Reflectance spectra characteristics from an SPR grating fabricated by nano-imprint lithography technique for biochemical nanosensor applications

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Abstract. In this paper, we report our research work on developing a Surface Plasmon Resonance (SPR) element with sub-micron (hundreds of nanometers) periodicity grating structure. This grating structure was fabricated by using a simple nano-imprint lithography technique from an organically siloxane polymers, which was then covered by nanometer thin gold layer. The formed grating structure was a very well defined square-shaped periodic structure. The measured reflectance spectra indicate the SPR wave excitation on this grating structure. For comparison, the simulations of reflectance spectra have been also carried out by using Rigorous Coupled-Wave Analysis (RCWA) method. The experimental results are in very good agreement with the simulation results.

1. Introduction
A sensor is a device that can convert a measurable physical quantity into an electrical signal, which often requires a transducer for that purpose [1]. One example of transducers is an optical transducer by utilizing the Surface Plasmon Resonance (SPR) phenomenon. SPR is a plasmon resonance phenomenon with electromagnetic waves causing quantized plasmon oscillation on the surface of metal-dielectric interface. SPR is very sensitive to the dielectric constant change of the dielectric medium so that it is widely applied for biochemical nanosensors applications [2]. The refractive index of may be strongly influenced by the type of molecule and intermolecular interactions. SPR based sensors are very suitable for label-free sensing and real-time sensing, which can measure the concentration and kinetic of biomolecules as well as distinguish the specific interaction between two molecule pairs, such as an antigen-antibody pair.

The requirement for excitation of SPR wave is that the vector component of light waves propagating at the boundary must be equal to the surface plasmon vector (SP) [3]. SPR wave can be created if the incident light can be coupled to the metal layer by using a prism, grating, or waveguide structure. This is related to the intersection between the dispersion curve of free-space light propagation and the dispersion curve of the SP wave on the metal/dielectric interface. SPR excitation by using grating has many advantages such as simpler instrumentation set-up and more practical. However, the measured SPR spectra are more complicated to be analyzed, particularly for a grating with non-sinusoidal structure, such as a square-wave periodic structure. In this case, the incident light will be also subjected to diffraction, where the diffraction pattern is more complex while some portions of the diffracted beams may be not coupled to the SPR waves [4].
In order to estimate the reflectance spectra of periodic structures, simulation based on the rigorous coupled wave analysis (RCWA) method may be very useful for that purpose. RCWA calculation is different from the coupled wave analysis (CWA) method in which RCWA is a full-vectorial calculation derived from the Maxwell equation without using an approximation as in CWA. [6-9] In this RCWA formulation, the dielectric constant of the structure and the light waves are transformed into their Fourier series representation. Therefore, this method is very relevant for periodic structure cases. The calculation results are then a representation of electric fields in each mode. Another benefit from RCWA is that the differential equations of Maxwell equation are transformed into a matrix form and solved as an eigenvalue problem. The wave equation (for two-dimensional structure) is then given by

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

where \( s_x \) and \( s_y \) are the electric fields, which can be found as the eigenvector solution, while \( \Omega \) stands for wave propagation constants. [6] All \( s_x \), \( s_y \), and \( \Omega \) are written in the matrix form.

In the present work, the grating structures with sub-micron (hundreds of nanometers) periodicity were made from an organically modified siloxane hybrid polymers by employing nano-imprint lithography. The advantages of this polymer are optically transparent and easy to be fabricated from its gel phase without requiring high temperature. The cross-linking formed in this polymer gives some advantages leading to good mechanical strength and thermal stability as well as chemical resistance so that the fabricated device can be more durable.

2. Experiments

2.1. Precursor preparations

The preparation of the polymer precursor was similar as in our previous work, where we have demonstrated the fabrication of sinusoidal corrugated grating structure with hundreds of nanometers periodicity by laser interferometry from this polymer precursor. [10,11] Cross-linking of siloxane groups of the 3-(Trimethoxysilyl) propyl methacrylate 98% (TMSPMA, Aldrich) monomer was formed during the sol-gel process. For that purpose, TMSPMA was dissolved in ethanol and added by HCl 1 N as the catalyst. The solution was continuously stirred for 72 hours at 50°C until forming a gel phase. This gel was added by photo-initiator Irgacure-819 (Ciba Speciality Chemical Inc.), which was then used as the polymer precursor for the nano-imprint lithography process. This process was carried out in dark room to avoid undesired photo-polymerization.

2.2. SPR grating fabrication

The sub-wavelength grating structure was made by employing the nanoimprint lithography technique. The polymer precursor was poured over a silicon stamp and then followed by a vacuum process for 30 minutes. The next step was UV-curing, where the polymer precursor layer on the top of the silicon stamp was irradiated by the 405 nm laser for 15 minutes. The resulted grating structure was peeled off from the silicon stamp and then evaporated with very thin layer of gold with the thickness of about 50 nm.

