

FABRICATION, CHARACTERIZATION AND SIMULATION OF GRATING-BASED STRUCTURES FOR SURFACE-ENHANCED RAMAN SPECTROSCOPY (SERS) SUBSTRATES

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Received: December 16, 2018; Revised: February 28, 2019; Accepted: March 01, 2019

Abstract

Surface Plasmon Resonance (SPR) is a resonance phenomenon between electron on the metal surface and the incident light which generates quantized-plasmons oscillation. There are several approaches to excite SPR wave, i.e. by using a prism coupler, grating-based structure, waveguide coupling and nanoparticles. Among those methods, diffraction grating offers more simplicity in fabrication and cost-effective. This paper presents the experimental results on the fabrication of grating-based structure and characterization in those fabricated grating. The fabricated structure is also analyzed using Rigorous Coupled-Wave Analysis (RCWA) method to maximize the SERS electromagnetic field as SERS substrates. SERS substrates are a method to enhance Raman signal.

Keywords: Surface-enhanced Raman spectroscopy, grating-based structure, surface plasmons resonance, rigorous coupled wave analysis

Introduction

Raman spectroscopy is a spectroscopy technique used to identify a material by measuring the way light scattered by a material. Applications of Raman spectroscopy are utterly diverse, such as pharmacy, environment, analytical chemistry (Fan *et al.*, 2011), biosensors (Yonzon

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et al., 2005), biomedical diagnostics and nanomedicine (Bálint *et al.*, 2010). Since, Raman signal is very weak, one method to enhance Raman signal is to use specialized SERS-substrates. SERS-substrate significantly increases the signal's intensities, with a wide variety of uses, ranging from, chemistry, materials science, medicine, biology, development and quality control of drugs, ecology, criminalistics, etc. The most common SERS substrates include gold, silver (less platinum, copper) rough surface or nanoporous films (Qian *et al.*, 2010), gratings (Xu *et al.*, 2012), photonic crystals (Kim *et al.*, 2008), hollow-core waveguides (Yan *et al.*, 2006), resonant cavities (Perney *et al.*, 2007), and noble metal nanoparticles with much smaller size than the wavelength of the incident light (Nie and Emory, 1997).

Nowadays there are many ways to improve synthesis of easy-to fabricate, cost-effective and stable SERS substrates. Metal grating on a dielectric substrate can be as SERS substrate. If metal surfaces are stimulated by laser light with a specific wavelength, electron on the surface experience forces, electron oscillates in phase with the laser light and surface plasmons is excited. As a consequence, molecules in the material not only experience the electromagnetic field of the laser, but also interact with the generated oscillating field. If molecules are irradiated with more powerful field, the signal is increased.

It is necessary to excite surface plasmons that enhance Raman signals. This paper presents results of simulation of grating geometrical parameters such as gratings period, depth, filling factor, type and thickness

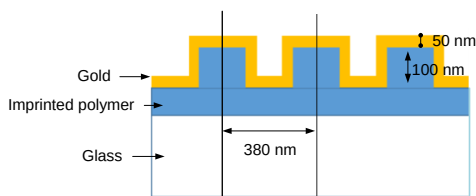


Figure 1. Grating-based structures

of the metal to enhance SERS electromagnetic field using RCWA methods, fabrication technique of grating-based structure, and also the Raman measurement of those fabricated grating.

Experiments

Fabrication of Grating-Based Structures

Polydimethylsiloxane (PDMS) was mixed with a cross-linking agent with the ratio of 10:1. The mixed solution was subject to continued stirring for five minutes. Vacuum chamber is used to remove air bubbles. The resulted gel was then poured into a mold while heated to obtain a replica of the mold. Meanwhile, a thin layer of imprint resist (SOG/Spin on Glass) was spin coated onto the sample substrate. Then the PDMS, which has predefined topological patterns, is brought into contact with the sample and they are pressed together under certain pressure. When heated up above the glass transition temperature of the polymer, the pattern on the PDMS is pressed into the SOG. After being cooled down, the PDMS is separated from the sample and the pattern resist is left on the substrate. 50 nm of gold thickness was deposited using DC magnetron sputtering (Figure 1).

Characterization

Scanning electron microscope (SEM) measurement was carried out to verify the

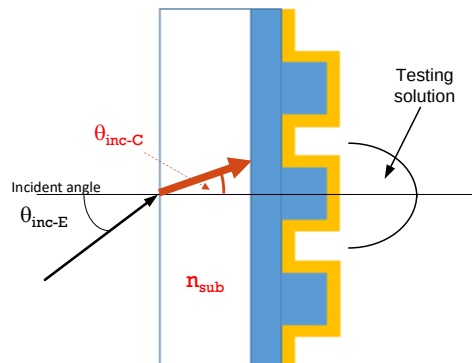


Figure 2. Measurement set-up to characterize sensitivity of sample

formation of the grating-based structure. The grating-based structures characterization was investigated in a manual configuration set-up and also using an Agilent spectrophotometer. To characterize sensitivity of substrate, the spectral shift of the resonance wavelength difference per unit change in the ambient refractive index was measured.

