Going Smaller, Raising Sensitivity

RAMAN spectroscopy has been used for decades to analyze the composition of complex liquids, gases, and solids. In this method, laser light excites molecular vibrations, which shift the energy of the laser light in a way that uniquely depends on the molecular structure. The method's popularity derives from both its high specificity and its noninvasiveness. Forensic investigators, when stymied by the diversity of sample mixtures they must analyze, often turn to Raman spectroscopy because it can produce

Researchers (clockwise from bottom) Tiziana Bond, Mihail Bora, Allan Chang, and Elaine Behymer fabricate rectangular arrays of vertical resonant cavities for use in surface-enhanced Raman spectroscopy (SERS).

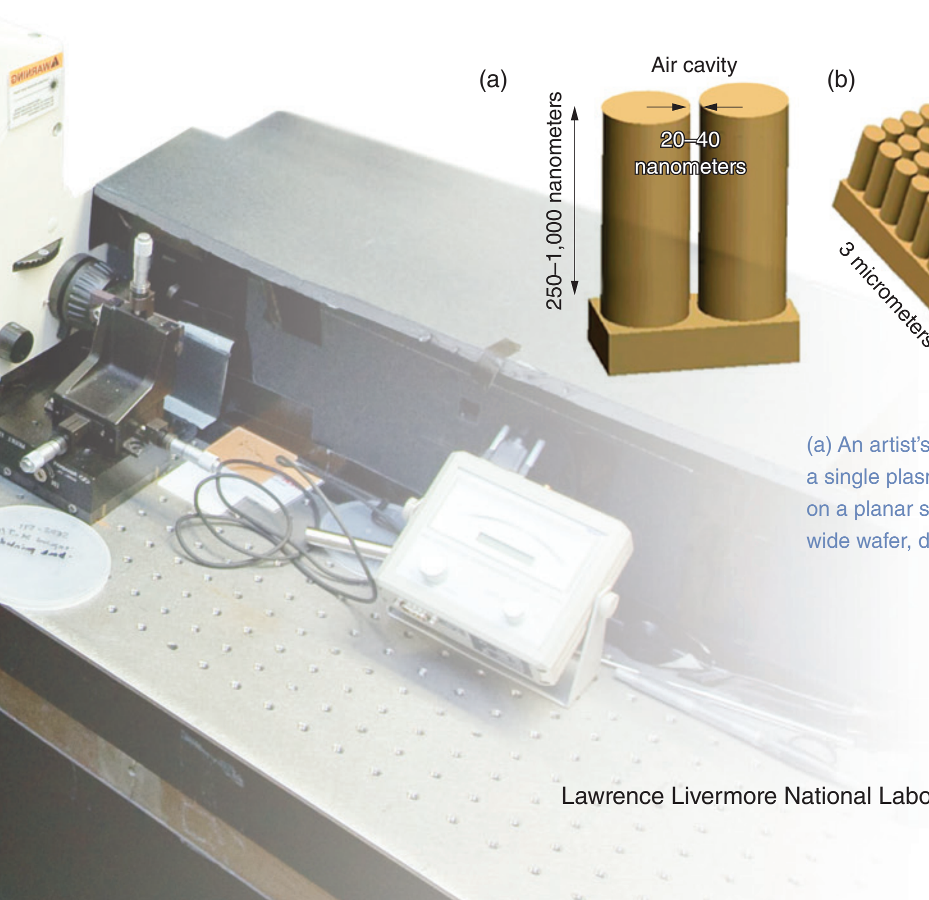
excellent analytic data. In the 1970s, scientists accidently discovered that a roughened silver surface smeared with metal nanoparticles would dramatically increase the light signal and improve the sensitivity. With this new modification, "surface-enhanced" Raman spectroscopy (SERS) allowed researchers to pick out one molecule among a million others, making it an excellent tool for nondestructively identifying substances for forensic analysis and other purposes. A problem lingered, however. Each roughened surface was slightly different—neither entirely uniform nor experimentally repeatable. For some testing procedures, these imperfections were not a problem. But for the detection of extremely low concentrations in a sample, a better technique was deemed essential.

