Fabrication of nanostructure grating polymer based coupling element for Surface Plasmon Resonance (SPR) sensors and its spectral reflectance characteristics

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Abstract. In this paper, we present nanostructure grating polymer, fabricated by employing the nano-imprint lithography technique, with gold nanolayer on its top surface as a coupling element for SPR sensors. The experiment results showed that the diffracted beams for \( m = \pm 1 \) were suppressed, which indicates the SPR wave excitation in this structure. For further clarification, SPR spectral shape simulation has been also done by using the Rigorous Coupled-Wave Analysis (RCWA) method. The simulation results are in agreement with the observed SPR dips in this experimental work.

1. INTRODUCTION

Surface Plasmon Resonance (SPR) is a resonance phenomenon between electrons oscillation on the metal surface and an incident electromagnetic wave causing quantized plasmon oscillations on metal surfaces. This SPR phenomenon produces an evanescent wave with strong electric field, which is considered can be utilized for enhancing the light excitation or light absorption of a tiny amount of analyte molecules on the metal surface. Therefore, this SPR phenomenon can be used for improving the sensitivity of optical-based bio-chemical or bio-medical sensors. [1]

There are several methods commonly applied to excite SPR wave, i.e. by using a prism, grating, and nanoparticles. Incident light coupling by using a prism, which is well known as the Kretschmann and Otto configurations, are the most commonly implemented method in SPR spectroscopy. However, this method requires delicate measurement set-up of their instrumentation so that rather difficult to be built as a portable or mobile sensor. In contrast, SPR excitation by using a grating as a coupling element requires simpler instrumentation setup. However, the fabrication of this coupling element requires more delicate technique. Moreover, this method also requires more complicated analysis on the measured SPR spectra, particularly when the grating shape is not simple sinusoidal form.

In grating coupling method, SPR excitation occurs when the resonance condition takes place where the propagation constant of the incident along the grating surface \( k_{inc} \) and the surface plasmon wave vector \( k_{sp} \) is given by the following relationship

\[
k_{inc} = \frac{n_{inc} \sin \theta_{inc}}{\lambda_0} \frac{2\pi}{\Lambda_x} - m \frac{2\pi}{\Lambda_x} = k_{sp}
\]

(1)

where \( n_{inc} \) is dielectric refractive index, \( \theta_{inc} \) is incident angle, \( \lambda_0 \) is light wavelength in vacuum, \( m \) is diffraction order, and \( \Lambda_x \) is grating periodicity. In the present work, we have successfully fabricated gratings having surface corrugated structure with square wave pattern and sub-micron periodicity.
These grating structures were made from hybrid polymer by simple nano-imprint lithography method, which then covered by a very thin gold layer of around 50 nm in thickness. The advantages of hybrid polymer are able to be shaped from its precursor gel by either photo- or thermal-polymerization, resulting a structure with good mechanical strength, thermal stability and optical clarity. [2]

In order to get an insight on the possible reflectance spectra or SPR spectra in those structures, calculations based on the Rigorous Coupled-Wave Analysis (RCWA) method have been also carried out. The RCWA method is different from the coupled wave analysis (CWA) because RCWA is a fully vectorial calculation for solving the Maxwell equation without using any approximation as in CWA. [3] In RCWA method, the light waves and the medium structure are formulated into their Fourier series expansions. This approach suits well with the grating structure in the present work. The calculation results are then a representation of electric fields in each mode. Moreover, as another advantage of RCWA, the differential equations of Maxwell’s equation are transformed into matrix forms. The wave equation (for two-dimensional structure) then can be written as

$$\frac{\partial^2}{\partial z^2} \begin{bmatrix} S_x \\ S_y \end{bmatrix} - \Omega^2 \begin{bmatrix} S_x \\ S_y \end{bmatrix} = 0$$

where \( S_x \) and \( S_y \) are the electric fields which can be found from the eigenvector solution of Eq. (2) and \( \Omega \) stands for wave propagation constants. All \( S_x, S_y \) and \( \Omega \) are in matrix form. [3]

2. EXPERIMENTS

2.1. Precursor gel preparation
The precursor gel was prepared by the sol-gel method from 3-(Trimethoxysilyl) propyl methacrylate 98% (TMSPMA, Aldrich) as in our previous work. TMSPMA was previously dissolved in ethanol and added by HCl 1 N as the catalyst. The precursor solution was continuously stirred 260 rpm for 72 hours at 50°C. The result of this process was a gel polymer precursor, which was then added by Irgacure-819 (Ciba Specialty Chemical Inc.) photo-initiator. This process was done in dark room to avoid undesired photo-polymerization.