SERS measurement was conducted using a portable Raman spectrometer with the laser wavelength of 785 nm (red) and reflection detection at zero degree. Methylene blue (MB) solution was dropped onto a grating-structures SERS substrate and then irradiated with the laser in order to take Raman spectrum.

Simulation is conducting using Rigorous coupled-wave analysis (RCWA). RCWA is a method to analyze diffraction from periodic dielectric structures (Moharam and Gaylord, 1981). The program used is written in Matlab. The simulation results are then compared with the experimental results.

Results and Discussion

Reflection spectrum was measured using Agilent spectrophotometer and manual set-up.

Figure 3 and 4 clearly show the presence of SPR phenomenon in this fabricated grating, which is indicated by the appearance of SPR dip in the reflection spectrum for the p-polarization or TM mode. At an angle of 20 degrees a dip can begin to observe at a wavelength of 630 nm, the dip shifts to the right while maintaining its shape but not its depth. The dip can still be clearly observed at an angle of 35 degree.

The dip is not observed for the s-polarization. Since SPR can only be excited in p-polarization mode.

Figures 3 and 5 show the reflectance spectra taken for several incident angles. The SPR dip is clearly shifted with increasing incident angle. Using manual set-up, at an angle of 15 degree a dip can begin to be observed at a wavelength of 604 nm and at an angle of 20 degree a dip observed at a wavelength 636 nm. This number approaches the results obtained by automatic measurements

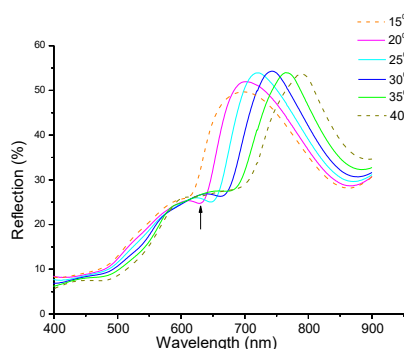


Figure 3. The reflection intensity spectra for the p-polarization

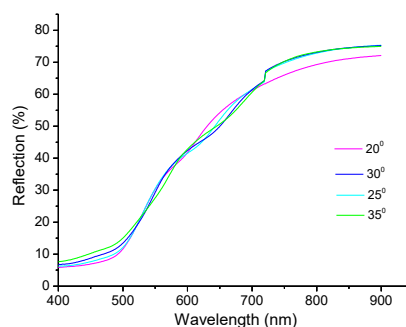


Figure 4. The reflection intensity spectra for the s-polarization

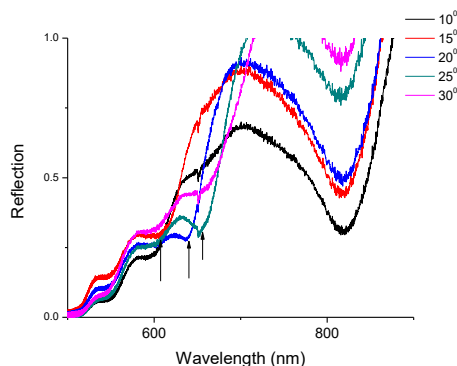


Figure 5. Reflection spectrum for the p-polarization using manual set-up

using Agilent. Using manual set-up, the dip can still be clearly observed at an angle of 25 degree. This is due to automatic set-up is more precise than manually built set-up.

Figure 6 shows simulation result. Comparing Figures 3, 5, and 6, we can see clearly that the calculated reflectance spectra are similar to the experimental reflectance spectra. Under simulation, incident angle θ_{inc} is called θ_{inc-C} (Figure 2). It is obtained using Snell's law:

$$\theta_{inc-C} = \sin^{-1} \left(\frac{\sin \theta_{inc-E}}{n_{sub}} \right) \quad (1)$$

$\sin \theta_{inc-E}$ is incident angle during experiment and n_{sub} is refractive index of the substrates. From Equation (1), the angle value obtained is 13 degree. Simulation result shows at an angle of 13 degree, a dip will be observed at a wavelength 626 nm.

Figure 7 clearly shows the reflection spectra obtained from the fabricated SPR sensor when dropped with the testing solution with different refractive indexes. The figure shows the change of reflection spectra. The refractive index of air and water are 1.00 and 1.33, respectively, while the refractive index of glycerol is larger than 1.33 depending on the concentration. While Figure 8 shows the reflection spectra obtained from simulation.

With the increase of concentration, we can observe the shift of the dip reflectance, although there is no significant change in the dip wavelength. Sensitivity can be obtained using Equation (2):

$$S = \frac{\Delta \lambda}{\Delta n_s} \quad (2)$$

λ is the wavelength when dip occurs while n_s is the refractive index of the superstrates at the same time. From the experiment, a sensitivity value of 0.0085 was obtained.

