RAMAN SPECTROSCOPY ENHANCED BY A BACK-ILLUMINATED SCMOS CAMERA

Operating in a climate-controlled lab or on the Martian surface, back-illuminated sCMOS detectors provide high sensitivity, high dynamic range, and low noise, even in low-light conditions.

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Raman spectroscopy serves a bevy of needs in numerous application areas. More complicated system designer requests and more demanding operational environments have prompted a need for more capable detectors.

In this respect, older Raman spectroscopy systems — such as those using photomultiplier tubes (PMTs) or avalanche photodiodes (APDs) — are at a disadvantage compared to more modern back-illuminated systems.

This article discusses the challenges inherent in working with older detector technologies, dispels some misconceptions associated with Raman spectroscopy detectors, and introduces readers to PCO's back-illuminated camera solutions.

UNDERSTANDING RAMAN SPECTROSCOPY

Raman spectroscopy provides detailed information about a material's geochemical composition by creating a "molecular fingerprint." The technique is used primarily for material identification, but it also is regularly leveraged to measure crystallinity, stress strain, etc.

Raman spectroscopy is accomplished by directing light source — typically, a laser — at a sample in a solid, liquid, or gas state. Shining monochromatic light of a certain wavelength onto the sample can cause molecules in the sample to vibrate, capturing some of the incident energy and altering the properties of the light that scatters off the sample. This scattered light is captured and analyzed. Raman spectroscopy specifically looks at vibrations induced in the sample by the light (i.e., the Raman shift).

Raman is a weak effect, in that the light coming back from samples is extremely weak. Thus, the evolution of sensitive detection sources and appropriate illumination sources has been critical to advancing and adapting the technique to different applications over the past 30 to 40 years — particularly in a natural environment or on a planetary surface (as discussed later in this article).

A number of technological options exist to carry out Raman spectroscopy, among them silicon APDs, PMTs, and 2D pixel array detectors including charge-coupled device (CCD) or scientific complementary metal oxide semiconductor (sCMOS) detectors.

PMTs are extremely sensitive, down to single photon counting. Thus, PMTs enjoy regular use in certain Raman applications (e.g., a Raman LiDAR for trace gas measurement in the atmosphere). However, PMTs are single-element detectors, limited to measuring one peak in the spectrum at a time. As with all point detectors, the wavelengths of interest must be sequentially scanned, which usually is a slow process.

