Micro-nano Structurized Gold Chip for SPR Imaging Sensor

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Abstract A micro-nano structurized gold chip was developed and applied to a surface plasmon resonance imaging (SPRi) sensor with polarization contrast method. Compared with the planar gold film, a total sensitivity enhancement (SEF=287%) was obtained.

1. Introduction
The demand for rapid high-throughput chemical sensor and biosensor technologies is increasing in many important areas such as life science, environment monitoring, and food safety. Due to the ability of multi-analyte interrogation and the high-throughput applications, surface plasmon resonance imaging (SPRi) has gained considerable interest in these areas. The general implementation for SPRi is based on analysis of the distribution of light intensity reflected from an SPR surface containing multiple sensing arrays. However, the main limitation of that is its poor refractive index resolution, which is lower than conventional angular or phase modulation SPR systems. So improving the performance of these sensors became particularly important. In recent years, a polarization contrast method for high-throughput SPR sensing has been developed. It converts changes of light polarization (phase and amplitude) into changes of light intensity, which was measured directly and thus it gains the same level of sensitivity as the phase modulation method.

In order to further improve the performance of the SPRi sensor, we proposed a micro-nano structurized gold chip for the SPRi sensor operated with polarization contrast method. The key innovations have two aspects. One is that a microwell structure is used to confine surface plasmon wave (SPW) inside the well, leading to a preliminary enhancement of sensitivity. The other is that a nano-gratings structure is designed inside the microwell to generate enhanced electric field due to localized surface plasmon resonance (LSPR) and SPR coupling, realizing a second enhancement of sensitivity. Bulk refractometric experiments are implemented to establish the real function of the micro-nano structure, and performance of the SPRi sensor is evaluated.

2. Micro-nano Structurized Gold Chip

2.1. Numerical Simulations
Numerical simulations were performed using finite-difference time-domain (FDTD) method. Non-uniform meshings were implemented during simulations. Models of microwell structure and nano-gratings structure are presented in Fig. 1. Both of the structures were illuminated with an incident
plane wave (\( \lambda = 633 \text{ nm} \), the incident angle \( \theta_1 = 75^\circ \)). The optical parameters of gold are derived from literature, and prism material is set as BK7 (\( n = 1.515 \)).

![Figure 1. FDTD models of (a) microwell structure and (b) nano gratings structure](image)

Figure 1(a) shows the xz cross-section of one circular sensing spot of the microwell structure. According to the results, microwell with a diameter of \( d = 10 \mu \text{m} \) was simulated in Perfectly Matched Layer (PML) absorbing boundary conditions. The thickness of the sensing gold film is 40 nm, and the optimal thickness for the gold film in background area \( t = 150 \) nm, considering difficulties in the fabrication of thicker patterns.

Figure 1(b) shows the xz cross-section of one period of the nano-gratings structure. This is a 2D model which is infinite in y axis since the length of the gratings is much larger than the period. It has a thin bottom gold film covered by a thin top gold film. The structure has parameters of period \( a \), width \( d \), thickness of the bottom film \( t_d \) and thickness of the top film \( t_g \). Due to its periodic property, the model was simulated in “Periodic” absorbing boundary conditions in x direction. When the structure parameters are \( a = 200 \) nm, \( d = 100 \) nm, \( t_d = 30 \) nm and \( t_g = 10 \) nm, there is a resonant peak at 635 nm, which coincides with the working wavelength of the SPRi sensor.

2.2. Fabrication of micro-nano structurized chip
Fabrication of microwell structure was realized by photolithography and two-layer deposition of gold film. The thick background film was firstly deposited on a thin, polished BK7 glass substrate by magnetron sputtering of gold with a 2-nm-thick chromium layer as an adhesion layer followed by a photolithography process. After etching the unprotected thick gold film, and then lifting off the photoresist using acetone, the microwell patterns were obtained. The exposed glass surface was cleaned by plasma, and then a thin gold film as the SPR-active layer and another 2-nm-thick chromium layer as an adhesion layer were sputtered onto the thick patterned gold film to finally form the microwell structure.

