Design, fabrication and testing of gain SPR sensor chip

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Abstract. The gain Surface plasmon resonance (SPR) chip can compensate for the SPR loss, which can improve the sensitivity of the SPR analysis system. In this paper, we design an SPR chip that includes a glass substrate, a gain layer, and a metal layer. Wherein the gain layer is a film obtained by adding IR-140 fuel to different concentrations of methylene chloride in which polymethyl methacrylate (PMMA) is dissolved. Then, we prepared a series of chips with a specific gravity of 0.4%, 0.8%, 1.2%, and 1.6% for the IR-140 in the gain dielectric layer. The fitting effect of the 2nd to 11th order polynomial fitting on the SPR curve is studied, and the SPR curve in this paper is processed by the preferred ninth order polynomial fitting. Finally, by studying the relationship between the thickness of the gain layer and the absorption peak generated by the SPR chip, a chip having an IR-140 dye specific gravity of 0.4% is preferred. The gain layer of the gain SPR chip is also expected to be further studied to further increase its sensitivity.

1. Introduction

SPR sensing technology is a physical optical phenomenon called Surface Plasmon Resonance (SPR). When a beam of light is directed from a refractive index to a light-diffusing medium having a refractive index, total reflection occurs when the incident angle is greater than a certain critical angle C. Due to the presence of a thin film of a suitable thickness on the SPR chip, the incident light illuminates the surface plasmon (SPW) along the surface of the metal conductor as it is totally reflected through the prism. Surface plasmon resonance (SPR) sensing technology is based on surface plasmons (SPPs).That has always been a hotspot in refractive index sensors due to its high resolution, high sensitivity, real-time and no markage. SPPs can be excited by an attenuated total reflection (ATR) based Otto or Kretschmann prism coupling structure [1-4]. However, the inherently high loss of SPPs limits the signal-to-noise ratio (SNR) and sensitivity of SPR sensors. The loss of SPPs can be compensated by using a gain medium in the vicinity of metals of different geometries, or by adding an active layer to the SPR sensor based on phase detection [5-7]. Recently, a five-layer SPR sensor model based on a gain dielectric layer has been proposed [8]. This sensor not only compensates for SPPs...
losses and can even amplify it. However, this chip has five layers, the structure is too complicated and requires an optical pump.

In this paper, a three-layer SPR sensor chip is proposed and fabricated and tested. The fabricated chip can improve the signal-to-noise ratio (SNR) of the SPR sensor and compensate for the loss of SPPs while finding that the sensor has a wider gradient measurement range \[9–10\]. It is expected that the ninth-order polynomial fitting algorithm will be applied to the SPR signal processing to improve the sensitivity of the SPR chip, and it is also expected to apply the gain SPR chip to multi-component detection.

2. Materials and Methods

2.1. Materials
The experimental materials required for this experiment include: IR-140 dye was purchased from Xibao Biotechnology (Shanghai) Co., Ltd.; powdered PMMA with a relative molecular mass of 350,000 Mw was purchased from Xibao Biotechnology (Shanghai) Co., Ltd. Slides are purchased from Beijing Chemical Reagent Company, China.

2.2. Preparation
The instruments required for this experiment include: Electric heating constant temperature air drying oven, purchased from Beijing Ying'an Meicheng Scientific Instrument Co., Ltd.; multi-functional magnetic enhanced reactive ion etching machine, model ME-3A, purchased from the Microelectronics Center of the Chinese Academy of Sciences; cleaning station, spin coating instrument; The step meter for measuring the thickness of the gain medium layer was purchased from KLA-Tencor, USA, and its model was ASIQ; the sputtering system was purchased from Denton Vacuum Equipment (Beijing) Co., Ltd.

In this paper, the gain dielectric layer used in the gain SPR sensor chip is obtained by dissolving PMMA and IR-140 dye in methylene chloride. Then, a metal film is sputtered on the gain medium layer to complete the fabrication of the sensor chip. The specific process is as follows:

1) Cleaning the glass substrate: sequentially boiling the glass substrate with concentrated sulfuric acid and deionized water, and drying;
2) 200 mg of PMMA having a relative molecular mass of 35,0000 Mw was dissolved in 3 ml of dichloromethane; The IR-140 dye was added to the mixed solution at a specific gravity of 0.4%, 0.8%, 1.2%, and 1.6% to prepare different kinds of gain SPR chips. The amount of PMMA in this step can then be determined by the experimental conditions, but it is guaranteed to be completely soluble in the dichloromethane solution.
3) The gain dielectric layer is prepared by spin coating. The spin coating is carried out by first homogenizing at 500 rpm for 15 s and then spin coating at 5000 rpm for 1 min; then, the gain dielectric layer film is used. Bake at 100 degrees Celsius for five minutes;
4) Using a sputtering or deposition method, a gold film is prepared on the glass substrate obtained in the step (3), thereby obtaining a gain SPR chip;

2.3. Testing
The thickness of the gain dielectric layer of four SPR chips with different concentrations of IR-140 dye is measured by the step meter(KLA-Tencor, USA). The SPR chip was tested in a multi-channel image SPR analysis system developed by the laboratory itself [11].