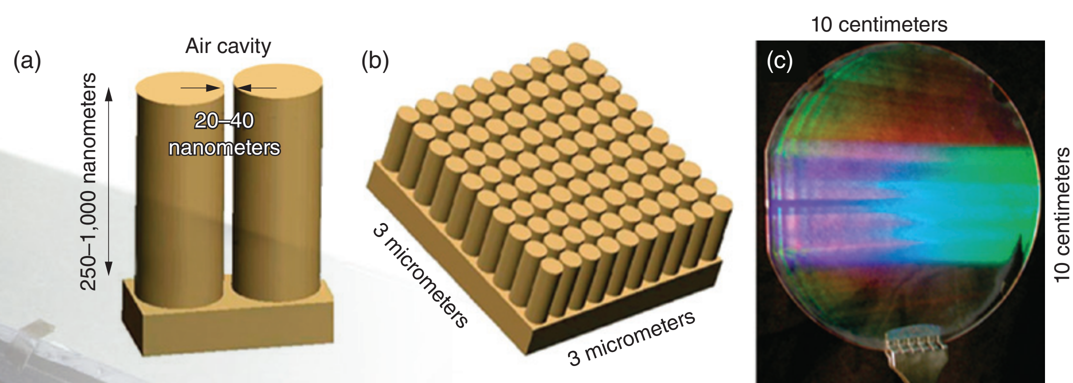
A team of scientists from Livermore and the University of Illinois at Urbana-Champaign has found a solution that enables researchers to detect solids, liquids, and gases with sensitivities thousands of times higher than previously possible. The team has replaced the irregular metal nanoparticle surface with carefully engineered nanoscale pillars. "We have exploited the Livermore speciality of laser interference lithography, which was developed for patterning over whole semiconductor wafers," says team leader Tiziana Bond of the Engineering Directorate's Center for Micro- and Nanotechnologies. The highly uniform SERS wafers are able to produce intense electric fields when laser-illuminated, which strengthens the Raman effect. For the first time, 10- to 15-centimeter-wide wafers can be identically fabricated. "Batch processing is essential for this tool to be truly useful," says Bond.

The Pillars of Raman

Although a roughened surface enhances interaction of the sample molecules with the metal surface, a substrate with uniform topographic features yields a more consistent Raman signal. The team's tapered and cylindrical nanopillars are just 100 to 150 nanometers in diameter and 250 to 1,000 nanometers tall. (For comparison, a human hair is about 50 micrometers across or approximately 1,000 times wider than one nanopillar.) Both pillar shapes perform as nanometer-size antennae, or so-called hot spots. The tapered pillars have generally offered better sensitivity than their straight-sided siblings.

The sensitivity of the cylindrical pillar has recently been raised by exploiting another step in the SERS wafer fabrication process to produce extremely small cavities between the tightly packed pillars. In these plasmonic resonant cavities, crowded electromagnetic waves concentrate energy into nanoscale dimensions thousands of times smaller than the wavelength of light. Incoming laser light interacts with the sample and coating on the nanopillar array, and the pillars act as highly confining waveguides at the interface with the sample, sending electronic oscillations upward and downward into the cavities. As is characteristic of Raman spectroscopy, the standing waves between pillars interact with the sample and, as a result, generate a shifted wavelength pattern. "By confining the light to such tight spaces, we can create intense electronic fields that increase the spectroscopic signal," says Bond. For the Defense Advanced Research Projects Agency, the team has successfully detected the explosive simulants bis(4-pyridyl)ethylene and benzenethiol



