Spectroscopy
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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.

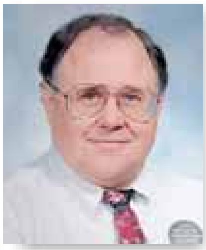
Turan Erdogan and Victor Mizrahi

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.



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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

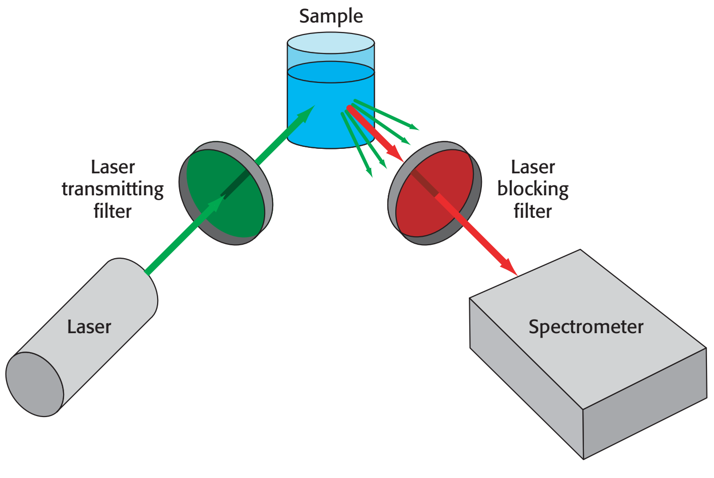

Figure 1. Laser transmitting and blocking filters in a typical Raman spectroscopy system.

the laser wavelength at an acute angle relative to the direction of the desired transmitted light. They also can serve as laser-line filters, where the desired laser light is diffracted at an oblique angle and a carefully aligned slit or pinhole is used to block unwanted light. The holographic gratings are exposed and developed in a thick gelatinous film that typically is sandwiched between two glass substrates.

Thin-Film Interference Filters

While holographic filters have long been popular, recent advances in thin-film interference filter technology have made it possible to produce the highest-performance optical filters for Raman spectroscopy applications with higher reliability and at lower cost. These new filters are manufactured using ion-assisted, ion-beam sputtering (IBS) deposition, a process perfected for coating precise ferrite thin films on magnetic disks, extremely low-loss mirrors for ring-laser gyro applications, and then ultimately high-performance optical filters for dense wavelength-division-multiplexed fiber-optic communications systems. The latter application fueled advances in IBS technology by providing a large market for extremely reliable filters with complex spectral profiles. These filters required hundreds of thin-film layers made with ultraprecise 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 possible by modern IBS technology. Figure 4 shows a photograph of some typical filters.

The graphs in Figure 3 highlight the most striking advantage of these modern thin-film filters over both holographic filters and other, older filter technologies: the complex and precise filter spectra. In general, these new filters stand out with their ability to offer steep edges to measure very small Raman shifts, deep blocking for maximum laser rejection, and high transmission of desired light to detect weak signals. Because these filters are based on hard oxide glass materials, operation in the near ultraviolet region is possible—holographic and soft-coated thin-film filter materials preclude operation even in the low 400-nm regime.

Table I compares the minimum specified performance of a modern

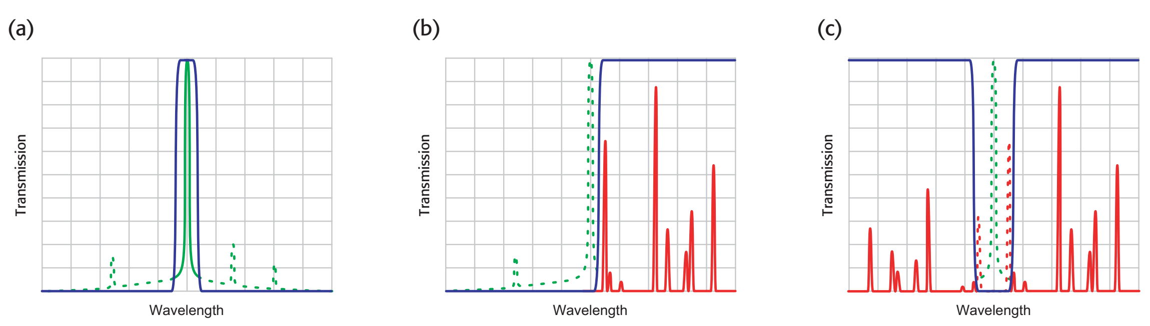

Figure 2. Schematic illustration of typical Raman filters, where blue lines represent the transmission spectra, green lines represent laser spectra, and red lines represent the Raman signal. (a) Laser-transmitting filter for both Stokes and anti-Stokes measurements. (b) Laser-blocking steep edge filter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