3. Results and discussion

3.1. Design of the gain SPR sensor chip
Based on the literature and the existing research in this laboratory [12], this paper designs a three-layer SPR chip, as shown in Figure 1. The chip comprises three layers, namely a glass substrate, a gain layer
and a metal layer. The chips in Figure 2 are the actual fabricated. Figure 2(a) is the chip prepared by the IR-140 dye having a specific gravity of 1.6%. Figure 2(b) is the chip prepared by the IR-140 dye having a specific gravity of 1.2%. Figure 2(c) is the chip prepared by the IR-140 dye having a specific gravity of 0.8%. Figure 2(d) is the chip prepared by the IR-140 dye having a specific gravity of 0.4%.

3.2. SPR sensor chip test
The thickness of the SPR chip in Figure 2 was tested and the SPR absorption peak was detected using the multi-channel image SPR biochemical analysis system of the laboratory. In this paper, the four different concentrations of IR-140 gain SPR chips were tested using our laboratory image SPR analysis system. The test is to install the gain SPR chip on the image SPR analyzer under normal temperature conditions and use deionized water as the analysis liquid layer to perform angle scanning and data acquisition.

The thickness of the gain dielectric layer of the SPR chip of Figure 2 was tested using a step meter (KLA-Tencor, USA), the thickness of which is shown in the following table:
Table 1. Gain level thickness.

| IR-140 specific gravity (percentage) | Gain dielectric layer thickness (um) |
|-------------------------------------|-------------------------------------|
| 0.4%                                | 3.5                                 |
| 0.8%                                | 4.0                                 |
| 1.2%                                | 5.0                                 |
| 1.6%                                | 6.5-8                               |

*a* percentage = IR-140 quality/ PMMA quality.

The SPR curve tested by the image SPR biochemical analysis system developed by our laboratory is shown in Fig. 3. In Figure 3, 0.4%, 0.8%, 1.2%, and 1.6% represent the specific gravity of IR-140 dye and PMMA, respectively. As can be seen from Figure 3, SPR characteristics have emerged.

![SPR raw test curve](image)

**Figure 3.** SPR raw test curve.

0.4%, 0.8%, 1.2%, and 1.6% represent the specific gravity of IR-140 dye and PMMA, respectively.

3.3. Optimize data processing parameters

Most SPR sensor data processing methods are based on the localization of the minimum SPR peak of the reflectance. These processing methods include nonlinear Lorentz curve method, centroid algorithm, optimized centroid algorithm and linear projection method, linear projection based on model parameters (MPLP) and 2-7 order polynomial fitting method. In this paper, we choose polynomial fitting for data processing. This is why the method is small in calculation and easy to implement, and it can also make the SPR curve smooth and reduce noise.

3.3.1. The mathematical model of the polynomial fitting algorithm. The mathematical model of the polynomial fitting algorithm is as follows:

\[ f(x) = a_1x^m + \cdots + a_mx^5 + a_{m+1} \]  

(1)

Here, \( m \) is the order of the polynomial, \( a_1, \ldots, a_{m+1} \) is the fitting coefficient.
The most common method of solving the coefficients in equation (1) is the linear least squares method. The coefficient is determined as follows:

$$J(a_1,\ldots,a_{m+1}) = \sum_{i=1}^{n} \delta^2 = \sum_{i=1}^{n} [f(x_i) - y_i]^2$$  \hspace{1cm} (2)

Where $J$ is the fitting error sum, $f(x_i)$ represents the value of the fitted function at $x_i$, $y_i$ representing the value corresponding to the original data.

In order to solve $a_1,\ldots,a_{m+1}$, Simply minimize the equation (2), which is $\frac{\partial J}{\partial a_k} = 0 \ (k = 1,\ldots,m)$.

Get the equations for $a_1,\ldots,a_{m+1}$.

$$\sum_{k=4}^{m} a_k \left[ \sum_{i=1}^{n} x_i^j \times x_i^k \right] = \sum_{i=1}^{n} x_i^j y_i, \ (j = 1,\ldots,m)$$  \hspace{1cm} (3)

Assume

$$R = \begin{bmatrix} x_1 & \cdots & x_i^m \\ \vdots & \ddots & \vdots \\ x_n & \cdots & x_i^m \end{bmatrix}_{j \times m}$$

$$A = [a_1,\ldots,a_m]^T, \ Y = (y_1,\ldots,y_n)^T$$

Then equation (3) can be expressed as

$$R^T RA = R^T Y$$  \hspace{1cm} (4)

Therefore, the coefficient matrix $A$ of the polynomial fitting can be obtained by the equation (4).