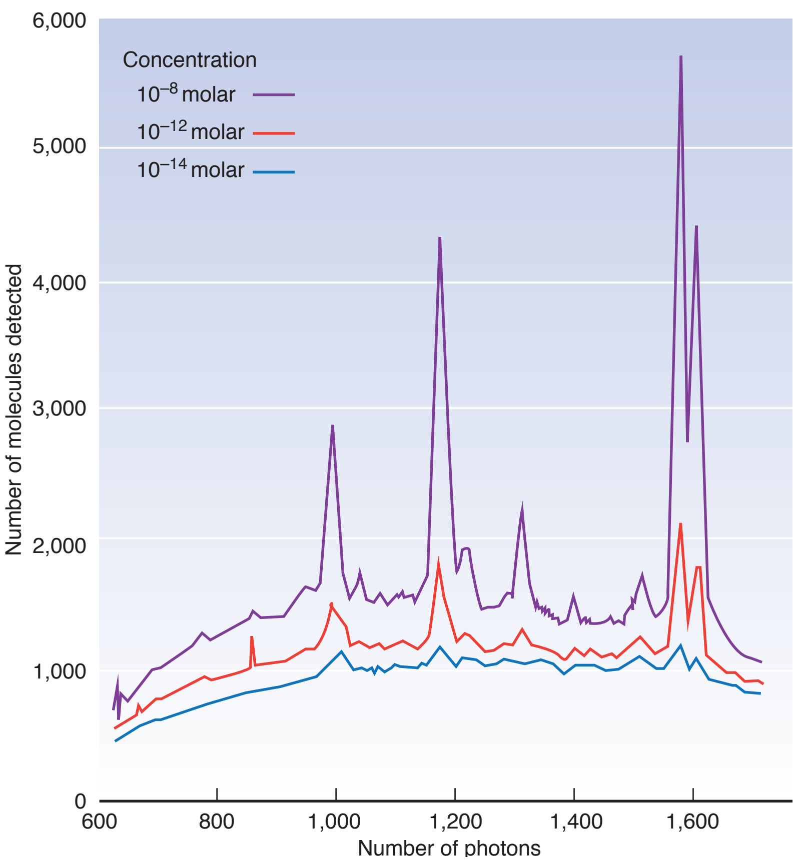


(a) An artist's rendering shows two gold nanopillar waveguides separated by a single plasmonic resonant cavity and (b) an array of pillars and cavities built on a planar substrate. (c) In an experiment using a fabricated 10-centimeter-wide wafer, diffraction patterns are observed at a high-viewing angle.

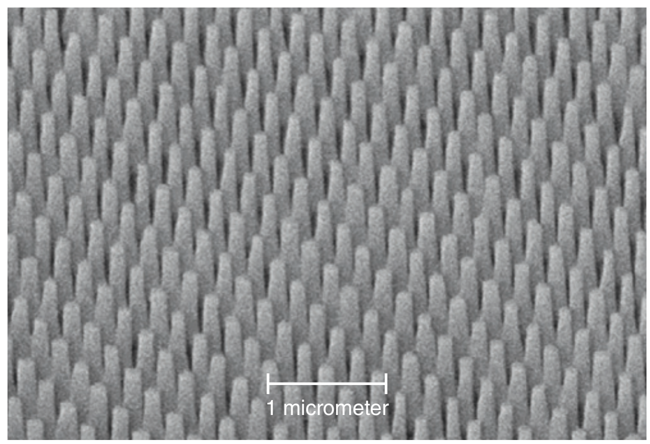
with femtomolar sensitivity, essentially picking out one molecule among a quadrillion others.

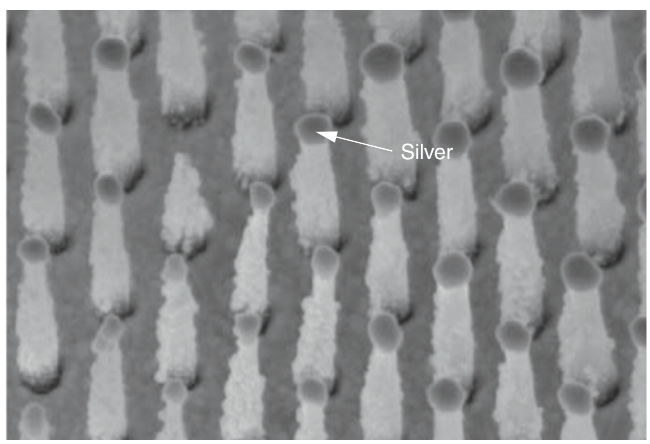
To achieve a deeper understanding of the observed improvement in SERS and its fundamental physical and chemical effects, the Livermore researchers collaborated with Gang Liu's NanoBionics Laboratory at the University of Illinois. The Illinois team used density functional theory, a quantum mechanical modeling method that aids in the investigation of the electronic structure of atoms, molecules, and solid materials, specifically their electron density. Using density functional theory and other studies, the team demonstrated computationally the mechanism that is potentially responsible for the remarkable enhancement: a strong local electrostatic field caused by what is known as the Schottky barrier at the junction of the metal wafer and the sample molecule. The study provided an explanation for the typical low repeatability of previous SERS experiments as well as the improved Raman peak shifts in raw spectra. These studies demonstrated that the strong electrostatic field at the metal–molecule junction along specific orientations could result in an enhancement in SERS of hundreds and even many thousands of times.

