The Effect of Temperature and Electric Current on the SPR Sensors

Shengming Zhang
Indiana University of Pennsylvania

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THE EFFECT OF TEMPERATURE AND ELECTRIC CURRENT ON THE SPR SENSORS

A Thesis Submitted to the School of Graduate Studies and Research

In Partial Fulfillment of the

Requirements for the Degree

Master of Science

Shengming Zhang

Indiana University of Pennsylvania

August 2011
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In this thesis, the history of SPR (Surface Plasmon Resonance) sensors and the details of the SPR theory and development are elucidated. An economical and practical SPR sensing reflectometer is introduced, including the manufacturing of the sensor film and measurement of the refractive indices of air and water.

Systematical theoretical simulations of multiple layer system SPR curves are developed. For this research, a NanoSPR 6 reflectometer with a ~0.5% resolution and ~2 sec response time is used. The dip of the SPR curve occurs at about 44.300 degrees, when the refractive indices of air and water are measured.

An integrated simulation of the temperature effects on a Kretschmann coupling configuration is modeled using Mathematica. The temperature effects of both the layers and the prism system are considered in this modeling. When the temperature is increased by 100 degree, the model shows that the minimum value of the SPR curve will shift to the right hand side by ~0.08 degree; the intensity of the SPR will decrease by ~ 3% and the full width at half maximum of the SPR curve will increase around 1.5 degree. We also shows that the electric current added to the gold film changed the SPR curve and find that the electromagnetic effect on the SPR curves is 10 times stronger than the temperature effect. An empirical formula is developed for the difference of the SPR curves (with current and without current) based on the experimental data using the Origin
software. The reduced Chi-Square of the formula is $1.022 \times 10^{-6}$ and the probability distribution is 0.9826, which shows that the empirical formula fitted the data well.
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CHAPTER 1

INTRODUCTION

1.1 Introduction of the SPR Sensors and SPR Phenomenon

Surface Plasmon resonance (SPR) sensors, which are based on a complex photoelectric phenomenon arising from the interaction of light with free electrons at a metal-dielectric interface, have been developed rapidly over the last two decades.

Due to the coherent charge density oscillations at a dielectric and metallic interface, some free electrons are excited collectively and generate a certain fluctuation wave, called surface plasmas (SPs). Under certain conditions, when a ray of photons is incident on the interface, their energies carried by the photons is transferred to the SPs, this phenomenon is called Surface Plasmon Resonance (SPR) or Surface Plasmon polariton (SPP) [1].

SPR can be excited by electrons or light rays. For optical excitation, the transfer of energy occurs only at a specific wavelength or incident angle of the light when the momenta of photons and plasma along the interface are matched [2]. Since the energy of the incident light is transferred to the SPs, there is a dip in the reflectance curve at the specific wavelength or incident angle. The specific wavelength or the incident angle is related to the SPs wave which is extremely sensitive to the refractive index near the metal surface within the range of the SP field [3]. Therefore, when an unknown solution passes on the metal surface, the refractive index of the surface will change, which will result in a shift of the reflectance signals. The magnitude of the difference is quantitatively related
to the refractive index of the solution. Based on the change of the refractive index, some key parameters, such as concentration or the reaction rate of the medium can be detected.

1.2 Reviews of SPR Studies

The first report of SPR phenomenon occurred in 1902, when Wood [2] observed an abnormal diffraction phenomenon during his experiment. In 1941, Fano first explained Wood’s observation by using the surface electromagnetic wave mode propagating along the interface.

In 1958, Turbader applied an attenuated total reflection method to excite the SPR phenomenon on the metal/dielectric interface. Later in 1959, Powell and Swan confirmed Ritchie’s mode using electrons to excite the “Plasmon”. Stern and Farrell created the concept “Surface Plasmon” in 1960 [1, 2, 4].

Otto (1968) [5] and Kretschmann (1971) [1], developed their own prism coupling configurations respectively to excite SPR by light, based on the “attenuated total reflection (ATR)” method. Nowadays, the Kretschmann configuration is widely used in the SPR sensing technique, due to its simplified user-friendly interface [6].

1.3 Development of SPR Sensor System

In 1976, Abeles first applied the SPR phenomenon to optical research of thin films [7] and then Liedberg (1983) was the first to use SPR to detect the interaction between an antigen(IgG) and its antibody in his PhD thesis [7].

Later in 1990, the first commercial SPR biosensor was developed by the Biacore AB Company, Sweden. From that time on, due to its label-free, real time monitoring and
other good advantages, SPR reflectometry has been widely used in chemical research, drug development, food safety, life science research and other biochemical researches.

Other SPR sensor systems have already been developed [8]. The most popular machines used for SPR reflectometry are listed in Table 1.1.

**Table 1.1 THE MOST WIDELY USED SPR REFLECTOMETERS AND MANUFACTURERS**

<table>
<thead>
<tr>
<th>The SPR reflectometer</th>
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<tr>
<td>Biacore</td>
<td>BIACore AB</td>
</tr>
<tr>
<td>IASys</td>
<td>Affinity Sensors</td>
</tr>
<tr>
<td>Speeta TM</td>
<td>Texas Instruments</td>
</tr>
<tr>
<td>Quantech SPR</td>
<td>Quantech</td>
</tr>
<tr>
<td>SPR-670</td>
<td>Nippon laser And Electronics Laboratory</td>
</tr>
<tr>
<td>Kinomics</td>
<td>Bio Tul Bio Instruments CambH</td>
</tr>
<tr>
<td>IBIS-ISPR</td>
<td>TBIS Technologies BV</td>
</tr>
<tr>
<td>Windsor Scientific</td>
<td>Windsor scientific</td>
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1.3.1 SPR Sensor Instrumentations

The devices that use SPs for optical sensing to detect a real time reaction on an interface are referred to as sensor systems. Now, the Kretschmann geometry of the attenuated total reflection method is the most commonly used setup.

Basic elements of a SPR sensor system include the light source, the sensor, sample cells and the photonic detector. The procedural sketch is illustrated in Fig. 1.1.
1.3.2 Classifications of SPR Sensors

Based on different SP exiting configurations, the SPR sensor system can be classified as prism coupling, grating coupling, fiber SPR sensor, waveguide SPR sensor and integrated coupling. Due to its simplicity, the prism coupling is the most commonly used configuration in practical applications [9].

