Conference Paper

Near-Field Hot Spots in Gold Nanoplasmonic Templates and Their Use for Surface Enhanced Raman Scattering Sensing Application

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Finite difference time domain (FDTD) method is adapted to investigate near-field enhancement effects on plasmonic structures (patterned in gold film) such as concentric rings with small separation, square, and rectangle. The near-fields effect on surface enhanced Raman scattering (SERS) is typically studied on square and rectangular structures. These metal structures are fabricated by laser interference lithography. Raman active molecules (Rhodamine 6G in PMMA (polymethyl methacrylate)) are spread onto patterned structure by spin coating, and Renishaw inVia Raman spectrometer was used to study SERS. Typical SERS enhancement of the order of 10^5 is seen for square and rectangular structures. It is observed that the corner points and edges of square and rectangular structures are most sensitive to concentrate near fields. In the case of concentric rings, huge near fields are seen to exist at the gap between the metal rings. Concentric rings are proposed to be very effective structure for SERS sensing applications such as molecular identification and biological mapping.

1. Introduction

Near-field assisted surface enhanced Raman scattering (SERS) is an efficient light scattering process which can be used for molecular sensing purpose. In SERS process, huge plasmonic near fields existing due to the localized and propagating surface plasmon resonances around the metal nanostructures have been the most important factors [1–5]. It can assist in achieving even 10^8 – 10^{10} times enhancement of the scattered signal. Thus, engineering the plasmonic structures to achieve densely packed near-field spots or hot spots is a prior must. This optimized structure can be used to explore trace molecular detection, biological sensing, and molecular vibrational studies [1–10].

Near-field localization and studies of SERS on a variety of plasmonic structures have been reported previously by various researchers [11–15]. It is also reported that two-dimensional (2D) structures are superior compared to one-dimensional (1D) structure. It is preferable if the plasmonic

structures are insensitive to the input excitation beam. In this work we propose a novel concentric ring structure (Figure 1) for the efficient near-field localization. Here concentric rings will be highly insensitive to the polarization state of the input light beam (unpolarized or transverse magnetic (TM) and transverse electric (TE)); thus SERS templates consisting of concentric rings will be very easy to perform SERS without prior information of the polarization of the input beam. Near-field localization is compared with square and rectangular geometries.

2. Designing of Plasmonic Structures for Simulation

The following designing parameters are considered for the computer simulation (3D). The finite difference time domain method (Optiwave) is utilized for the analysis of the near fields. The enhanced near field around the edges and corners

FIGURE 1: Design parameters for the structures under investigation. Concentric rings (top-left), unit cell of the square array of gold (top-right), and unit cell of rectangular array of gold (bottom-left).

of plasmonic metal nanostructures is caused by propagating or localized plasmon resonances or coupled modes of both of them [2, 3]. To understand the effect of near-fields localization and the interaction with Raman active probe molecules plasmonic structures, that is, concentric rings, square array and rectangular array are modeled as free standing templates. The structures are very similar to the structures shown in Figure 1. All the structures are designed to have a depth of 100 nm. For square and rectangular structures the duty cycle is assumed to be 50 : 50. Concentric rings have width of 50 nm. Periodic boundary conditions are applied along x - and y -axes, and in the z -direction, anisotropic perfectly matched layers are applied. A normally incident plane wave having wavelength of 785 nm is used for the excitation. Polarization of incident pump is set to x -pol. The periodicity of the lattice is fixed at 800 nm for square and 800 nm and 1200 nm for rectangular lattice.

3. Experimental Details

Square and rectangular plasmonic structures are fabricated by using laser interference lithography. The details of the fabrication procedure have been reported previously [2, 3]. As the dimensions of the concentric rings structure are very small and the fabrication is only possible through

either electron beam lithography or focused ion beam approach, the testing of SERS at this moment is not feasible. For SERS measurement typical square and rectangular plasmonic structure are considered. Rhodamine 6G (R6G) probe molecules (50 micromolar) in PMMA (PMMA in chlorobenzene: MICROCHEM, Germany) were spin coated (resulted in ~ 50 nm thick film) onto the plasmonic structures. Renishaw inVia Raman spectrometer typically with 785 nm laser at 3 mW input power was employed to conduct the SERS experiments. The laser was focused through 50x objective (0.75 NA, spot size $\sim 5 \mu\text{m}$) and the back scattered signal was collected through the same objective. The signal was integrated for 20 s and 2 accumulations.

4. Analysis of Simulation Results

The (E_z, E_x, E_y) field distribution for concentric ring structure is shown in Figure 2. The polarization of input field was set to x -polarization (parallel to x -direction). The distribution of E_x field in Figure 2(a) shows concentrated near fields around the metal ring edges. The strength of the concentrated field is much higher, about 100 times compared to that from flat portion. The field is enhanced throughout the structure in a modulated fashion (field is stronger at about $x = 200$ nm and 600 nm). This trend is also observed in the case of E_y

FIGURE 2: Distribution of near fields for the gold concentric rings with the electric field components as E_x (a), E_y (b), and E_z (c). The coloured scale bar represents the field strength throughout the structure.

field distribution as well as E_z . The strength of the near field confined along the vertical direction (E_z) is weaker compared to in-plane confinement (E_x and E_y). The field distribution and large enhancements suggest the effectiveness of the structure for SERS as the scattering process varies with E^4 [16]. The modulated enhancement is the result of combined effect of localized and propagating plasmon resonances.

Electric field distribution for square array of gold lattice is shown in Figure 3. Near field is concentrated at the corners and edges. Field enhancement is clearly observed from E_x and E_y field distributions, whereas field confinement along the vertical direction is not significant. Similar field distribution is observed for rectangular structure (not shown here). Comparing with the field confinement in ring structure it is observed that the overall field strength is higher compared to square and rectangular structures.

5. SERS Results

Raman spectra of R6G-PMMA molecules spin coated onto 2D square and rectangular patterned templates are shown in Figure 4. Raman spectrum from flat (unpatterned gold film) gold is plotted as inset of the figure. The spectra for square and rectangle samples show strong characteristic peaks at 613, 775, 1190, 1312, 1363, 1507, 1602, and 1650 cm^{-1} of R6G and PMMA probe molecules as reported earlier [2, 3].

6. Discussions and Conclusions

Concentric ring structure is proposed to be highly effective for near-field confinement and surface enhanced Raman scattering. The proposed structure is insensitive to incident beam polarization and thus easy to perform SERS experiment. The field confinement is observed to be modulated

FIGURE 3: Distribution of near fields for the square array of gold as described in Figure 1. Electric field components are E_x (a), E_y (b), and E_z (c). The coloured scale bar represents the field strength throughout the structure and is kept as in Figure 2 for easy comparison.

FIGURE 4: Raman spectra obtained from R6G-PMMA probe molecules deposited on 2D square and rectangle plasmonic templates. Inset shows the spectrum obtained from flat gold film keeping all other parameters identical.

in nature which is indicative of near-field contribution from propagating plasmon resonance. The total field enhancement for unit area is very high compared to that for other plasmonic structures.

It is much challenging to further enhance near field in the proposed ring structure to make it densely packed.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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