Optimization of sputtered Au film on grating structure as SERS substrate for detection of pesticide

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Abstract. Here, we report an efficient approach to optimize the performance of surface enhanced Raman scattering (SERS) substrate. The geometry of the SERS substrate consists of the Au film deposited on polymer grating. The SERS substrate were fabricated by the laser interference lithography (LIL) and magnetron sputtering of Au thin films. The effect of the Au thin film prepared by magnetron sputtering at different deposition time (5-180 s) and operated pressure (3-5 mTorr). The morphology of the obtained samples was observed by field-emission scanning electron microscopy (FE-SEM). The results indicated that optimal SERS substrate with deposition time of 180 s and 3 mTorr-operated pressure was obtained. The limit of detection for methylene blue (MB) and methyl parathion were evaluated at $10^{-4}$ M and $10^{-2}$ M, respectively. Moreover, our SERS substrate shows the application of a portable Raman spectrophotometer which also promising for on-site pesticide substance detection.

1. Introduction

Methyl Parathion (MPT), an organophosphate (OP) pesticide, is one of the most hazardous pesticides that are used to protect the fruit and vegetables plantations from the insects [1]. In 2004, World Health Organization reported that 0.1-0.2 ng of MPT accumulated in our body per day [2]. Due to its hazardous, the use of MPT is restricted by Indonesian Ministry of Agriculture [3]. Some methods have been done by researchers to detect MPT, such as liquid chromatography [4], gas chromatography [5], capillary electrophoresis [6], colorimetry [7], Mass Spectrometry [8], InfraRed, and Raman [9]. With this background, this study has aim to analyse Raman spectra of MPT using SERS based on Au film on grating structure. SERS offers many advantages such as being able to use with solids, liquids or gases, non-destructive, label-free measurement, multiplexing capabilities, high resolution, speed of analysis [10, 11]. To improve the enhancement of SERS-methods, photonic crystal [12], hollow-core waveguides [13], resonant cavities [14], nanoporous films [15], and gratings [16] are used. Grating has several advantages, especially in terms of high response homogeneity and high enhancement factor, an increase in electrical field strength not only occurs at hot spots, but also spreads homogeneously across the entire active sample layer [17]. Some tuning parameters provide high electric field enhancement thus maximizing the Raman signal on SERS, such as grating period, grating depth,
refractive index of superstrate and Au film thickness [18]. In this study we will focus on the effect of sputtering time and operated pressure in sputtering chamber.

2. Methodology

2.1. Laser interference lithography

The grating structure with 850 nm-period, 0.5 fill-factor, 310 nm-depth was prepared by Laser interference lithography (LIL) [19,20]. Figure 1 shows the scheme of laser interference lithography technique. The period pattern of rectangular grating $\Lambda$ was controlled by the angle of two collimated interfering beams $\theta$ hitting a mirror.

![Figure 1. Laser Interference Lithography](image)

To get grating period pattern, we calculated it using following formula

$$\Lambda = \frac{\lambda}{2 \sin \theta}$$

where $\Lambda$ is desired grating period, $\lambda = 442$ nm is the wavelength of the used laser source. The two exposures of interfering collimated beams form the pattern that already simulated.

2.2. Substrate fabrication.

Polydimethylsiloxane (PDMS) liquid mixed together with cross linking-agent in a 10:1 by volume ratio. Then we stirred it thoroughly for 5 minutes to ensure it homogeneously mixed. Then degassed under vacuum to remove the bubbles on the surface. The mixed-liquid was put in the vacuum chamber for an hour then casted on the master. Then heated at 70 °C temperature for 5 hours to get a replica of PDMS cross-linked template. After cooling down to room temperature, the PDMS mold can be peeled off from the substrate and be used for stamping.

Glass substrates were cleaned by washing liquid then rinsed and soaked in an acetone, isopropanol liquid and deionized water before washed thoroughly in the water with an ultrasonic cleanser for 20 minutes. Eight drops of SOG are placed on glass substrates. Then it was spin-coated onto the glass substrates at a speed of 3600 rpm for 90 seconds. The PDMS stamp is brought into physical contact with the substrate heated on the hot plate at 150 °C for 20 minutes. Then the PDMS stamp were separated from the substrates.

The gold layer sputtered on the substrates using DC magnetron sputtering under room temperature. The supplied power was 100 watts, Argon flow rate was kept constant at 20 sccm. The sputtering time was varied from 5 s to 180 s. The operated pressure in the chamber was varied from 3 mTorr to 10 mTorr.
2.3 Characterization
We observed the presence of thin film thickness using Field Emission Scanning Electron Microscope (FE-SEM). The SERS performance of obtained substrates was tested with probe molecules such as $10^{-3}$ M and $10^{-4}$ M Methylene Blue (MB) concentration. MB were dropped on the substrates and dried, later $10^{-2}$ M Methyl Parathion were dropped and acquired the SERS signal by utilizing portable Raman spectrometer of 785 nm wavelength.