Based on the detection methods of the SPR, the SPR reflectometers can be classified as intensity modulation, angular modulation, wavelength modulation, phase modulation and the polarization modulation. The intensity detection method is the simplest, but it has the least sensitivity. Phase modulation and the polarization modulation have the highest sensitivity but their configurations are very complex.
Therefore, the angle and wavelength modulations are the most commonly used SPR sensors systems.

1.4 Significance and Motivation

SPR sensing is a useful tool not only for identifying these interactions and quantifying their equilibrium constants as well as kinetic constants, but also for employing them in very sensitive, label-free biochemical assays. Therefore, it had been demonstrated in the past decade to be an exceedingly powerful and quantitative probe of the interactions of a variety of biopolymers. There is a continuously increasing number of publications related to SPR sensing as shown in Fig. 1.2.

Figure 1.2 The number of the SPR related publications in the last 2 decades.
The main advantage of SPR sensors is its high sensitivity without any fluorescent labeling or other analysis of the interactants. The field of SPR is currently undergoing an exciting period of discoveries. With SPR, the IUP researchers can be facilitated with a highly sensitive and highly accurate detecting technique to study the properties of nanometer scale thin films, to detect the interaction between trace amounts of chemical reagents, and to monitor the real-time biological enzymatic interactions.

Another motivation of this project is to study the electromagnetic effect on SPR based sensors. The electromagnetic effect plays a rather important role in the material science study, since it may excite a phase transition of a paramagnetic material; it also influences the chemical reactions and biological interactions. Additionally, the electric current through the sensor chip can generate heat, and increase its temperature. This temperature change will affect the accuracy of the sensor as well as the sample’s activity; therefore, it is important to study the temperature dependent effects of the SPR biosensors first.

1.5 Outline of the Present Thesis

a. First, in the present thesis, the detail of the SPR theory and the development will be elucidated clearly.

b. Further on, an economical and practical SPR sensing system will be introduced, including the production of the sensor film, and measurement of the refractive index of the analytes.
c. Theoretical simulations of multiple layer SPR curves will be built. An integrated simulation of the temperature effects on a Kretschmann coupling configuration will also be built by computer simulation.

d. Finally, the electric current effect on the SPR curve will be analyzed and a proposed explanation will be given.
2.1 Introduction

As introduced previously, a wave of surface plasmons (SPs) can be excited by an incident beam of light. This has been demonstrated in optical experiments by Otto and Kretschmann-Raether [1, 5].

Since the interaction between the photons and the surface electrons is governed by electromagnetic theory, this chapter starts with a review of Maxwell’s equations and then applies them to the SPs excitations at the interface.

2.2 Light Propagation in a Medium

Light is an electromagnetic wave, which can be demonstrated using Maxwell's equations. Maxwell’s equations in a medium can be expressed as follows:

\[ \nabla \cdot \vec{D} = \rho \]  
\[ \nabla \cdot \vec{B} = 0 \]  
\[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \]  
\[ \nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \]

where \( \vec{D}, \vec{E}, \vec{B}, \) and \( \vec{H} \) represent the dielectric displacement, the electric field, the magnetic field, and the magnetic induction or magnetic flux density; \( \rho \) represents charge density while \( \vec{J} \) represents the current density and \( \frac{\partial \vec{D}}{\partial t} \) represents the displacement current.
density. Also, Eq. (2.1) through Eq. (2.4) represent Gauss’s Law, Biot-Savart Law, Ampere’s Law and Faraday’s Law, respectively.

When light travels through a certain medium, the properties of the medium will affect the propagation of the wave. In this project, the media are limited to linear, isotropic and nonmagnetic materials, and the constitutive relations in a continuous medium are defined as:

\[
\begin{align*}
J &= \sigma E \\
\mathbf{D} &= \varepsilon \mathbf{E} \\
\mathbf{B} &= \mu \mathbf{H}
\end{align*}
\]  
(2.5)  
(2.6)  
(2.7)

where, \(\sigma, \varepsilon,\) and \(\mu\) represent the conductivity, the relative electric permittivity, and the relative magnetic permeability.

Considering an infinite, bulky material, \(\varepsilon\) and \(\mu\) are constants and there are no free charges or induced charges; therefore, \(\rho\) and \(J\) should both be equal to zero.

Substituting the constitutive relations Eqs. (2.5-2.7) into the Maxwell equations, we have:

\[
\begin{align*}
\nabla \cdot \mathbf{E} &= 0 \\
\nabla \cdot \mathbf{B} &= 0 \\
\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\
\nabla \times \mathbf{H} &= \varepsilon \cdot \mu \frac{\partial \mathbf{E}}{\partial t}.
\end{align*}
\]  
(2.8)  
(2.9)  
(2.10)  
(2.11)

Taking the curl of Eq. (2.10), then substituting it into Eq. (2.11), we get:

\[
\nabla \times (\nabla \times \mathbf{E}) = -\frac{\partial}{\partial t} (\nabla \times \mathbf{B}) = -\varepsilon \mu \frac{\partial^2 \mathbf{E}}{\partial t^2}.
\]  
(2.12)

Together with \(\nabla \times (\nabla \times \mathbf{A}) = \nabla \cdot (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}\) and \(\nabla \cdot \mathbf{E} = 0\), it follows that:
\( \nabla \times (\nabla \times \vec{E}) = -\nabla^2 \vec{E} \). \hfill (2.13)

Substituting Eq. (2.13) into Eq. (2.12), the relation becomes:

\[ \nabla^2 \vec{E} = \varepsilon \mu \frac{\partial^2 \vec{E}}{\partial t^2}. \] \hfill (2.14)

Therefore, \( \vec{E} \) and \( \vec{H} \) are harmonic wave functions with an amplitude that is transverse to the direction of propagation and with a speed \( v = \frac{1}{\sqrt{\varepsilon \mu}} \). Assuming the light propagates along the \( x \)-direction as shown in the Fig. 2.1, the solution of Eq. (2.14) can be expressed as:

\[ \vec{E} = E_0 \exp [i \omega (t - \frac{x}{v})] \] \hfill (2.15)

where \( \omega \) is the angular frequency \( (\omega = \frac{2 \pi}{\lambda} v (k)) \), \( \lambda \) is the wavelength of the light; and \( v \) is the speed in the medium, which is a function of the frequency \( (k) \) [10].

