidth – wavelength (for 532-nm filter)	< 20 nm	< 19 nm	< 10 nm
Laser-line blocking	> 6 OD	> 6 OD	> 6 OD
Transmission	> 85%	> 90%	> 85%

ble to those of holographic filters. Table II compares the minimum specified performance of a modern thin-film notch filter to that of performance- and premium-grade holographic notch filters. As can be seen from this comparison, the thin-film notch filter

performance exceeds that of the holographic notch filters in every respect except bandwidth, which is comparable. In addition to Raman spectroscopy, these notch filters also are finding wide use in laser-based fluorescence instrumentation and biomed-

superior reliability and durability because the all-dielectric coatings are based upon hard refractory oxide materials. These dense, all-glass coatings also enable almost-zero temperature dependence to maximize the operating temperature range of instruments without the need for expensive compensation hardware.

Finally, a significant advantage of the new thin-film filter technology is that very sophisticated spectral profiles can be realized with the same compact, single-substrate filter format. For example, double-, triple-, and even quadruple-notch filters (Figure 6) can be manufactured with the same exacting spectral performance, convenience, and reliability of the laser-line, edge, and single-notch filters described above.

Summary

Modern thin-film filters, as described in this article, are a boon to a variety of spectroscopic applications, especially Raman-based process analysis. They are simpler, sharper, more rugged, and more reproducible than older thin-film filters and holographic filters. Raman spectroscopy has been gaining in popularity, and the introduction of the latest optical filter technology will further hasten its broader acceptance.

Turan Erdogan is chief technology officer and **Victor Mizrahi** is president and CEO of Semrock, Inc. (Rochester, NY; www.semrock.com).

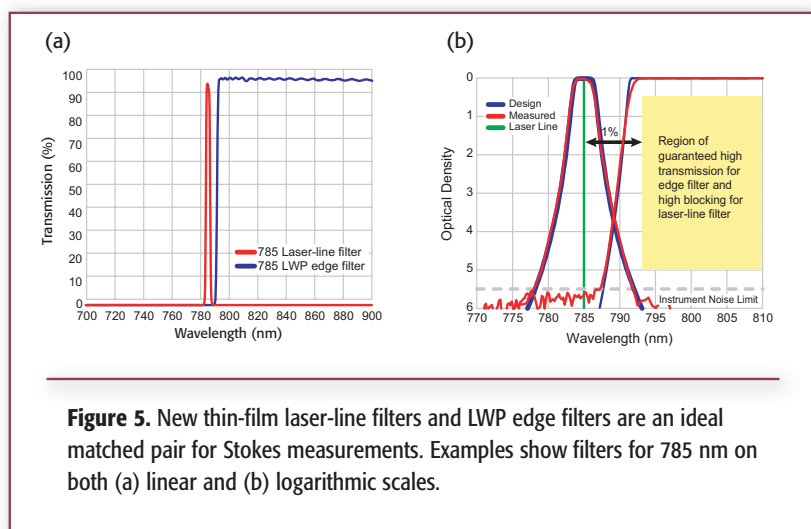


Figure 5. New thin-film laser-line filters and LWP edge filters are an ideal matched pair for Stokes measurements. Examples show filters for 785 nm on both (a) linear and (b) logarithmic scales.

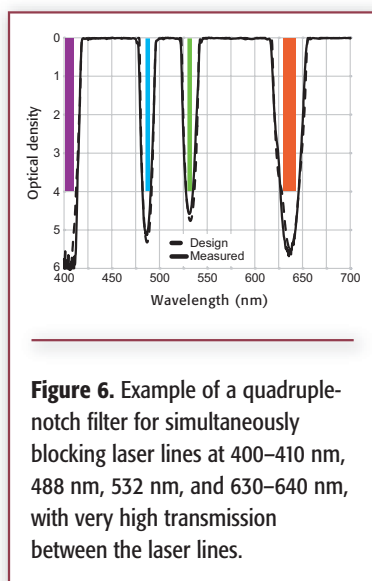


Figure 6. Example of a quadruple-notch filter for simultaneously blocking laser lines at 400–410 nm, 488 nm, 532 nm, and 630–640 nm, with very high transmission between the laser lines.

ical laser systems.

This new breed of thin-film filters offers many other advantages over holographic filters in addition to the spectral advantages already noted. Blocked light is back-reflected, rather than diverted at an acute angle, simplifying system layout and improving stray-light management. Thin-film filters are very compact and simple to integrate into a variety of optical systems. And thin-film filters are inherently lower in cost because many filters are manufactured simultaneously in a parallel approach. Furthermore, compared to both holographic filters and thin-film filters made with older technologies (for example, soft coatings), these modern filters offer far