2.3. SPR Characterization

The fabricated grating SPR structure was characterized by measuring its reflectance spectrum by using an experimental setup as shown in Figure 1. A tungsten lamp was used as the polychromatic light source. Slit and pin holes were used to keep the light beam from spreading out beyond the grating size. The polarization was adjusted by using a polarizer. The reflectance light beam was measured by a CCD based spectrophotometer.
3. Results and Discussions

Figure 2 shows the scanning electron microscopy (SEM) images of the fabricated grating structure with a periodicity of about 500 nm. These images show that the grating has a surface corrugated structure of a periodic square wave shape with corrugation depth of around 200 nm.

Figure 3 clearly shows 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. The dip is not observed for the s-polarization. For both s- and p-polarization, there is a strong light absorption by
gold at wavelengths shorter than 550 nm. The s-polarization shows even stronger absorption because the direction of the electric field in the s-polarized is parallel to the grating structure repetition.

![Graphs showing reflection intensity and reflectance spectra](image)

Figure 3. (a) The reflection intensity spectra and (b) the reflectance spectra of the zero order diffraction beam \((m = 0)\) measured from the fabricated metal grating for the s- and p-polarization at an incident angle of 10°.

Figure 4 shows the reflectance spectra taken for several incident angles. For s-polarization, there is no dip and no change of spectral shape with increasing incident angle. For the p-polarization, however, the SPR dip is clearly red-shifted with increasing incident angle. The third dip (3) shifts to a longer wavelength, while the first and second dips (1 and 2) seem to shift and merge into one dip. The appearance of multi dips here is slightly different from the SPR spectrum characteristics in perfect sinusoidal SPR grating. [10]

![Graphs showing reflectance spectra at different angles](image)

Figure 4. The reflectance spectrum for (a) the s-polarization and (b) the p-polarization of the grating for diffraction order \(m = 0\) taken at several incident angles.

Comparing Figure 4 and Figure 5, we can clearly see that the reflectance spectra calculated from the RCWA method are similar to the experimental reflectance spectra. The simulation was done by using a modified computation program initially developed by the Zhang group of the Georgia Institute of Technology. [12] The spectral shape and the trend of dip shifting dip are almost similar, where the maximum difference between the dip wavelengths obtained from the simulation results and from the experimental measurements, for the same incident angle, is just about 3%.
4. Conclusion
The nano-imprint lithography technique and hybrid polymer precursor used in this work is very effective for fabricating submicron (hundreds nanometer periodicity) grating structure. The SPR wave can be effectively excited in the fabricated grating structure, which is indicated by red-shifting of SPR dip with increasing incident angle. This systematic SPR dip shifting will be useful as a sensing tool in a biochemical nanosensors. The experimental results are in good agreement with the simulation results calculated by using the RCWA method.

5. References
[1] Wilson J 2005 Sensor Technology Handbook (Oxford: Elsevier Inc)
[2] Homola J et al 2006 Surface Plasmon Resonance (SPR) Sensors Surface Plasmon Resonance Based Sensors (Springer Series on Chemical Sensors and Biosensors vol 4 ) ed J Homola (Berlin: Springer) chapter 2 pp 69 - 91
[3] Maier S A 2007 Plasmonics: Fundamentals and Applications (UK: Springer)
[4] Liang G et al 2016 Fiber Optic Surface Plasmon Resonance–Based Technique: Fabrication, Advancement, and Application Crit. Rev. Anal. Chem. 46 213-223
[5] Wismanto W Y et al 2012 Emission enhancement characteristics of oxazine in pmma matrix influenced by surface plasmon polariton induced on sinusoidal silver grating J. Nonlinear Opt. Phys. Mater. 21 1250013
[6] Merhari L 2009 Hybrid Nanocomposites For Nanotechnology (US: Springer)
[7] Pathak A et al 2016 SPR Based Cone Tapered Fiber Optic Chemical Sensor for the Detection of Low Water in Ethanol AIP Conference Proceedings vol 1728 (US: AIP Publishing) pp 020017
[8] Han K S et al 2013 Fabrication of 3D nano-structures using reverse imprint lithography Nanotechnology 24 045304
[9] Peng S and Morris G M 1995 Efficient implementation of rigorous coupled-wave analysis for surface-relief gratings J. Opt. Soc. Am. A. 12 1087-1096
[10] Hidayat R et al 2012 Journal of Engineering and Technological Sciences 44 207-219
[11] Hidayat R et al 2012 Polymer. Adv. Tech. 23 1264-1270
[12] http://zhang-nano.gatech.edu/

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