![Figure 2.1 A light ray propagates along the x direction in a medium.](image)

However, considering a metallic material, \( \sigma \neq 0 \), then:

\[ \frac{1}{v^2} = \varepsilon \mu - i \frac{\sigma \mu}{\omega}. \] \hfill (2.16)
Defining the complex refractive index of a metal as:

\[ N^2 = (\varepsilon \mu - i \frac{\sigma \mu}{\omega})/\varepsilon_0 \mu_0. \]  

(2.17)

Therefore, \( N = n - ik \) and \( n = \frac{c}{\nu} \), where \( n \) is the refractive index and \( k \) is the extinction coefficient which determines the optical absorption of the electromagnetic wave. Eq. (2.15) can be written as:

\[ \bar{E} = E_0 \exp \left[ i \left( \omega t - \frac{2\pi Nx}{\lambda} \right) \right] = E_0 \exp(i\omega t) \cdot \exp\left(-\frac{2\pi kx}{\lambda}\right) \cdot \exp\left[i \left( -\frac{2\pi nx}{\lambda} \right) \right]. \]  

(2.18)

Eq. (2.18) demonstrates that the wave in a metallic medium is a dissipating wave. Therefore, part of the wave’s energy will be absorbed by the metal and the absorption can be measured by the extinction coefficient \( k \).

2.3 Total Internal Reflection and Attenuated Total Reflection

2.3.1 Total Internal Reflection

When a ray of light strikes the second medium (\( n_2 \)) from the first medium (\( n_1 \)), define \( n_1 > n_2 \), where \( n_1 \) and \( n_2 \) are the refractive indices, according to Snell’s law, we have

\[ \frac{\sin \theta_2}{\sin \theta_1} = \frac{n_1}{n_2} > 1. \]  

If \( \sin \theta_1 < \frac{n_2}{n_1} \), then \( \sin \theta_2 > 1 \). This situation is physically impossible so there is no refraction ray, and all light will reflect back into the first medium (\( n_1 \)). This phenomenon is called total internal reflection (TIR).
2.3.2 Evanescent Waves

According to the condition of continuity for components of Maxwell’s equations, the solution for TIR contains a transmitted wave into the second medium and the wave propagates along the interface in a wavelength pattern. Additionally, along the z direction the wave shows an exponential decay pattern as shown in Fig. 2.2 [11]. This is called an evanescent wave [12].

![An evanescent wave](image)

Figure 2.2 An evanescent wave. [11]

Considering total internal reflection in the interface between two media, e.g. the vacuum \((n_1=1)\) and the glass \((n_2=n)\), the interface is on the x-y plane and the normal direction is along the z axis. The transmitted wave is:

\[
\overline{E}_2 = E_{0t} \exp[i(\overline{k}_2 \overline{r} - \omega t)] \quad (2.19)
\]

where, \(\overline{k}_2\) is the wave number of the wave in the second medium \((n_2)\). Therefore, \(\overline{k}_2\) is in the incident plane \((x-z \text{ plane})\) and Eq. (2.19) can be rewritten as:

\[
\overline{E}_2 = E_{0t} \exp[i(\overline{k}_{2x} \overline{x} + \overline{k}_{2z} \overline{z} - \omega t)] \quad (2.20)
\]
where, $\vec{k}_{2x}$ and $\vec{k}_{2z}$ are the elements of $\vec{k}$ along the x and z direction respectively.

Defining $\theta_t$ as the angle between the normal direction and the propagating direction of the transmitted wave in medium 2 as well as defining $\theta$ as the angle between the incident ray and the normal direction, we can obtain,

$$\vec{k}_{2x} = \vec{k}_2 \sin \theta_t = \vec{k}_2 \frac{\sin \theta}{n}$$  \hspace{1cm} (2.21)

Using Snell’s law Eq. (2.21) can be converted to:

$$\vec{k}_{2z} = \vec{k}_2 \cos \theta_t = \vec{k}_2 \sqrt{1 - \sin^2 \theta_t} = i\vec{k}_2 \sqrt{1 - \frac{\sin^2 \theta}{n^2}}.$$  \hspace{1cm} (2.22)

Defining $\theta$ as the critical angle of TIR, we have $\sin \theta = n$ and $\cos \theta = 0$. For angles that satisfy $\sin \theta > n$, TIR will occur. Therefore, $\cos \theta_t$ becomes pure imaginary and an “$i$” appears in Eq. (2.22), which indicates the light attenuates in the z direction.

Defining $\alpha = \vec{k}_2 \sqrt{\frac{\sin^2 \theta}{n^2} - 1}$, the transmitted wave may be expressed as:

$$\vec{E}_2 = E_{ot} \exp(-\alpha z) \times \exp[i(\vec{k}_{2x} \vec{x} - \omega t)].$$  \hspace{1cm} (2.23)

The first factor, $E_{ot} \exp(-\alpha z)$, describes an exponential decrease in the amplitude of the wave, see Fig. 2.3 as it enters the less dense medium along the x direction. The other exponential factors include “$i$”, making them harmonic functions with unit amplitude. This is why it is defined as an “evanescent wave”. When the amplitude is decreased by a factor of $1/e$, the wave penetrates into the rare medium by an amount of

$$z_0 = \frac{1}{\alpha} = \lambda \left( \frac{\sin^2 \theta}{n^2} - 1 \right)$$  \hspace{1cm} (2.24)
where $z_0$ is defined as the penetration depth which depends on the refractive index of the material. The exponential dependence of the field $E_z$ is shown in Fig. 2.3 [13].

![Diagram of exponential dependence of light ray in E_z direction](image)

**Figure 2.3** The exponential dependence of the light ray in the $E_z$ direction.

### 2.3.3 Attenuated Total Reflection (ATR)

Now, consider that the medium ($n_2$) has a limited thickness $d$, and $d < z_0$. If it is a metallic material, the energy of the ray will be absorbed by the medium. As a result, the reflectance $R$ is less than 1. This phenomenon is called “attenuated total reflection” [14].
Another situation of $R < 1$ is when the medium is transparent and part of the reflected ray is scattered by the interface causing the light to lose energy. This phenomenon is called “frustrated total reflection”, or FTR.