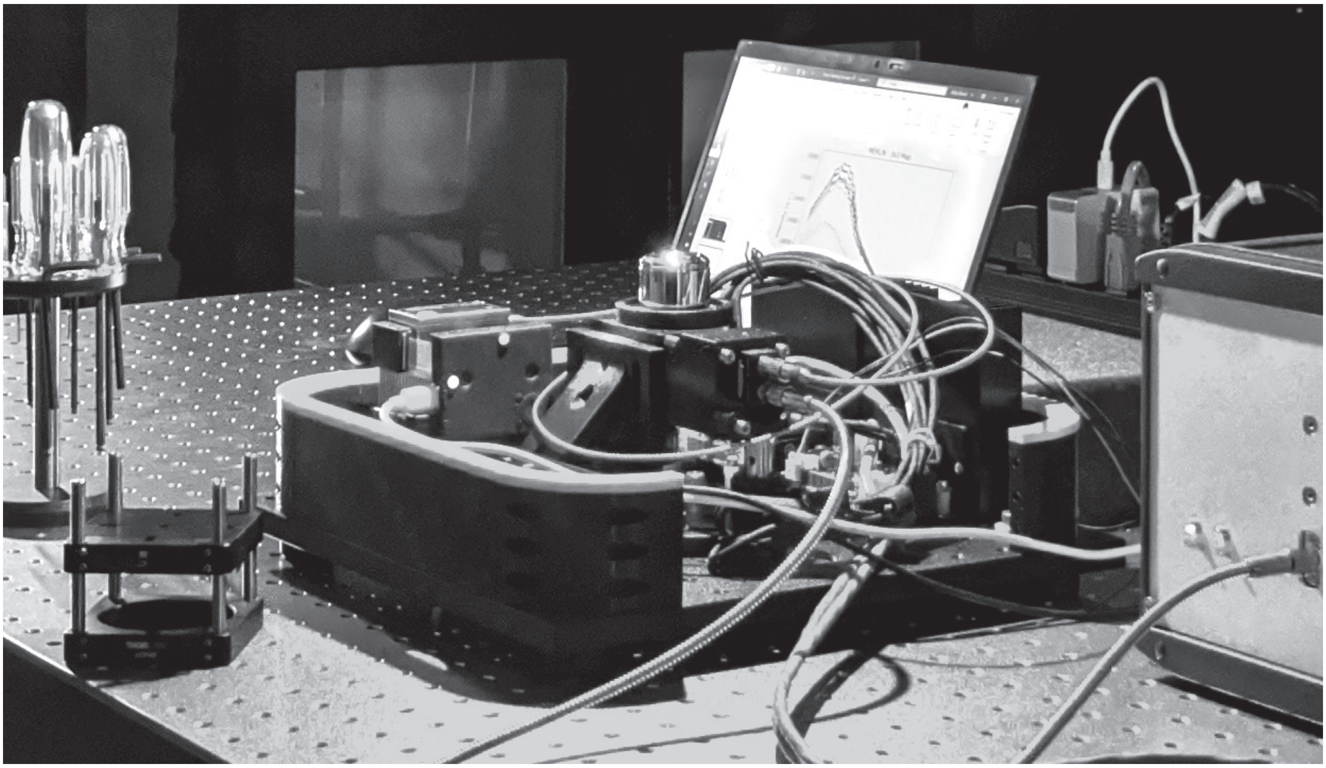
Hardware intended to look at rocks and natural surfaces, as well as scan over large areas (in less time) while preserving sensitivity, calls for the capabilities provided by 2D pixel array, CCD, or sCMOS detectors.

Detector sensitivity and low readout noise are keys when discussing low-light measurements. In this context, CCDs — often used in conjunction with an intensifier and/or some form of nitrogen cooling — generally have been preferred to sCMOS detectors. However, advances in sCMOS technology have empowered it with comparable (and, in some cases, superior) capabilities to CCDs in low-light applications.

BACK-ILLUMINATED SENSOR BENEFITS

In the context of very low-light measurement, back-illuminated sensors provide higher quantum efficiency (QE). In short, the user's ability to detect the low light (e.g., weak Raman signals) improves.

To maximize your chance of detecting very low-light signals, a back-illuminated sensor affords broad spectral response: sensitivity from ultraviolet (UV) down to near infrared (NIR). An intensi-



fied CCD detector not only is costlier, it registers only visible to NIR or UV – they cannot be combined in a single CCD detector. PCO, meanwhile, has integrated both options in its back-illuminated sCMOS camera systems.

The other advantage offered by back-illuminated cameras stems from their deep cooling: the user sees very low dark current, leading to a very homogeneous image and helping with the detection of weaker signals at longer exposure times. Due to the camera's wide dynamic range, if you have one signal significantly brighter than another (admittedly, uncommon in Raman), you could resolve both in the same image, rather than having to capture multiple images from that perspective.

Consider as an example Impossible Sensing, which is using PCO devices to develop instruments for planetary exploration applications. Specifically, Impossible Sensing has integrated the pco.edge 4.2 bi for Raman spectroscopy applications based upon a number of its performance features:

- **2048 x 2048 Resolution** — Impossible Sensing's measurement goal for its device is to determine sample composition, resolving a large number of peaks across a spectral window at a high spectral resolution. A detector with the 2048 x 2048 resolution can achieve those measurements.
- **Broadband Light Source** — Using a broadband light source, the same camera is capable of detecting light from 190 nm all the way up to 1100 nm, a broad spectral range.