This is strengthened by simulation result, dip shifted no more than 10 nm for corresponding refractive index. In the same way sensitivity is obtained through simulation with a value of 0.0031. The difference

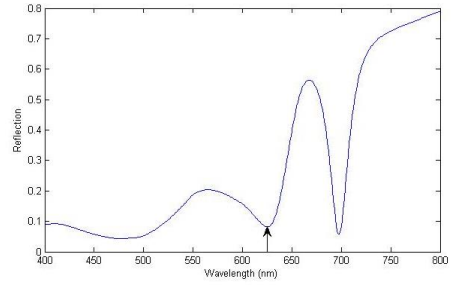


Figure 6. Reflection spectrum for incident angle equal to 13 degrees

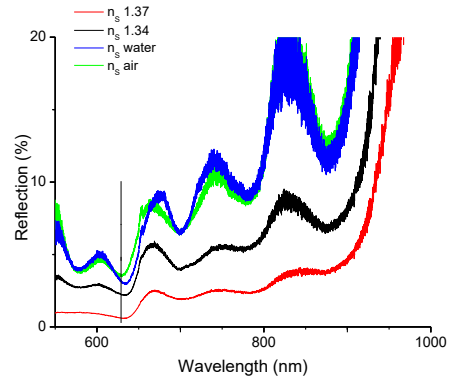


Figure 7. Reflection spectrum for different ambient refractive indices obtained from experiment

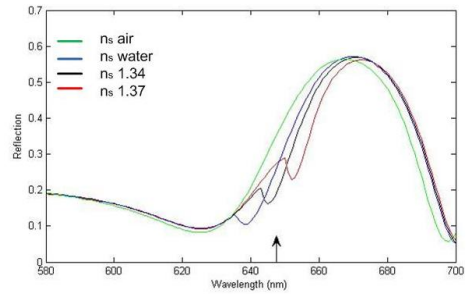


Figure 8. Reflection spectrum for different ambient refractive indices obtained from simulation

obtained from the experimental and simulation results of 0.0054 is a very good value.

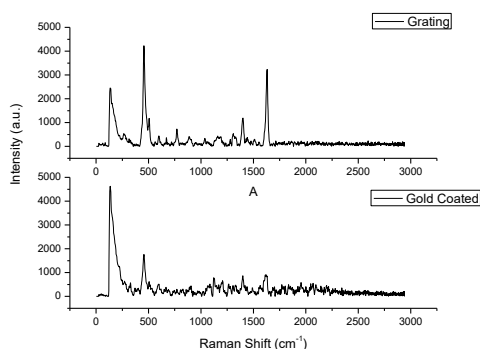


Figure 9. SERS intensity of MB with concentration of 10^{-3} M

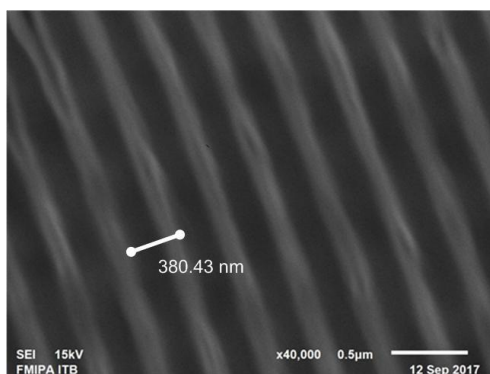


Figure 10. The SEM images of one-dimensional grating fabricated in this work

SERS measurement was conducted using a portable Raman spectrometer (Enwave

Optronics Field-type EZRaman-M) with the laser wavelength of 785nm (red) and reflection detection at zero degree. Before MB detection, Raman spectrum of SERS substrate was measured in order to determine the baseline signal. Afterwards, MB solution was dropped onto a SERS substrate and then exposed to the laser in order to take Raman spectrum. Figure 9 shows SERS intensity of MB with concentration of 10^{-3} M. It is seen that two main MB characteristic peaks of at 446 and 770 cm^{-1} can be clearly observed in the SERS spectra for grating and gold-coated surfaces. In

addition, SERS intensity of MB peak at grating surface increases than gold-coated only surface. From overall results, grating fabricated has shown high SERS enhancement factor and excellent MB detection sensitivity.

Figure 10 shows the scanning electron (SEM) images of the fabricated grating structure with of about 380 nm. This image shows that the grating has a corrugated structure surface of a periodic square wave shape.

Conclusions

Gold film coated grating-based structure have been calculated and fabricated for excitation $0.785\text{ }\mu\text{m}$ to obtain maximum enhanced Raman signals. The experiment results showed that optimized substrates on base of rectangular gold grating-based structures have a SERS sensitivity of about 10^4 - 10^5 for some different molecules indicating the high efficiency of their use in Raman spectroscopy. The proposed gold film coated grating-based structure is relatively cheap and simple to manufacture.

Acknowledgement

This research was funded by Sandwich Program, World Class University, Institut Teknologi Bandung and the authors are grateful for facilities supported from Optical Thin-Film Technology Laboratory (OTL) and Photonic Technology Laboratory (PTL) in National Electronics and Computer Technology Center, Thailand.

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