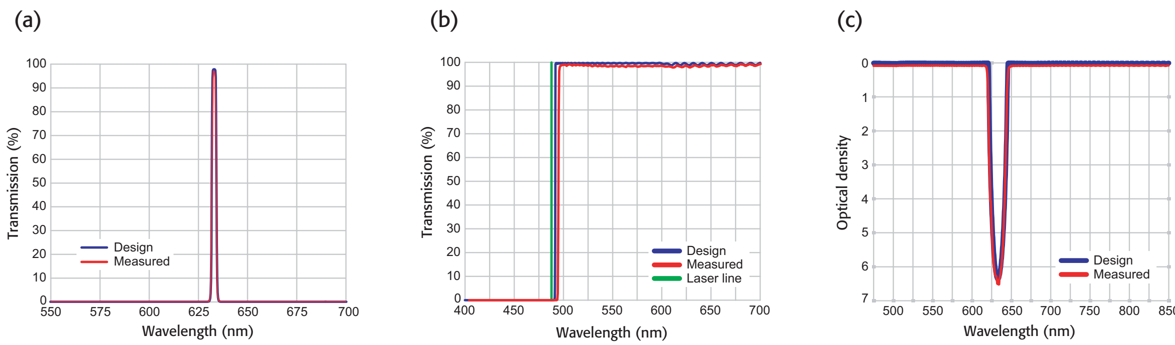

Figure 3. Spectra of modern thin-film filters, showing both target design and typical measured example spectrum: (a) 632.8-nm laser-line filter; (b) 488.0-nm LWP edge filter; and (c) 632.8-nm notch filter.

LWP edge filter for laser-blocking to that of a premium holographic filter. In fact, typical performance can exceed an optical density (OD) of 8 or more at the laser-line, and the average transmission typically is around 98% (see Figure 3).

It is important to keep in mind that the best overall system performance is achieved when the laser-transmitting and laser-blocking filters work together as a matched pair. For example, for Stokes measurements a properly matched high-performance thin-film laser-line filter and LWP edge filter, both made with modern IBS technology, are ideal. The steep edges and high transmission exhibited by both filters allow them to be spectrally positioned very close together, while still retaining complementary transmission and blocking characteristics (Figure 5). The laser-line filter provides greater than 90% transmission immediately in the vicinity of the laser wavelength, and then rolls off rapidly to achieve high blocking (OD > 5) at wavelengths within 1% of the laser line. The edge filter provides extremely high blocking (OD > 6 or more) at the laser line itself, and then rapidly climbs to achieve very high transmission (> 93%) of the desired signal light at wavelengths only 1% away from the laser line.

Table I. Comparison of the minimum specified spectral performance of a new thin-film filter to that of a premium holographic notch filter

Property	Premium Performance Holographic Filter	Thin-Film Raman Edge Filter
Edge steepness — frequency (50% to OD 4)	< 150 cm^{-1}	< 50 cm^{-1}
Spectral edge width — wavelength (50% to OD 4 at 532 nm)	< 4 nm	< 1.4 nm
Laser-line blocking	> 6 OD	> 6 OD
Transmission	> 85%	> 93%

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

Spectral Performance and 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-

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 biomedical laser systems.

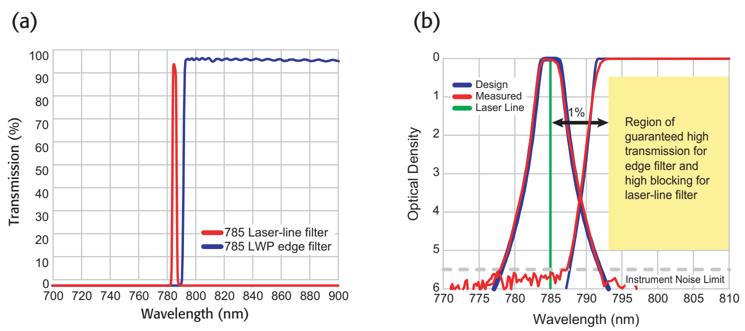

Figure 5. New thin-film laser-line filters and LWP edge filters are an ideal matched pair for Stokes measurements. Examples show filters for 785 nm on both (a) linear and (b) logarithmic scales.

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 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.

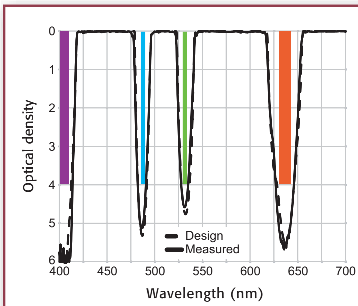

Figure 6. Example of a quadruple-notch filter for simultaneously blocking laser lines at 400–410 nm, 488 nm, 532 nm, and 630–640 nm, with very high transmission between the laser lines.

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.

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