$$A = \left( R^T R \right)^{-1} R^T Y$$

In this paper, a prepared gain SPR chip with an IR-140 concentration of 0.4% was selected and tested using the image SPR biochemical analysis system of the laboratory to collect data. The fitting order of the selected polynomial is 2-11, and the fitting error is calculated by using equations (1) and (2), the fitting coefficient is calculated by equation (4). The fitting coefficient is shown in Table 2, where in Table 2, only the fitting coefficients of the 2nd to 5th order polynomials are given. And the fitting curve is drawn, as shown in Figure 4 and Figure 5. In Figure 4, Figure 4(a) is a fitting error curve, and Figure 4(b) is a fitting curve of 2-5 steps. In this paper, a 2-11 fitting error graph is made, but in this analysis, only the 2-5-order graph in Figure 4 is given, and the remaining fitting error graphs are in the appendix. 4 is an enlarged view of Figure 4(b). Referring to Figure 4(a) and Figure 5, the effect is ideal when the fitting order is 5 or more.

| Fitting order | $a_1$    | $a_2$    | $a_3$ | $a_4$ | $a_5$ | $a_6$ |
|---------------|---------|---------|-------|-------|-------|-------|
| 2             | 36914.632 | -0.690 | 0     |       |       |       |
| 3             | 78101.859 | -2.362 | 0     | 0     |       |       |
| 4             | 90026.686 | -3.023 | 0     | 0     | 0     |       |
| 5             | -11033.421 | 4.070 | -0.002 | 0     | 0     | 0     |
Figure 4. Fitting error and fitting curve of prepared gain SPR chip with IR-140 concentration of 0.4%.

(a) fitting error curve  (b) fitting curve of 2-5 steps.

Figure 5. Magnified image of the prepared gain SPR chip with IR-140 concentration of 0.4%.

3.3.2. Determining the polynomial fitting order of multiple sets of SPR chips. From the above analysis, the fitting order of the polynomial is determined to be 5 or more. The fitting error calculations were performed on the four IR-140 concentration gain SPR chips and plotted. As shown in Figure 6. In Figure 6, it can be seen that for four different gain layer thickness SPR chips, when the fitting order is greater than 5, the fitting error does not change much, but it can be seen from the four curves. When the order number is greater than or equal to 9, the fitting error curve becomes more gradual. Considering the comprehensive consideration, this paper chooses the 9th-order polynomial fitting.
Figure 6. Four IR-140 concentration gain SPR chips for fitting error map.

0.4%, 0.8%, 1.2%, and 1.6% represent the specific gravity of IR-140 dye and PMMA, respectively.

3.4. SPR absorption peak curve under optimized conditions

In this paper, a layer of gain medium film was prepared by dissolving PMMA and IR-140 in 3 ml of dichloromethane. Based on the IR-140 concentration, four gain layers were fabricated and tested using our laboratory image SPR analysis system. Figure 7 is a graph of experimental results. Figure 7 shows the polynomial-fitted curve obtained by testing the gain SPR sensor chip prepared with four different concentrations of IR-140 dye; Figure 7 is normalized. The principle of normalization is: first select the lowest point of the SPR curve measured by the bare chip, that is, the SPR peak, and obtain its coordinates; then, based on this coordinate point, the four SPR curves in this experiment are also translated. That is normalized, so that its SPR peak is in the same position. It can be seen from Fig. 7 that the lower the IR-140 concentration, the smaller the half width of the prepared SPR sensor chip, and the higher the slope near the SPR peak. When the concentration of IR-140 is 1.6%, the half width is higher than the half width of 1.2%. It is speculated that the higher concentration of IR-140 may reduce the half width.

Figure 7. Nine-order polynomial fitting SPR absorption peak curve.

0.4%, 0.8%, 1.2%, and 1.6% represent the specific gravity of IR-140 dye and PMMA, respectively.
4. Summary
This paper describes in detail the working principle of the gain SPR sensor and the process flow of its fabrication. In order to compensate the loss caused by the SPPs excited by the SPR sensor, a layer of gain layer medium is added to the SPR chip by using the Kretschmann prism coupling structure. Experiments have shown that the SPR absorption peak of this gain-type SPR sensor will increase, that is, it will compensate for the SPPs loss. And this paper also gives an SPR signal processing algorithm based on 9th order polynomial fitting. During the fabrication of the gain SPR sensor, the spin-on speed and the ratio of PMMA to IR-140 dye have an important effect on the thickness of the gain layer. Next, we will delve into the characteristics of the gain dielectric layer. For example, the effect of the thickness of the gain dielectric layer on the SPR chip and the specific gravity of the IR-140 dye on the sensitivity of the chip.

5. Appendices

![Graphs of SPR curves](image)

Figure 8. Magnified image of the prepared gain SPR chip with IR-140 concentration of 0.4%.

![Graphs of SPR curves](image)

Figure 9. Magnified image of the prepared gain SPR chip with IR-140 concentration of 0.4%.
Acknowledgments
This work has been supported by the National High Technology Research, the National Basic Research Program of China (973 Program) (Grant No. 2014CB744600), and the National Natural Science Foundation of China (Grant Nos. 31571007, 61571420, 61372055).

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