2.2. Grating SPR fabrication
The sub-micron polymer grating structure was then made from that precursor gel using the nano-imprint lithography method. The precursor was poured over a silicon stamp, followed by a vacuum process for 30 minutes. The next step was UV-curing process where that precursor gel was irradiated by 405 nm laser light for 15 minutes. Finally, the formed grating structure was coated with the gold layer of around 50 nm in thickness by the sputtering technique.

![Figure 1](image-url) Figure 1. Schematic diagram of the measurement setup of SPR spectrum.
2.3. SPR Spectra Characterization
The fabricated grating SPR elements were characterized by measuring the reflectance spectra with a measurement setup as shown in Fig. 1. A tungsten lamp was used as the polychromatic light source. The incident light was polarized either to be the p- or s- (TM or TE) polarization light beam by using a polarizer. A slit and a pinhole were used to keep the light beam with an appropriate small diameter. The reflected light beam was captured by a CCD based spectrophotometer that was connected to a computer.

2.4. Simulation
The RCWA calculations were performed by using a modified computation program initially developed by the Zhang group of the Georgia Institute of Technology. [4] The grating structure model in the simulation was made to be same as the fabricated grating structure.

3. RESULTS AND DISCUSSION

![Figure 2](image)

**Figure 2.** The SEM images obtained from (a) the surface and (b) cross-section of the fabricated polymer grating structure with grating periodicity of about 700 nm.

Figure 2 shows the scanning electron microscopy (SEM) images indicating the formation of surface corrugated or surface relief grating structure with a periodicity of about 700 nm. This formed grating structure has almost the same structure and periodicity as the template. Grating structure with periodicity up to around 150 nm can be made by using this polymer precursor gel and nano-imprint lithography.

![Figure 3](image)

**Figure 3.** The reflection spectra obtained from the diffracted light beams at diffraction order \( m = \pm 1 \) and incident angle 45° for (a) the s-polarization (TE mode) and (b) the p-polarization (TM mode).
The diffraction light beams were observed for $m = 0$ and $m = +1$ at incident angles of 40°, 45°, and 50°. The zero-order diffracted light ($m = 0$) looks like a polychromatic beam spot, whereas the first order diffracted light ($m = +1$) looks like a monochromatic light beam with wavelength depending on the diffraction angle. In order to analyze the complete reflection spectrum at this first diffraction order, we added these first order diffraction spectra for all diffraction angles and took the envelope from the resulting total spectrum, as shown in Figure 3. This envelope spectrum was then divided by the incident light spectrum, taken from a flat Au layer at the same incident angle, to get the complete reflectance spectrum. Figure 4 shows these complete spectra for the s-polarization (TE mode) and the p-polarization (TM mode), giving an evidence of the appearance of SPR dip in the p-polarized light spectrum. Moreover, this figure also shows that this SPR dip was red-shifted with increasing incident angle.

![Figure 4](image)

**Figure 4.** The comparison of the complete spectra of the s-polarization (TE mode) and (b) the p-polarization (TM mode) from the first order ($m=+1$) diffraction light.

![Figure 5](image)

**Figure 5.** The comparison of the SPR spectra obtained from (a) the experimental results and (b) the simulation results for the first order ($m=+1$) diffraction light.

As shown in Figure 5, the SPR dips in the simulation spectra are almost similar as in the experimental results. The SPR dips from the simulation spectra are 582, 599, and 620 nm for incident angles of 40°, 45°, and 50°, respectively. The corresponding SPR dips from experimental results are 594, 611, and 627 nm.
In order to clarify the origin of SPR dips, the experimental SPR dips were plotted in the dispersion relation given by Eq. (1), as shown in Fig. 6. Interestingly, the SPR dips are around the blue line for the surface plasmon dispersion relation with $m = +2$. So diffraction order which was generated SPR in the visible light is $m = +2$. The origin of SPR dips seems to be caused by SPR excitation from the second order diffraction, not from the first order diffraction. This fact means that the excitation SPR wave is caused by the second order diffraction light beam and absorbs the light energy at the resonance wavelengths. Due to this light absorption, the first order diffracted light intensity then becomes much weaker.

4. CONCLUSION
We have successfully fabricated some surface-corrugated polymer gratings with sub-micron periodicity by using nano-imprint lithography from hybrid polymer precursor, which can exhibit SPR excitation after the deposition of 50 nm thin gold layer. The SPR dips were observed in the first order ($m = +1$) diffraction light beams. The observed SPR spectrum shows an agreement with the SPR spectrum from the simulation results based on RCWA method. Interestingly, the dispersion curve shows that SPR dips are from the second order ($m = +2$) diffraction. These facts then lead to a conclusion that, in the present case, the observed SPR in the present case is not directly from the resonance condition with the first order diffraction, but from the second order that has resonance wavelength coincidentally matched with the first order diffraction wavelength.

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Acknowledgment
Authors acknowledge the support from Desentralisasi research program from ITB-Ristekdikti.