

Metasurface development for SERS-based optical sensors

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Summary:

Using both numerical simulations and nano-fabrication techniques, we experimentally demonstrated the SERS functionality of a novel nanostructure by employing a drop-casted thiabendazole analyte. The nanostructure was specifically designed with tailored shapes and dimensions to achieve plasmon resonance within the visible range.

Keywords: Nanopatterning, SERS structures, pesticide detection.

Introduction

The advancement of nanotechnology has led to innovative nanomaterials and technological applications across a range of fields, including electronics and sensing [1-2]. Surface-enhanced Raman spectroscopy (SERS) is an effective method for detecting ultra-low concentrations of analytes, enabling detailed structural and molecular identification. Nanotechnology offers a wide array of plasmonic nanostructures, such as gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and 3D plasmonic substrates, that significantly enhance SERS performance [3]. The efficiency of SERS sensors relies on the manufacturing of complex nanostructured architectures, which enhance the electromagnetic field, amplifying the Raman scattering signals.

This paper presents the simulation results, the manufacturing process, and the Raman characterization of metasurfaces used for SERS applications.

Optical Design and Simulations

The nanostructures were designed with specific C shapes, arranged in a lattice, with sizes of 80 nm width and 430 nm diameter to achieve plasmon resonance within the 650-750 nm wavelength range, considering electron-beam lithography (EBL) as fabrication technology. This wavelength range was chosen to enhance the Raman peaks of pesticide Thiabendazole (TBZ), which exhibit significant vibrations when using a 633 nm excitation wavelength. However, it is important to note that most pesticides will have Raman peaks in a similar wavelength range. The

simulations were conducted using the Finite-Difference Time-Domain (FDTD) method, implemented in Ansys Lumerical commercial software. The simulations include full 3D model of the nanostructures: C-shape particles (60 nm high), Au layer (40 nm thickness) and Si substrate (Fig. 1a). Three C-shaped structures were included in a rectangular simulation volume, with the perfectly matched layer (PML) boundary conditions in the X direction (the propagation direction) and periodic boundary conditions in the Y and Z directions. The substrate was illuminated from the top by a broadband plane wave. The reflected intensity was measured above the substrate, while the electric field distribution was recorded at the gold–air interface.

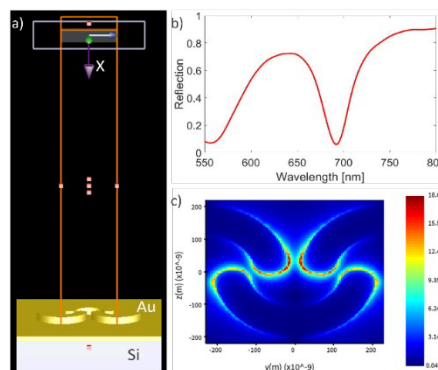


Fig. 1. a) Cross-section of the simulation model; b) Simulated reflection; c) Simulated electric field distribution

The simulated reflection with strong resonance around 691 nm wavelength is presented in Fig. 1b, while the electric field distribution around the nanostructures is presented in Fig. 1c.

Metasurface fabrication and SERS detection

The metasurface manufacturing process started with the spin-coating at 2500 (rpm) of a thin polymer film (polymethyl methacrylate: PMMA 950k A4), followed by a thermal treatment on a hot plate performed at a temperature of 160°C for 3 minutes. The pattern transfer was carried out via electron beam exposure using the dedicated RAITH e_Line system, with the following parameters: acceleration voltage – 30 kV, beam current – 200 pA, and a clearing dose of 300 $\mu\text{C}/\text{cm}^2$. Proximity effect correction was applied using the PECS software module.

The subsequent step consisted in the structures developing by immersing the wafers in a solution of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) in a 1:3 ratio at 22°C for 60 seconds. A thin Au film with a thickness of 60 nm was then deposited using the electron beam (e-beam) vacuum evaporation method, performed with the TEMESCAL FC-2000 system, which provides high-quality deposition suitable for the lift-off process.

The following step in the fabrication process involved selective metal removal by dissolving the polymer together with the Au film on its surface (lift-off technique). The scanning electron microscopy (SEM) image illustrated in Fig. 2 reveals the nanopatterned C shapes on the silicon substrate. The patterned area was 250 μm ×250 square micrometres. In the end, the metasurfaces were covered with 40 nm thickness Au to generate the plasmonic effect.

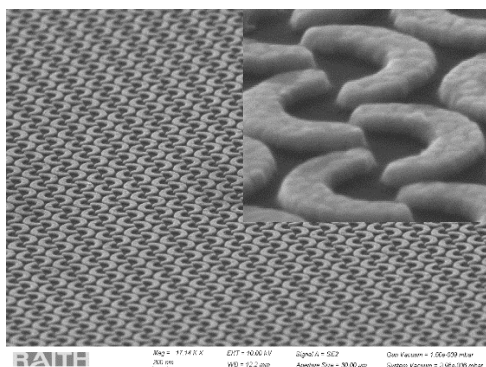


Fig. 2. Side-view SEM micrograph of the nanopatterned metasurfaces on Si substrate (a) and detail of an area containing the nanopatterned C shapes.

SERS investigation

To test the SERS functionality, Raman measurements of the patterned and un-patterned areas using the thiabendazole as an analyte were performed. 5 μl from a stock solution of 10 mM thiabendazole dissolved in ethanol were drop-casted onto the Au-SERS (patterned) surface and Au area (un-patterned). Raman spectra were measured with a Horiba LabRAM HR Evolution Spectrometer. The samples were excited

with a 633 nm wavelength using 50x objective and 25% of the maximum power (17mW). The spectra were recorded, focusing the laser on the thiabendazole crystallites found on the analysed substrates with 10 s of acquisition time and 10 accumulations. The differences in the Raman spectra for the needle-like filament crystallites formed onto the Au-SERS and un-patterned gold area are illustrated in Fig.3.

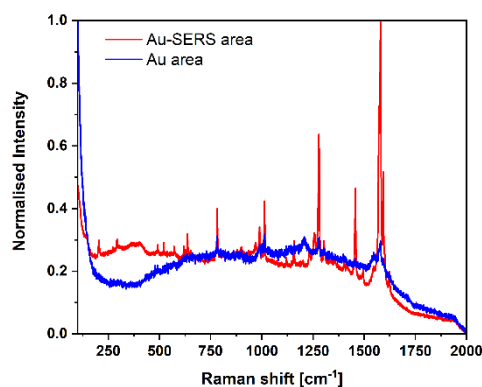


Fig. 3. The normalized Raman spectra of the thiabendazole films

Conclusions

We developed a novel SERS nanostructure obtained by using numerical simulations and EBL fabrication technique. We demonstrated the SERS functionality using thiabendazole as an analyte. Further SERS investigations will be carried out to explore the pesticide sensing performances.

References

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