The loss of energy of the incident light in ATR is due to the excitement of the SPs in the interface of media 1 and 2.

2.4 Polarization of Waves

Classifying a beam of light as s- or p- polarized (TE or TM mode wave) is relative to the plane of the incidence ray and the interface that the ray will shine on. The polarization state of a ray is not just a character of the beam itself [15].

The electric field of the light is described by a vector $E$ that has components $(E_x, E_y, E_z)$ which are all complex-valued. The ray propagation vector $k$ has components $(l, m, n)$ where $l$, $m$, and $n$ are the direction cosines of the ray in the $x$, $y$, and $z$ directions. The electric field vector $E$ must be orthogonal to the propagation vector $k$ so that: $k \cdot E = 0$; therefore, $Ex \cdot l + Ey \cdot m + Ez \cdot n = 0$. The $x$, $y$, and $z$ axes are arbitrary chosen. For example, we can choose $z$ to go from left to right across the paper, $y$ from bottom to top, and $x$ into the paper. Or, we might choose $z$ to point out of the paper, $y$ to go left to right, and $x$ to go bottom to top, as long as it is consistent everywhere in the definition of the coordinate axes.

However, when a ray intercepts the surface of an optical component, we define a plane called the plane of incidence, which is not arbitrary. The plane of incidence
contains both the k vector and the surface normal vector n at the intercept point. The s component of the field is the projection of E that lies along the axis orthogonal to the plane of incidence, while the p projection lies within the plane of incidence. The electric field E is then divided into $E_T$ and $E_P$ components, both of which are complex valued.

In summary, s and p are defined relative to the plane of incidence of the ray on the surface, and are not characteristics of the beam itself. Therefore, since the SPs are p-polarized wave in dielectric/metal interface [explained in the next section], a necessary condition of SPR is that the incident ray should be p-polarized.

2.5 The Dielectric Function and Dispersion Function of the Surface Plasmons

2.5.1 The Dielectric Function of the Surface Plasmons

Assuming we have a bulky, metallic material, we can consider the free electrons as a gas in the metal according to the Drude Theory of metals [16], which is constructed by applying the highly successful Kinetic Theory of gases to a metal. The gas of free electrons can be treated as an ideal gas whose number density can be described as a Maxwell distribution. If the number density of the free electrons gas is $\rho$ at a certain time $t$, and the distance that the electron travels in the x direction is $\bar{x}_x(t)$, which is a function of time [4]. Then the displaced electron’s contribution to the macroscopic polarization is:

$$\bar{P} = \rho e \bar{x}_x(t).$$

(2.25)
Therefore, the electric field caused by the polarization is $\vec{E}_0 = -4\pi \rho e \vec{x}(t)$, and the electric force is $e \vec{E}_0 = -4\pi \rho e^2 \vec{x}(t)$.

Then the equation of motion for an electron inside of the plasma subjected to an external electric field $E$ is [4, 16]:

$$m \ddot{x} + m \gamma \dot{x} = -eE$$  \hspace{1cm} (2.26)

where, $\gamma$ is the characteristic collision frequency defined as $\gamma = 1/\tau$. $\tau$ is known as the relaxation time of the free electron gas. ($\tau \sim 10^{-14}$ s, and $\gamma \sim 100$ THz). If we neglect the collision decay term in Eq.(2.26) and use $e\vec{E}_0 = -4\pi \rho e^2 \vec{x}(t)$, we have

$$m \ddot{x} = -4\pi \rho e^2 \vec{x}(t) = -\omega_p^2 \vec{x}(t).$$

Solving it and incorporating with $\vec{P} = \frac{n e^2}{m(\omega^2 + i\gamma \omega)}E(t)$ and $D = \varepsilon_0 \varepsilon E + P$, then the dielectric function of the free electron gas is:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega}$$ \hspace{1cm} (2.27)

where $\omega_p = \sqrt{\frac{4\pi \rho e^2}{m}}$ is the volume plasma frequency of the free electron gas in an unattenuated medium [4, 10, 16].

2.5.2 The Dispersion Function of the Surface Plasmons

The surface of the metallic material will retard the motion of free electrons in the normal direction ($z$ direction), which changes the number density of electrons in the $z$
direction. Therefore, the electron charge on a metal boundary will perform coherent fluctuations that are so called Surface Plasma Oscillations [17]. The oscillation of the surface plasma generates an electromagnetic wave propagating along the metal surface and decaying in the z direction. The fluctuation wave will disappear as |z| becomes infinite and will reach its maximum at z=0 as shown in Fig. 2.4. This is why SPR is highly sensitive to the surface properties of a material changing.

![Diagram of SPs wave propagating on a surface along x direction.](image)

**Figure 2.4** The schematic of SPs wave propagating on a surface along x direction. [18]

Defining the propagation direction of the SPs wave in the x direction, see Fig. 2.4, and assuming ε depends only on the normal direction (z), the electrical field of the wave can be described as:

\[
\vec{E} = E_0^\pm \exp[i(\vec{k}_x x \pm \vec{k}_z z - \omega t)]
\]  

(2.28)

where, + is used for z \geq 0, - for z \leq 0; \vec{k}_x and \vec{k}_z are the components of the wave vector in the x and z direction. \(k_z\) should be an imaginary number because the field \(E_z\) decays exponentially in the z direction. The decay length equals the reciprocal value of \(k_z\)
i.e. \( z = 1/|k_x| \). The wave vector in the x direction, \( k_x \), equals \( 2\pi/\lambda_p \), where \( \lambda_p \) is the wavelength of the volume plasma oscillation and \( \omega_p = \frac{2\pi}{\lambda_p} \cdot \nu(k) \).