  Further, combining a 6.5 x 6.5 µm² pixel size with 2048 x 2048 resolution allows users to resolve fine details without compromising light-gathering capacity. Larger-pixel back-illuminated cameras exist, but their light is dispersed on a much larger area, and therefore larger optical systems may be necessary to accommodate the larger detector footprint.
- **High Quantum Efficiency** — The pco.edge 4.2 bi also offers a peak QE of 95% and low noise (less than 1.9 electrons).
- **Speed** — Older systems leveraging PMTs or APDs to detect and analyze Raman spectra (RS) by scanning over multiple wavelengths can take minutes to hours to produce results. The pco.edge 4.2 bi can achieve the same results in a few hundred milliseconds.
- **Ease of Integration** — Impossible Sensing sought to build proof of concept for a prototype version of a novel optical

instrument to look for geochemical compounds on planetary surfaces. The task involved a multitude of optical, mechanical, and electronic parts that had to be combined in a short period of time.

Designers were able to secure the detector in less than a month and quickly integrate it; the included software developer kit (SDK) enabled smooth plug-and-play access. Conversely, a PMT might require a bench-top, high-voltage power supply or a downstream amplifier, making integration a more complex endeavor.

The next-generation DiSCO (Dual in-situ Spectroscopy and COring) system by Impossible Sensing is being funded by NASA via a small business grant. DiSCO integrates “drilling/coring/caching, imaging, and laser spectroscopic mapping systems” by combining fiber-based optical imaging, laser Raman spectroscopy (LRS), laser-induced breakdown spectroscopy (LIBS), and a laser-induced native fluorescence (LINF) system into a drilling and coring platform.

DiSCO’s most significant attribute is its ability to focus on a specific layer or location on the core surface — something that no previous or current surface missions have the capability to do. The Mars Exploration Rovers exposed the rock surface and identified round nodules, but the arm-mounted instruments were unable to analyze the nodules themselves; instead, they recorded an “average” of the area. Both the Curiosity and ExoMars orbiters require complex sample acquisition, processing, and handling systems prior to analysis.

Equipped with PCO back-illuminated detectors, DiSCO empowers lander/rover-based planetary exploration with unprecedented analytical capabilities, including in-situ, co-registered, high-resolution imaging and LRS+LIBS+LINF core mapping. The pco.edge 4.2 bi has allowed Impossible Sensing to dramatically reduce the resources needed to perform Raman and LIBS measurements of the planetary subsurface.

Gone is the need for core processing and delivery systems, or robotic arm movement between the rock and an instrument aboard the rover. Novel mission architectures now are possible: coring, analysis, and caching capabilities are offered within a single, highly modular, arm-mounted instrument. As planetary subsurface environments are key scientific targets but remain technologically challenging, these advantages cannot be overstated.

Impossible Sensing also is integrating PCO detectors into other instruments for potential space and deep ocean exploration applications. Because PCO detectors enable rapid and sensitive measurements, they can drive real-time exploration and deployment of AI tools.

CONCLUSION

Raman spectroscopy has been an established technique for decades, but even now it is being adapted to new applications – in the case of PCO and Impossible Sensing, it is being introduced into space for planetary exploration. Further, back-illuminated sensors are improving upon current Raman spectroscopy techniques and enabling next-generation systems to boldly operate where no spectrometer could function before.

While these advances are groundbreaking, they merely represent the next step in PCO cameras’ planned evolution. PCO detectors’ benefits for Raman spectroscopy — high sensitivity, high dynamic range, and low noise — also provide for UV fluorescence, modern microscopy techniques (e.g., SIM, LSFM, and SMLM), 3D metrology, and LIBS applications, as well as photovoltaic inspection.

To learn more, contact the authors at altaf.ramji@pco-tech.com or eeshelman@impossiblesensing.com, or visit https://www.pco-tech.com/ and https://www.impossiblesensing.com/.

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RESOURCES

- Basics/principles of Raman spectroscopy https://youtu.be/SslYDEma_cU and https://youtu.be/qBDtlY5vClo
- Impossible Sensing is using the pco.edge 4.2 bi in this application:
  - https://sbir.nasa.gov/SBIR/abstracts/19/sbir/phase2/SBIR-19-2-S1.07-2925.html
  - https://sbir.nasa.gov/SBIR/abstracts/19/sbir/phase1/SBIR-19-1-S1.07-2925.html

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