Nano-gratings structure was fabricated just inside the microwell structure by etching the thin sensing gold film using a focused-ion-beam (FIB) system (30 K eV Ga ions, resolution 5 nm). Periodic hollows were obtained by etching and the top gold films were formed, leaving the rest as the bottom gold film.

3. Experimental and setup
A home-built SPRi sensor comprising of a 635 nm LED light source and a 12-bit CCD with a resolution of 1392 \times 1040 pixels as the detector, was established based on the polarization contrast method. The LED light was first collimated, and then passed through a polarizer. The transmitted light contains both p (vector of electric intensity parallel to the plane of incidence) and s (perpendicular to the plane of incidence) polarizations. It illuminated a right-angle BK7 prism with an incident angle of 75 degree. After reflected by the sensing surface, it passed through a \( \lambda/4 \) waveplate and an analyzer,
and was finally captured by the CCD camera. The micro-nano structurized gold chip was mounted on the surface of prism by matching liquid ($n = 1.515$). A 350 μL flow cell was attached on the chip.

To study the refractive index sensitivity of the micro-nano structurized chip, a series of NaCl (0, 20, 50, 100, 150, and 200 g/L) solutions were prepared and measured. The refractive indices of these solutions cover the range of 1.3315–1.3632 RIU, which had been previously measured by an Abbe refractometer. Before measurement, deionized water was pumped through the flow-cell to the sensor surface until a stable baseline was established. Liquid samples were then injected sequentially with a loop of water-NaCl-water at a controllable flow rate. Each concentration was injected thrice to reduce measurement error.

4. Results and discussion

The sensitivity enhancement factor (SEF) to evaluate the improvement of sensitivity, which is defined as the ratio of sensitivity of the micro-nano structure to that of the reference chip, i.e. $SEF = \Delta I_{\text{micro-nano}} / \Delta I_{\text{reference}}$.

4.1. Microwell chip

The gold microwell chip was characterized by high sensitivity to bulk refractive index changes in NaCl solution. Figure 2 depicts sensor response to sequential concentration changes of NaCl (0–200 g/L) from the sensing spots.

The signal value was normalized by the intensity of air to eliminate the influence of light intensity fluctuations. Using the refractive indices obtained from the Abbe refractometer as horizontal coordinates, a refractive index calibration curve was established, and linear fit of the curve can be achieved. Sensitivity can be obtained as the slope of the linear curve, which was 3521 %/RIU. The responses of NaCl solutions from the reference chip were also recorded for comparing, and the calculated sensitivity of the reference chip is 2237 %/RIU. So the SEF here is 157%.

4.2. Nano gratings chip

Sensitivities of gold microwell spots with nano gratings and without nano gratings in detection of NaCl are compared. Linear fits of the curves are implemented within the low refractive index range ($n = 1.3315–1.3394$ RIU, corresponding to 0–50 g/L of NaCl), which is shown in Figure 3.

Sensitivity of microwell spot without nano gratings is 2526 %/RIU, while with nano gratings is 4619 %/RIU (SEF=183%). Combined with the afore obtained sensitivity enhancement of microwell to planar gold film (SEF = 157%), a total enhancement of the micro-nano chip can be calculated by $SEF_{\text{total}} = 157\% \times 183\% = 287\%$. 

![Figure 2. Sensor response to NaCl (0 – 200 g/L)](image-url)
5. Conclusion
A micro-nano structurized gold chip was developed and applied to a SPRi sensor with polarization contrast method. A total sensitivity enhancement (SEF = 287%) was obtained. These improvements are attributed to: (1) sensitivity enhancement (SEF = 157%) due to the electric field enhancement in the microwell caused by SPW interference; and (2) a second sensitivity enhancement (SEF = 183%) due to LSPR-SPR coupling in the nano gratings structure.

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