At the metal surface, the SPs wave propagates in the x direction. So there is no y direction dependence of the wave vector as shown in Fig. 2.5. As a result, the SP’s electromagnetic field in the material 1 and 2 can be described as [1, 2, 4]:

\[
z \geq 0 \quad \vec{H}_1 = (0, H_{y1}, 0) \exp[i(k_{x1}x - k_{z1}z - \omega t)] \quad (2.29)
\]
\[
\vec{E}_1 = (E_{x1}, 0, E_{z1}) \exp[i(k_{x1}x - k_{z1}z - \omega t)] \quad (2.30)
\]
\[
z \leq 0 \quad \vec{H}_2 = (0, H_{y2}, 0) \exp[i(k_{x2}x - k_{z2}z - \omega t)] \quad (2.31)
\]
\[
\vec{E}_2 = (E_{x2}, 0, E_{z2}) \exp[i(k_{x2}x - k_{z2}z - \omega t)] \quad . (2.32)
\]

**Figure 2.5** The schematic of the SPs on a dielectric/metal surface.

Eqs. (2.29- 2.32) satisfy the Maxwell equations:

\[
\nabla \times \vec{H}_i = \frac{\omega}{c} \frac{\partial \vec{E}_i}{\partial t} \quad (2.33)
\]
\[
\nabla \times \vec{E}_i = -\frac{1}{c} \frac{\partial \vec{H}_i}{\partial t} \quad (2.34)
\]
\[
\nabla \cdot \varepsilon_1 \vec{E} = 0 \quad (2.35)
\]
\[
\nabla \cdot \vec{H}_i = 0 \quad . (2.36)
\]
And the fields follow the continuity relations:

\[ E_{x1} = E_{x2} \]  \hspace{1cm} (2.37)

\[ H_{y1} = H_{y2} \]  \hspace{1cm} (2.38)

\[ \epsilon_1 E_{z1} = \epsilon_2 E_{z2}. \]  \hspace{1cm} (2.39)

From Eqs. (2.37-2.38), we have:

\[ k_{x1} = k_{x2} = k_x. \]

Substituting Eq. (2.29) and Eq. (2.32) into Eq. (2.33), gives:

\[ \frac{\partial H_i}{\partial z} = -\epsilon_1 \cdot \frac{\omega}{c} E_{x1} \] or

\[ k_{x1} H_{y1} = \epsilon_1 \cdot \frac{\omega}{c} E_{x1} \]  \hspace{1cm} (2.40)

\[ k_{x2} H_{y2} = -\epsilon_2 \cdot \frac{\omega}{c} E_{x2}. \]  \hspace{1cm} (2.41)

From Eq. (2.37), Eq. (2.38), Eq. (2.40) and Eq. (2.41), we can see that:

\[ H_{y1} - H_{y2} = 0 \]  \hspace{1cm} (2.42)

\[ \frac{k_{x1}}{\epsilon_1} H_{y1} + \frac{k_{x2}}{\epsilon_2} H_{y2} = 0. \]  \hspace{1cm} (2.43)

To obtain a solution of Eqs. (2.42-2.43), the determinant of Eqs. (2.42-2.43) has to be zero,

\[ D = \frac{k_{x1}}{\epsilon_1} + \frac{k_{x2}}{\epsilon_2} = 0. \]  \hspace{1cm} (2.44)

This is the dispersion relation of the SPs in the system as shown in Fig. 2.5. Using Eq. (2.33), Eq. (2.34) and Eq. (2.40-2.41), we have the following:

\[ k_x^2 + k_{x1}^2 = \epsilon_1 \left( \frac{\omega}{c} \right)^2. \]  \hspace{1cm} (2.45)

Substituting Eq. (2.44) into Eq. (2.45), gives:

\[ k_x = \frac{\omega}{c} \left( \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^{1/2} \]  \hspace{1cm} (2.46)
assuming that \( \omega \) and \( \epsilon_2 \) are real numbers, and \( \epsilon_1 = \epsilon_1' + i\epsilon_1'' \) is a complex number. Additionally for a metal, we usually have \( \epsilon_1'' < 0 \) and \( \epsilon_1'' < |\epsilon_1'| \), the wave vectors \( k_x \) and \( k_z \) should be complex numbers too. Then, we have \( k_x = k_x' + ik_x'' \), with:

\[
k_x' = \frac{\omega}{c} \left( \frac{\epsilon_1' \epsilon_2}{\epsilon_1' + \epsilon_2} \right)^{1/2}
\]

\[
k_x'' = \frac{\omega}{c} \left( \frac{\epsilon_1' \epsilon_2}{\epsilon_1' + \epsilon_2} \right)^{3/2} \frac{\epsilon_1''}{2(\epsilon_1')^2}
\]

For most metallic medium, \( \epsilon_1'' < 0 \) and \( |\epsilon_1'| > \epsilon_2 \). This indicates that \( k_x' \) is a real number and \( k_x' > k_{x0} = \frac{\omega}{c} \).

Finally, we have the wave vector \( k_x = k_x' + ik_x'' \) of SP. Now we can obtain the dispersion relation of SPs using \( k_x' \), which is the real part of the wave vector. For convenience, we can use \( k_x \) instead of \( k_x'' \) in the rest of this thesis. \( k_x'' \) is the imaginary part of the wave vector, which determines the internal absorption.

Therefore, from Eq. (2.48) we have \( k_x = \frac{\omega}{c} \left( \frac{\epsilon_1' \epsilon_2}{\epsilon_1' + \epsilon_2} \right)^{1/2} \), or \( \frac{k_x}{k_0} = \left( \frac{\epsilon_1' \epsilon_2}{\epsilon_1' + \epsilon_2} \right)^{1/2} \), where we define \( k_0 = \frac{\omega}{c} \) by imagining that a SPs wave is like a light wave propagating in a medium. This definition is for the convenience of the discussion about “the excitation of SPR” in the next section.
The dispersion relations are normalized using $\omega_p$ as shown in Fig. 2.6. The program codes of Fig. 2.6 are attached in Appendix 1. According to the Drude model, the dielectric function of the free electron gas is expressed as Eq. (2.27),

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i \gamma \omega},$$

where $\gamma$ is the collision frequency as defined in Eq. (2.26). If neglecting the collision and assuming there is no damping in the SPs wave, the dielectric function becomes

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2},$$

or

$$\omega_{sp} = \left(\frac{\omega_p}{1 + \varepsilon_2}\right)^{1/2}.$$  \hspace{1cm} (2.50)

Substituting Eq. (2.50) into Eq. (2.48), we can get the dispersion relation of SPs, i.e. the relation between $\frac{\omega}{\omega_p}$ and $\frac{k_x}{k_{x0}}$ using Mathematica 7.0 as shown in Fig. 2.6. If
choosing air as the dielectric medium, which means $\varepsilon_2 = 1$, it can be shown the

dispersion limit of the SPs wave to be $\frac{\omega_p^2}{\sqrt{2}}$.