3. Result and Discussion
Figure 2 shows the SEM images of gold films deposited on glass substrates. AJA International, Inc. DC Magnetron sputter coating device was used to obtain gold layer. The operated pressure on the sputtering chamber was set on 5 mTorr. The morphologies are significantly affected by the increase of sputtering time. The sputtering devices that is used did not have a film thickness measuring device. The cross section of the substrates which identified the film thickness only can be seen on FE-SEM. 20 nm gold film thickness was produced using 45 s sputtering time, 54 nm gold film thickness was produced using 90 s sputtering time, and 83 nm of film thickness was produced using 180 s sputtering time. As shown in the FE-SEM image of Figure 2(a), The Au nuclei in this layer appear homogeneously divided an are smaller than those obtained in the sputtered layer as shown in Figure 2. Figure 2(b) shows rather small particles, though not very uniform in shape and size. The grey background suggests the presence of still smaller particles. Figure 2 (c-g) shows particles in this layer slightly larger. The FE-SEM shows some substructures. The particles show a less uniform shape, very small particles are found between the relatively large particles. The agglomeration is larger for larger thickness.

![Figure 2](image)

**Figure 2.** The SEM images of the glass substrates with varied sputtering times: (a) 5 s, (b) 10 s, (c) 15 s, (d) 30 s, (e) 45 s, (f) 90 s and (g) 180 s
The fabricated substrate has period and grating depth of 850 nm and 310 nm. Methylene blue dropped on the substrates and dried. Raman spectra was measured using portable Raman. First measurement without Methylene blue on the substrates, shown on Figure 3. We can see in Figure 3 (a), the peak was obtained at 1400 cm\(^{-1}\) Raman Shift which identified as the peak of the thin film [21] while on the SERS substrate no Raman peak was obtained. 2µl of volume Methylene Blue liquids dropped on SERS substrates using micropipette. Figure 4 shows the Raman spectra of Methylene Blue with 10\(^{-3}\) M concentration.

The characteristic peaks of MB at around 1618 and 445 cm\(^{-1}\) obviously exhibit in the Raman spectra. They have been assigned to C–C stretching and C–N–C skeletal bending [22]. They are indicating that...
the molecules were adsorbed on the SERS substrates well. One of the band in the spectra has a little shift in position relative to the corresponding normal Raman spectra, as shown in Figure. 4(b) the peak at 1396 shift to 1390 cm\(^{-1}\). Raman peak of MB on the SERS substrate with grating structure has higher intensity than on the flat gold film. Grating structure addition on the SERS substrates increased the intensity of Raman spectrum. The substrates can detect MB with concentration up to 10\(^{-4}\) M.

Gold layer deposited by using DC magnetronspattering and the influence of operated pressure was investigated in the present work. The sputtering time of gold was set on 180 s. Figure. 5. Shows the Raman spectrum of MB with the varied operated pressure.

We can see on Figure. 5 that operated pressure in sputtering process affected on Raman spectra. The highest intensity of MB was obtained on the operated pressure 3 mTorr and occurred at 452 cm\(^{-1}\). When the operated pressure was increased, particle density in the chamber will be increased which affect the collision and acceleration of particles [23]. It minimizes the particles deposited on the substrates.

Methyl parathion with concentration 10\(^{-2}\) M was dropped on the substrates with varied operated pressure, the Raman spectra is shown on Figure. 6. Variations in the Raman peaks at 1629, 1397, 1306, 1157, 769, 507, and 452 cm\(^{-1}\) were monitored at different pressure.

![Figure 5. Raman Spectra of the Methylene Blue 10\(^{-3}\) M on the SERS substrates with varied operated pressure](image)
The observed Raman wavenumbers are listed in Table 1.

![Figure 6. Raman Spectra of the substrates with variated operated pressure on $10^{-2}$ M of Methyl Parathion](image)

**Table 1. Observed Raman wavenumbers of MP powder and on SERS**

| Vibration Description | Obtained Powder$^a$ | Obtained SERS$^b$ |
|-----------------------|---------------------|------------------|
| Phenyl Stretching     | 1596                | 1593             |
| C-H bending           | 1349                | 1348             |
| C-O stretching        | 1216                | 1231             |
| C-N                   | 1107                | 1114             |
| P-O stretching        | 857                 | 861              |
| Ring Breathing        | -                   | 645              |
| N-C-N bending         | +                   | -                |
| NH$_2$ twisting       | -                   | 592              |

a Raman spectrum of MP powder sample
b SERS spectrum of MP liquid absorbed gold film on grating.
3.1. Operated Pressure

In particular, the P=S stretching Raman peak, centered at 645 cm\(^{-1}\), was used as a quantitative evaluation of MP\([9]\). This strong Raman feature is the most useful characteristic group frequencies for the identification of this OP. Its variation in peak area and the corresponding calibration curve are shown in Figure 7.

4. Conclusion

SERS substrate that has been fabricated exhibited enhancement in Raman intensity. The grating structure has grating period 850 nm, grating depth 310 nm, time deposition 180 s, and operated pressure 3 mTorr. Fabricated SERS substrate make it possible to detect Methylene Blue with a concentration of \(10^{-4}\) M and Methyl Parathion with a concentration of \(10^{-2}\) M.