Ongoing efforts to optimize the system include experimenting with various metallic coatings on the pillars and with a range of pillar geometries. The goal is to maximize the absorbance and subsequent light emission as well as the adsorption of the sample molecules on the coatings, which together can enhance spectroscopic analysis and therefore sensitivity. Livermore

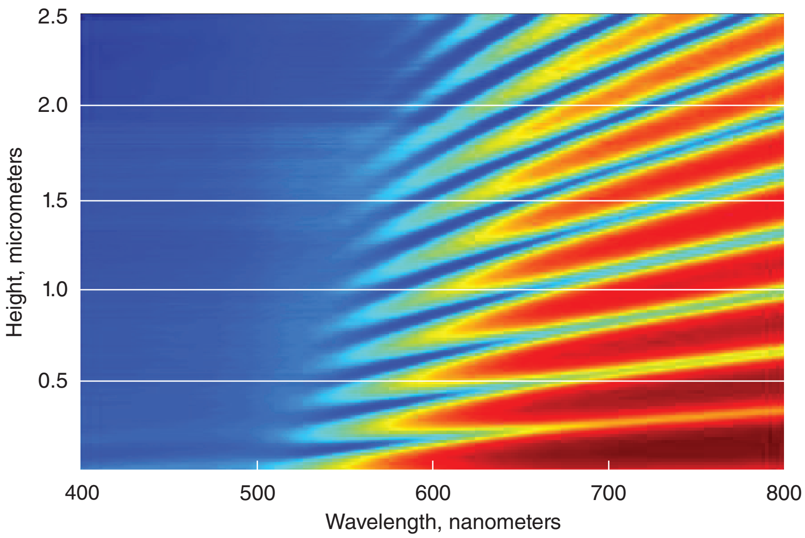


This graph shows Raman vibrational resonances of bis(4-pyridyl)ethylene molecules at various concentrations when they are excited by 660-nanometer laser light on a nanopillar substrate. The bottom (blue) curve represents the lowest concentration for effective detection.





(top) A SERS substrate is built with tapered pillars. (bottom) The substrate then receives an 80-nanometer silver coating.



Electromagnetic simulations measure the reflected power of gold coating as a function of wavelength and pillar height. Enhancing absorbance is a primary goal and it is derived as a function of reflectivity. The taller pillars, with more blue, indicate more resonances and greater absorbance.

photonics experts build the wafers of silica pillars, and electrical engineer Allan Chang evaporates a metallic coating onto them. “So far, we have worked with gold, silver, aluminum, and most recently an alloy of silver and palladium coatings,” says Chang. After coating the nanopillar arrays, he examines test objects spectroscopically to determine the coating’s effectiveness. Physicist Mihail Bora uses electromagnetic modeling to test the benefits of different pillar geometries. “We have found that with the taller pillars, the number and depth of resonances increases, and the absorbance rate is higher,” says Bora.

A Future of Enhancement

With funding from the Laboratory Directed Research and Development Program, the researchers have been testing SERS for use in the detection of gases in nuclear weapons. To advance this capability, a member of the Lawrence Scholar Program from the University of California at Santa Cruz recently began work on incorporating advanced SERS into microscale fiber-optic sensors. “Initially,” says Bond, “a sensor will have a tiny SERS device on its tip. In the future, we want to develop a technique to coat the optical probe.”

The new SERS technology is expected to eventually be enormously useful for monitoring aging weapons materials and assessing the health of closed systems. The Laboratory is responsible for ensuring the safety and reliability of the Livermore-designed nuclear weapons in the nation’s stockpile. Sensors are embedded in the weapons to constantly and nondestructively monitor changes over time.

Jim McCarrick, who leads embedded sensor development in the Engineering Directorate, is excited about SERS nanosensors because of their extraordinary sensitivity. “We already have a gas detection capability, but the SERS technology increases the sensitivity available by many thousands of times,” says McCarrick.

A further step toward higher enhancements is to increase the number of hot spots. More closely packed nanopillar arrays are being set in miniature bowls, or dimples, using block copolymers, which are combinations of chemical “blocks” that can be coupled in various ways to create exotic structures of all kinds. Recent research suggests that they may be useful for creating semiconductor and carbon nanotube arrays. This new platform could be used not only for SERS but also for advanced lithography. A student from the Swiss Federal Institute of Technology in Zurich is at Livermore for a year working on developing these higher density arrays.

In addition to applying SERS to defense efforts and forensics, a future goal is to detect very small amounts of biological material in a sample. Says Bond, “All of these applications are critical for the Laboratory’s national security mission.”

—Katie Walter

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