2.6 The Excitation of Surface Plasmons (SPs)

2.6.1 Surface Plasmon Resonance (SPR)

The mathematical descriptions of the SPs wave and the evanescent wave of light were introduced in the above section. Now, if defining the wave vector of the evanescent wave along the interface ($\vec{k}_{2x}$) as equal to the wave vector of the SPs wave ($\vec{k}_{sprx}$), the energy of the evanescent wave will be absorbed by the SPs wave, and the intensity of the reflective ray will decrease dramatically. This is the so-called surface plasmon resonance (SPR) since the SPs on a metal surface were excited by the photons of the evanescent wave, just as a “resonance” of the SPs. Historically, the first instance of the excitation of SPs was using an electron beam [19, 20]. However compared to emitting a beam of electrons, a laser beam is easier to generate, therefore the laser beam is usually used to excite the SPs. The value of $\vec{k}_{2x}$ is related to both the incident ray and the dielectric function of the metal, and the value of $\vec{k}_{sprx}$ is $k'_{sx} = \frac{\omega}{c} \left( \frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2} \right)^{1/2}$. 
2.6.2 Excitation of SPs by Light

As shown in Fig. 2.6, the dispersion relation of SPs lies to the right side of the dispersion relation of the light in the metal (propagating along the interface between air and the gold film; therefore, \( \bar{k}_{2x} = \sin \theta \cdot k_0 < k_0 < \bar{k}_{\text{sprx}} \)). As a result, the photons cannot excite the SPs directly [1]. To excite the SPs using photons, the wave vector of the photon, \( \bar{k}_{2x} \) (point 1 as shown in Fig. 2.6), has to be increased by a certain amount, \( \Delta k \), to reach the value of the wave vector of the SP, \( \bar{k}_{\text{sprx}} \) (point 2 in Fig. 2.6).

Therefore, the wave-vectors matching of SPs and photons can be achieved in a three-layer system as shown in Fig. 2.7. If we take one of the dielectric mediums to be air with \( \varepsilon = 1 \) for simplicity and another layer is a prism with a higher dielectric constant of \( \varepsilon_0 = 1.5 \). When a beam shines on the interface of the prism (higher \( \varepsilon \)) and the metal, the wave vector of the evanescent light wave in the metal will be:

\[
k_{mx} = k_0 \sqrt{\varepsilon_0 \sin \theta},
\]

(2.51)

where \( \varepsilon_0 \) is the dielectric constant of the prism [1, 4]. Then, \( k_{mx} \) is large enough to excite the SPs at another interface between the metal and the air (lower \( \varepsilon \)).
Figure 2.7 Prism coupling to SPs using attenuated total internal reflection in the Otto and Kretschmann configurations. [4]

Fig. 2.7 shows two well-known constructions for exciting SPR using light, Otto and Kretschmann Configurations. In the Otto setup, the light is first shined through a glass block, typically a prism. A thin metal (for example gold) film is positioned close enough that the evanescent waves can interact with the plasma waves on the surface between the thin air layer. This interaction can excite the SPs. In the Kretschmann configuration on the other hand, the metal film is evaporated onto the glass block in an ultra-small thickness. The light is first incident through the glass block, an evanescent wave with higher wave vector will penetrate through the thin metal film and excite the SPs at the outer side of the film.

Using Eq. (2.51) and the dispersion relation Eq. (2.48), the dispersion curves of SPs on the interface of metal/air and of metal/prism can be plotted, see Fig. 2.8. Between the light line (c) in the air and the light line in the prism ($\frac{c}{\sqrt{\epsilon_0}}$), when the incident angle $\theta$ is bigger than the critical angle of the TIR, the excitation of the SPs by the light can be
achieved and can be identified as a dip in the reflective intensity curve. However, as discussed in Section 2.3.3, there are other factors that cause the decrease of the reflective energy, e.g. the inherent absorption inside the metal and the prism. Therefore, the detected value of the minimum might be smaller than the simulated values using a modeling system based on the Fresnel equations [4].

Figure 2.8 The dispersion curves of a three layer system. Only the wave vector of light below point 3 can excite the SPs. [1]
2.7 Calculation of the Reflection Intensity

The quantitative description of the minimum value of the reflective intensity can be determined by Fresnel’s equations and Snell’s equations, when SPR happens in a Kretschmann configuration (see Fig. 2.9). According to Fresnel’s equations, the reflection and transmission coefficient of the p-polarized light are [12]:

\[ r_{12} = \frac{n_2 \cos \theta_1 - \tilde{n}_1 \cos \theta_2}{n_2 \cos \theta_1 + \tilde{n}_1 \cos \theta_2} \]  \hspace{1cm} (2.52)

\[ t_{12} = \frac{2 \tilde{n}_1 \cos \theta_1}{n_2 \cos \theta_1 + \tilde{n}_1 \cos \theta_2} \]  \hspace{1cm} (2.53)

where, \( \tilde{n}_i \) indicates the refractive index of medium 1 or 2, and by definition \( \tilde{n}_i = \sqrt{\varepsilon_i} \). Since \( \varepsilon \) of metals is a complex number, \( \tilde{n}_i \) is also complex for metals, and the “~” indicates complex number. \( \theta_1 \) is the reflective angle and \( \theta_2 \) is the refractive angle.

![Diagram](image)

Figure 2.9 The multiple reflections between the two parallel surfaces. (3 layers)
Using Eqs. (2.52), (2.53) and Snell’s law, \( \tilde{n}_2 \cos \theta_1 = \sqrt{\tilde{n}_2^2 - \left( \frac{\sin \theta_1}{\tilde{n}_1} \right)^2} \), we have [21]:

\[
\begin{align*}
t_{12} &= 1 + r_{12} \\
r_{21} &= -r_{12} \\
t_{21} &= 1 - r_{12}.
\end{align*}
\]

(2.54)  
(2.55)  
(2.56)

Then, the recursive method is used to calculate reflection intensity [21, 22] of the multiple reflections between the two parallel surfaces as shown in Fig. 2.9.