5. References

[1] Pablos, Espada M. C et al 1999 Analysis of Pesticides in water samples using GC-ECD and GC-MS/MS techniques, Int. J. Environ. Anal. Chem, 75, 165-179.
[2] Regulation of the Minister of Agriculture of the Republic of Indonesia 2015 Pesticide Registration, Number 39/Permentan/SR.330/7/2015, 39, 22-30.
[3] Daniel, C et al 1977 Determination of ethyl and methyl parathion in runoff water with high performance liquid chromatography. Anal. Chem, 49, 1551-1554.
[4] Da Silva, D.F et al 2015 Determination of methyl parathion insecticide in rice samples by headspace solid-phase microextraction-gas chromatography-mass spectrometry. Pest management science, 71, 1497-1502.
[5] Du, F and Fung, Y.S 2018 Dual-opposite multi-walled carbon nanotube modified carbon fiber microelectrode for microfluidic chip-capillary electrophoresis determination of methyl parathion metabolites in human urine. Electrophoresis, 39 1375-1381.
[6] Chang, Po-Ling et al 2016 Recent advances in the determination of pesticides in environmental samples by capillary electrophoresis, Int J Environ Res Public Health, 13 1-20
[7] Anh, D. H et al 2011 A colorimetric assay for determination of methyl parathion using recombinant methyl parathion hydrolase, Biotechnol. J., 6 565-572
[8] Barr, D. B et al 2002 A multi-analyte method for the quantification of contemporary pesticides
in human serum and plasma using high-resolution mass spectrometry, J. Chromatogr, B, 9 (99) 778-784

[9] Peter, Tanner A and Hung Leung, Kim 1996 Spectral interpretation and qualitative analysis of organophosphorus pesticides using FT-Raman and FT-Infrared spectroscopy, Applied Spectroscopy, 5 565-571

[10] Boss, Pamela A et al 2017 Review of SERS substrates for chemical sensing, Nanomaterials, 7 1-30

[11] Bruzas, I et al 2018 Advances in surface-enhanced Raman spectroscopy (SERS) substrates for lipid and protein characterization: sensing and beyond, Analyst Critical Review, 143 3990-4008

[12] Kim, W. Zhang and Cunningham, B.T 2008 Photonic crystal with SiO$_2$-Ag “post-Cap” nanostructure coatings for surface enhanced Raman spectroscopy, Appl. Phys. Letter, 93 143112-143117

[13] Yan, H. C et al 2006 Hollow core photonic crystal fiber surface-enhanced Raman probe, Appl. Phys. Lett., 89204101-204208

[14] Perney, N et al 2007 Tuning localized plasmon cavities for optimized surface enhanced Raman scattering, Phys. Rev. B, 76 035426-035431

[15] Qian, L et al 2010 Giant Raman enhancement on nanoporous gold film by conjugating with nanoparticles for singlemolecule detection, Journal of Materials Chemistry, 206891-6895

[16] Xu, X. D et al 2012 Guided-mode-resonance-coupled plasmonic-active SiO$_2$-nanotubes for surface enhanced raman spectroscopy, Appl. Phys. Lett., 100 191114-191119

[17] Guselnikova, Olga et al 2019 Preparation of selective and reproducible SERS sensors of Hg$^{2+}$ ions via a sunlight-induced Thiol-Yne reaction on gold gratings, Sensors, 19 1-12

[18] Yaremchuk, H et al 2017 Optimization of the grating-based structures for the efficient SERS substrates, IEEE 37th International Conference on Electronics and Nanotechnology (ELNANO), 2017 119-123

[19] Seo, Jung Hun et al 2014 Nanopatterning by laser interference lithography, Journal of Nanoscience and Nanotechnology, 14 1521-1532

[20] Lu, Cheng and Lipson, R. H 2010 Interference lithography: a powerful tool for fabricating periodic structures, Laser Photonics Reviews, 4 568-580

[21] Wu, Cheng et al 2009 Hybrid surface-enhanced Raman scattering substrate from gold nanoparticle and photonic crystal: Maneuverability and uniformity of Raman spectra, OpticsExpress, 17 21522-21529

[22] Naujok, R and Corn R. M 1993 Fluorescence and Fourier Transform surface-enhanced Raman scattering measurements of methylene blue adsorbed onto a sulphur modified gold electrode, Langmuir, 9 1771-1774

[23] Zeman et al 2001 Effect of total and oxygen partial pressures on structure of photocatalytic TiO$_2$ films sputtered on unheated substrate, Surface and Coating Technology, 153 93-99

Acknowledgements

This research was partially supported by Sandwich Program 2019 (World Class University – InstitutTeknologi Bandung). Authors acknowledge the support from NSTDA (National Science and Technology Development Agency), Thailand and we also thank our colleague Assc. Prof. Herman from Bandung Institute of technology who provided insight and expertise that greatly assisted the research.