SURFACE-ENHANCED RAMAN SPECTROSCOPY AND CONFOCAL IMAGING OF PERIODIC NANOHOLE ARRAYS SURROUNDED BY PLASMONIC BRAGG MIRRORS
Nathan C. Lindquist1, Hyungsoon Im1, Kyle C. Bantz2, Antoine Lesuffleur1, Christy L. Haynes2, and Sang-Hyun Oh1
1Department of Electrical and Computer Engineering, 2Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

ABSTRACT
Recent progress in the field of plasmonics, and the subwavelength confinement and manipulation of optical fields with metallic nanostructures, offers many new opportunities for the design of novel surface-enhanced Raman spectroscopy (SERS) substrates. The addition of surface plasmon (SP) optical elements, such as Bragg mirrors and surface cavities, allows further substrate optimization. Here, we demonstrate nanostructured SP optical elements as a SERS substrate that provides flexible optimization, tuning, as well as enhancement factors of $10^7$ to $10^8$. A confocal scanning microscope is used to image and characterize the SERS substrates.

KEYWORDS: Nanophotonics, surface plasmon (SP), surface-enhanced Raman spectroscopy (SERS), enhanced transmission

INTRODUCTION
Surface-enhanced Raman spectroscopy (SERS) is a powerful technique that can be readily applied towards ultra-sensitive chemical detection. It is known that the local enhancement of the optical field is a primary factor for a strong SERS signal [1]. However, the measurements are typically performed on roughened or randomly structured metallic substrates with poor control over the location and strength of the enhancing fields [2]. A SERS substrate that is both highly reproducible and that can offer high signal enhancement due to controlled field localization can offer immediate benefits to a broad range of disciplines where efficient and accurate chemical detection is necessary.

Properly structured metallic films and nanoparticles [3] that take advantage of surface plasmons (SPs)—electromagnetic surface waves coupled to the free electron plasma of metals—can provide these benefits. Indeed, the last decade has seen greatly renewed interest in the role that SPs play in the optical properties of nanostructured metallic surfaces, largely due to the discovery of “Extraordinary Optical Transmission”, whereby the local field enhancements due to SPs generated by a periodic nanohole array increases the transmission through the nanoholes [4]. The SP-enhanced optical fields can also be used to increase SERS [5]. The possibility of using simple nanohole arrays as a well-defined and efficient SERS substrate shows promise. Beyond this, SP optical elements provide many free design parameters, such as the periodicity of the array or incorporation with other plasmonic
nanostructures. Previously, we introduced Bragg mirrors surrounding a nanohole array to further confine the SP energy, forming a lateral SP resonant cavity [6]. Multiple such devices can be arranged into a larger microarray-type matrix, creating individually unique and isolated sensor spots [7]. In this paper we present high-resolution chemical mapping and SERS imaging of nanohole arrays and matrices of sensor spots on a 200-nm-thick silver film on a glass microscope slide.

EXPERIMENTAL

Figure 1 shows an SEM image of a 2-by-2 matrix of sensor spots, each with a slightly different periodicity. The sensor spots were created with an FEI Quanta 3D™ Focused Ion Beam (FIB) milling tool. The surrounding Bragg mirrors, milled halfway through the silver, serve to enhance the SP field by coherently reflecting SPs back into the area of the nanoholes, as well as to prevent cross-talk between adjacent nanohole arrays [7]. A WITec Alpha300R™ confocal Raman microscope was used to image and characterize the SERS substrate, using a 100x objective and an excitation wavelength of 514 nm. With such a setup, it is straightforward to characterize the enhancement, reproducibility and optimization of the devices.

![Figure 1. SEM image of a 2-by-2 matrix of nanohole arrays surrounded with Bragg mirror grooves, which serve to reflect and confine the SP energy and increase the local field intensity. Each nanohole array has unique plasmonic properties.](image1)

The nanoholes each have a diameter of 180 nm, and the multiple arrays have periodicities that range from 400 nm to 480 nm, to find the best tuning conditions using a fixed excitation wavelength. The wavelength of maximum SP field and enhanced Raman is, to first order, a function of the periodicity of a nanohole array. Figure 2 shows the transmission spectrum for a single sensor spot with an excitation peak near 514 nm. Standard rhodamine 6G (R6G) dye molecules were deposited on the silver substrate, and the SERS activity was measured.

![Figure 2. Sample transmission spectrum of a single nanohole array surrounded with Bragg mirror grooves. The periodicity of the array is 460 nm, which gives an excitation peak near the imaging wavelength of 514 nm.](image2)
RESULTS AND DISCUSSION

Figure 3 shows a sample Raman spectrum of the R6G dye molecules extracted from a single spot within a nanohole array, the peaks providing the “molecular fingerprints” that make Raman spectroscopy so attractive. Figure 4 shows an image obtained by scanning and mapping the intensity of specific Raman peaks. The surrounding Bragg grooves are also seen, with a horizontal excitation polarization, since they also introduce a SERS-active “roughness.” The top right array shows the most enhanced and homogeneous SERS signal within the nanohole array. With similar nanohole array devices tuned to excitation at 633 nm, SERS enhancement factors of $10^7$ to $10^8$ have been achieved with a self-assembled monolayer of benzenethiol molecules. In conclusion, we present the use of confocal Raman imaging to characterize a nanofabricated SERS substrate that combines the enhancement and design freedoms of nanohole arrays and SP optics. Plasmonic elements such as Bragg mirrors and nanoholes can be a powerful tool to further optimize SERS-active substrates.

REFERENCES


Figure 3. Sample Raman spectrum of the R6G dye molecules extracted from the area of a single nanohole array. There is also a large background fluorescence signal.

Figure 4. A high-resolution Raman scan. Each nanohole array can be clearly seen, and the enhancement above the silver substrate background can be quantified.