First, we defined “Pr”, “1” and “2” to represent the prism, metal and air respectively, and “\( r_{pr12} \)” to represent the total reflective intensity of the p-polarized light from the three layers see Fig. 2.9. We have

\[
r_{pr12} = r_1 + r_2 + r_3 + r_4 + \cdots
\]

(2.57)

where,

\[
r_1 = r_{pr1}
\]

\[
r_2 = \left\{ t_{pr1} e^{(ik_z d_1)} \right\} \cdot \left\{ r_{12} e^{(ik_z d_1)} \right\} \cdot t_{1pr} = t_{pr1} r_{12} t_{1pr} e^{(i2k_z d_1)}
\]

\[
r_3 = \left\{ t_{pr1} e^{(ik_z d_1)} \right\} \cdot \left\{ r_{12} e^{(ik_z d_1)} \right\} \cdot \left\{ r_{21} e^{(ik_z d_1)} \right\} \cdot \left\{ r_{12} e^{(ik_z d_1)} \right\} \cdot t_{1pr} = t_{pr1} r_{12} r_{21} t_{1pr} e^{(i4k_z d_1)}
\]

\[
\vdots
\]

\[
\vdots
\]

\[
\vdots
\]
Therefore, Eq. (2.57) can be written as:

\[ r_{pr12} = r_{pr1} + t_{pr1} r_{12} t_{pe} e^{i(2k_z_1 d_1)} + t_{pr1} r_{12} r_{21} r_{12} t_{pe} e^{i(4k_z_1 d_1)} + \ldots . \]

Together with Eqs. (2.54-2.56), gives:

\[
\begin{align*}
    r_{pr12} &= r_{pr1} + (1 + r_{pr1}) r_{12} (1 - r_{pr1}) e^{i(2k_z_1 d_1)} + (1 + r_{pr1}) r_{12} (-r_{12}) r_{12} (1 + r_{pr1}) e^{i(4k_z_1 d_1)} + \\
    &= \{ r_{pr1} + r_{12} e^{i(2k_z_1 d_1)} \} - \{ r_{pr1} r_{12} e^{i(2k_z_1 d_1)} + r_{pr1} r_{12}^2 e^{i(4k_z_1 d_1)} \} + \\
    &\{ r_{pr1}^3 r_{12}^2 e^{i(2k_z_1 d_1)} + \ldots \} - \{ \ldots + \} + \\
    &= \{ r_{pr1} + r_{12} e^{i(2k_z_1 d_1)} \} \{ 1 - r_{pr1} r_{12} e^{i(2k_z_1 d_1)} + (r_{pr1} r_{12} e^{i(2k_z_1 d_1)})^2 - \ldots - \ldots \}.
\end{align*}
\]

Using geometric series, Eq. (2.57) finally becomes:

\[
r_{pr12} = \frac{r_{pr1} + r_{12} e^{i(2k_z_1 d_1)}}{1 + r_{pr1} r_{12} e^{i(2k_z_1 d_1)}}. \tag{2.58}
\]

The reflective intensity definition is:

\[
R = |r_{pr12}|^2 = \left| \frac{r_{pr1} + r_{12} e^{i(2k_z_1 d_1)}}{1 + r_{pr1} r_{12} e^{i(2k_z_1 d_1)}} \right|^2 \tag{2.59}
\]

where \( d_1 \) is the thickness of the metal film, and \( k_{z1} d_1 \) is the optical path difference, which equals:

\[
k_{z1} d_1 = k_1 d_1 \cos \theta_1 = (\vec{n}_1 \frac{\omega}{c}) d_1 \sqrt{1 - \left( \frac{\vec{n}_1 \sin \theta_{pr}}{\vec{n}_1} \right)^2} = \frac{\omega}{c} d_1 \sqrt{\varepsilon_1 - (\vec{n}_1 \sin \theta_{pr})^2} \tag{2.60}
\]

Eq. (2.59) yields the reflective intensity of SPR, where at a certain angle, the reflection intensity reaches its minimum value. The minimum value is related to the thickness, dielectric function of the metal film, and other properties of the system. And the reflection is also very sensitive to the changing of the surface properties. The
reflection intensity can be detected by a spectroscope, so that the property changes in the surface can be inferred.
CHAPTER 3

THE PRELIMINARY EXPERIMENTAL INVESTIGATIONS

3.1 Introduction

In this chapter, the methods of this research will be clarified, including the experimental steps, equipment, materials and methods used in this thesis. The basic usages of the SPR reflectometer and the preliminary simulation of the SPR curves in multiple layer system are also illustrated.

3.2 The Design of the Experiment

At the beginning of this project, a preliminary study was completed including calibration of the SPR sensor system, production of the gold thin film chips and measurements of the refractive index of air and water.

Later, the experimental data are compared to the published data to test the sensitivity and accuracy of the NanoSPR 6. After preliminary experiments, the sensor chip is connected to a DC power supply to detect the electromagnetic effect on the SPR phenomenon and determine the sensitivity of the SPR sensor system.

The difference between the SPR curves with an electric current going through the gold film and without such a current will be measured. We will try to explain the change of the SPR curve caused by the current effect.
3.3 Flowchart of this Thesis

- Lectures review
  - Simulation of SPR curves
  - Set up the SPR and calibrate
  - Preparation of the sensor chips

Preliminary Study
- Measure the refractive indices of air and water
  - Evaluate the sensitive of the SPR
- Feedback
  - Compare data to evaluate the SPR system
  - Optimize the system

Electromagnetic Effect
- Connect the sensor chips to a DC power supply and detect the electromagnetic effect of SPR
- DC power supply
- Measure the refractive indices of air/gold film interface when a current going through the gold film
- Analysis the data
  - Build temperature SPR model to evaluate the data
  - Determine if the external current will affect the SPR curve
  - If there is an obvious shift of the SPR curve, suggest an explanation
3.4 Equipment and Materials

The most crucial device in the thesis is the NanoSPR 6 SPR sensor system, which is a dual channel Kretschmann prism SPR reflectometer, as shown in Fig. 3.1.
The NanoSPR 6 has a thermo stabilizing system and it can stabilize the temperature of the sensor from room temperature (20 °C) to 60 °C. It can measure a refractive index in a range from 1.0 to 1.5 and the sensitivity is theoretically 0.00002, with time resolution of 2 sec for kinetics measurements and angular precision 5 angular sec. The light source is a Gallium Arsenide (GaAs) semiconductor laser whose wavelength is 650 nm.

