Au-Coated PDMS grating for SERS substrate: Comparison of two different grating depths

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Abstract. Surface enhanced Raman scattering substrate was an alternative analytical tool with ultrahigh sensitivity and rapid response for chemistry, medicine and forensics science. In this work, the surface enhanced Raman scattering (SERS) substrate based on PDMS grating structure created by laser interference lithography using excimer laser modification and further 80 nm-thick Au thin film deposition by dc magnetron sputtering was proposed. We investigated the effect of the grating depth on SERS performance. The methylene blue solution of different concentration was employed to test the SERS performance using the portable Raman spectrometer. The optimal SERS performance can be optimized by fabricating the PDMS grating structure with 850 nm-period, 310 nm-depth and 0.5-filling factor.

1. Introduction

Surface enhanced Raman scattering (SERS) is one of versatile vibrational spectroscopic technique that provides rapid determination and detail information of chemical analysis thus has been applied as ultrahigh sensitive technique in chemistry, medicine and forensic science. Since its discovery in 1974, SERS substrate has wide variety and is still being developed and fabricated for broader application. Mostly SERS substrate development focuses on optimizing ‘hot spot’, a place where strong enhancement Raman of adsorbs molecules occurs, due to generation localized surface plasmon resonance (LSPRs) of noble material nanostructures. \cite{1,2,3,4}

Nanostructures for instance nanospheres, nanowires, nanopillar and nanotriangles, only exhibit short-range SERS effect. To get wider area sensing, an alternative substrate is one-dimensional (1D) metallic grating with depth and nano-periodic grooves. The transverse magnetic (TM) light excites propagative surface plasmons (PSPs) that provides long-range SERS effect on grating surface. 1D metallic grating also offers regularity surface that can increase reproducibility and control the desired signal amplification by numerical approach. \cite{5,6}

Plasmons resonance condition is achieved if light coupling on grating overcome mismatch between wavevector of incident light and surface plasmon at metal-dielectric interface. Resonance will occur if following condition is achieved,

\begin{equation}
 k_0 \sin \theta = k_0 \sqrt{\frac{\varepsilon_0}{\varepsilon_m(\omega)}} \pm \frac{2\pi}{p}
\end{equation}
Where $\lambda$ is the excitation wavelength, $k_0 = \frac{2\pi}{\lambda}$ is the free space wavevector, $n_d$ is refractive index of dielectric medium, $\varepsilon_m(\omega)$ is complex permittivity of metal and $P$ is a grating constant. Other studies have reported that metal thickness, period and grating depth can change the phase although these parameters are not shown explicitly in Eq.1.

There have been some studies on optimizing grating as SERS substrate [7]. In this work, we further developed alternative cost efficient and high reproducibility SERS substrate that is a reflective 1D Au-coated PDMS as SERS substrate for portable Raman instrument, 785 nm-excitation wavelength and incident angle at normal. Grating structure created by laser interference lithography using excimer laser modification. We discussed possibility grating depth effect on Raman enhancement based on experiment results using Methylene Blue (MB) solution by comparing two different fabricated grating depths.

2. Experiment

2.1. Grating Preparation

In order to preparation of the grating, we used nanoimprint lithography method. Laser interference lithography technique as shown in Figure 1 was used to make master mold. Two adjusted coherent He—Cd laser with certain angle in between create coherent periodic pattern that impinge photoresist surface substrate. Desired grating period calculated using following formula

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

where $\Lambda$ is desired grating period, $\lambda$ is laser wavelength and $\theta$ is an angle of two collimated interfering beams hitting a mirror.

![Figure 1](image)

**Figure 1.** Diagram of laser interference lithography

Master mold pattern performance will decrease inprecision after multiple usage therefore we created PDMS master mold replica. PDMS master mold replica can be reused three times before deterioration. Polydimethylsiloxane (PDMS) liquid mixed together with cross linking-agent in a 10:1 by volume ratio. After 5 minutes stirring continuously in normal speed, PDMS solution was poured over master mold and degassed under vacuum for 1 hour then heated in the oven for 5 hours at 70°C. PDMS mold replica cooled down after a while then it can be peeled off from master mold.

2.2. Grating Fabrication

The schematic of our proposed grating is shown in Figure 2. Firstly, the spin on glass (SOG) solution was prepared as grating substrates by spin-coating technique. The PDMS stamp was brought into physical contact with SOG surface and degassed under low-vacuum for 10 minutes in order to remove the bubbles on PDMS and SOG interface. Then it was heated in the oven at 150°C for 20 minutes. The PDMS was lifted from the glass substrate after transferring the pattern. Then, the imprinted grating was coated by 80 nm-thick gold (95.5% Au) using a commercial dc reactive magnetron sputtering system (AJA International, Inc. ATC 2000-F).
Figure 2. Schematic of our proposed grating in this experiment

The physical structures of the prepared samples were characterized by field-emission scanning electron microscope (FE-SEM; Hitachi, S-5200). For SERS spectra measurements, the methylene blue (MB) was used as probing molecules on the prepared samples in order to determine the SERS activity. Raman measurements were conducted with the portable Raman spectrophotometer (EZ-Raman-M; Enwave Optronics), with an included built-in computer, utilized a 785-nm diode laser, which allowed a probing area of 100 μm in diameter.

3. Result and Discussion

Figure 3 and Figure 4 shows scanning electron microscopy (SEM) images of fabricated grating at grating period 850 nm and two different grating depths, 210 nm and 310 nm. We obtained grating with sinusoidal grooves and filling factor at 0.5.

Figure 3. SEM images of cross-section 1D grating tg= 210 nm

Figure 4. SEM images of cross-section 1D grating tg= 310 nm

Figure 5 Shows relative intensity of Raman spectrum with $10^{-3}$ M-concentration on different substrates. 1D grating at grating depth 210 nm showed the highest intensity at 1620 cm$^{-1}$ Raman shift for $t_f= 40$ nm and at 440 cm$^{-1}$. The highest intensity showed for $t_f= 60$ nm. Otherwise, 1D grating at grating depth 310 nm showed the highest intensity at 1620 cm$^{-1}$ for $t_f=80$ nm.
Figure 5. Raman spectrums of MB $10^{-3}$ M-concentration and without MB on 80 nm-thick Au-coated substrates.

Figure 6 shows limit detection of 1D grating for both grating depths. It can detect up to $10^{-4}$ M for portable Raman 785-nm wavelength excitation. This result can be potential for further application in forensic such as explosive material and others chemical compound detection.

Figure 6. Relative intensity of MB Raman spectrums with variation concentration start from the bottom are respectively $10^{-3}$ M, $10^{-4}$ M, $10^{-5}$ M and $10^{-6}$ M (a) 1D grating tg=210 nm; tf= 60 nm, (b) 1D Grating tg= 310 nm; tf= 80 nm

4. Conclusion
Au-coated PDMS grating was fabricated successfully at grating period 850 nm. Two different grating depths showed different signal enhancement with different metal thickness combination. In this work, it is shown that we can achieve maximum enhancement for a certain wavelength excitation under certain combinations depth. The optimal structures were obtained at grating depth 310 nm, Au thickness 80 nm, filling factor 0.5. This structure can detect MB up to $10^{-4}$ M.
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