Another important instrument is the thin film deposition device, a vacuum sputtering system (VSS). The VSS used in this research includes the sample chamber, vacuum system, cryo-system, control system and power supply (see Fig. 3.2). The vacuum pump system is the central part of the VSS, which consists of a mechanical pump providing a pressure below 0.1 Torr (1 Torr =133.322 Pa), and a cryo pump (10⁻⁶ Torr or smaller). Following the evacuation of the sample chamber to reach its base pressure, the
process gas (Argon) is admitted into the vessel. The pressure of this process gas is maintained at a user-selectable pressure around 10 mTorr using a set of upstream mass flow controllers to regulate the process gas. After an electric bias is applied to the gold target, electrons will be emitted by the target and strike on Argon gas molecules. These electrons will ionize the Argon gas in the vicinity of the target. Therefore, the positive Argon ions will be accelerated towards the gold target (cathode) by the applied negative bias. When the positive ions collide with the gold target, the kinetic energy transferred is sufficient to eject gold atoms from the target. The ejected (sputtered) gold atom will deposit on the surfaces of the pre-cleaned glass slide. The depositing rate can be collected by the Argon gas flow. The glass slide can be cut by a diamond knife for proper shapes.
Figure 3.2 (A) A picture of the vacuum sputtering system. (B) A sketch of the vacuum sputtering system diagram (Copyright by David Bernot).

The major pieces of equipment used in this project are tabulated in Table 3.1, and the major materials used in this thesis are tabulated in Table 3.2.

**Table 3.1 APPARATUS AND EQUIPMENT**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Model</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPR sensor system</td>
<td>NanoSPR6 Model 425</td>
<td>Nano SPR, US</td>
</tr>
<tr>
<td>Vacuum sputtering system</td>
<td></td>
<td>Lad Setups</td>
</tr>
<tr>
<td>DC power Supply</td>
<td>72-2005</td>
<td>TENMA, JP</td>
</tr>
<tr>
<td>Thermometer (type-k)</td>
<td>EW-91210-45</td>
<td>Cole-Parmer, US</td>
</tr>
<tr>
<td>Equipment</td>
<td>Model</td>
<td>Manufacturer</td>
</tr>
<tr>
<td>----------------------------</td>
<td>------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Thermocouple Probes</td>
<td>EW-08113-28</td>
<td>Cole-Parmer, US</td>
</tr>
<tr>
<td>Glass slides</td>
<td>Refractive index 1.5</td>
<td></td>
</tr>
<tr>
<td>Electric Balance</td>
<td>V-1200</td>
<td>Globaltec Corp, CA</td>
</tr>
<tr>
<td>Ultrasonic cleaner</td>
<td>Model 50T</td>
<td>VWR Scientific Products, US</td>
</tr>
</tbody>
</table>

Table 3.2 MATERIALS AND REAGENTS

<table>
<thead>
<tr>
<th>Materials</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>Our lab</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>Fisher Scientific, US</td>
</tr>
<tr>
<td>Magnesium Chloride</td>
<td>Fisher Scientific, US</td>
</tr>
<tr>
<td>High Purity Gold foils</td>
<td></td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>Fiber Instrument Sales, Inc. US</td>
</tr>
<tr>
<td>High Purity Copper foils</td>
<td></td>
</tr>
<tr>
<td>Lens Tissue</td>
<td>Newport Corporation, US</td>
</tr>
<tr>
<td>High Purity Silver Paint</td>
<td>Structure Probe, Inc. US</td>
</tr>
</tbody>
</table>
3.5 Experimental Procedures

3.5.1 Preliminary Study

Before the laboratory work, we used the theories provided in Chapter 2 and the parameters provided by the NanoSPR company to simulate the SPR curves using Mathematica and Matlab.

3.5.1.1 The Simulation of the SPR Curve

First, the fundamental theory of SPR phenomenon was studied to construct a theoretical curve as shown in Fig. 3.3 using Matlab. Eqs. (2.58-2.60) were used to calculate the reflection intensity of the SPR curve as discussed at the end of Chapter 2.

Eq. (2.60) is the excitation condition of the SPs and photons:

\[ k_{z1} = \frac{\omega}{c} \sqrt{\bar{\varepsilon}_1 - (\bar{n}_{pr} \sin \theta_{pr})^2} \]  \hspace{1cm} (2.60)

Additionally, the reflection intensity is

\[ R = |r_{pr12}|^2 = \left| \frac{r_{pr1} + r_{12} e^{i2k_{z1}d_1}}{1 + r_{pr1}r_{12} e^{i2k_{z1}d_1}} \right|^2 \]  \hspace{1cm} (2.59)

where, \( r_{ij} = (\varepsilon_j k_{zi} - \varepsilon_i k_{zj})/(\varepsilon_j k_{zi} + \varepsilon_i k_{zj}) \) is the Fresnel’s equations for p-polarized light; i and j represent different layers, and \( k_{zi} \) can be calculated from Eq. (2.60). [1, 12]
The parameters used in this model and program for the SPR plot are provided in Appendix 2.

Figure 3.3 The simulated SPR curve when a laser light source at 650.0 nm wavelength is used (room temperature).

Based on this model, we can learn how these key parameters of the SPR sensor systems such as the different materials (different dielectric function), different wavelength, and the thickness of different layers affect the appearance of the SPR curves. More detail can be found in Homola 2007 [2].

If the thickness of the glass slide is increasing to 10000 nm, the SPR curve will become as follows:
Figure 3.4 The simulated SPR curve with a 10000 nm thickness of the glass slide.

Fig. 3.4 shows a waveguide coupling SPR pattern, which means the system is no longer a multiple layer system. The waveguide coupling SPR systems, as shown in Fig. 3.5, usually have higher sensitivity, compact nature and better evanescent wave enhancement than multiple layer systems [23]. Therefore, the waveguide SPR system has become a hot research topic of the SPR sensing technology [2].
3.5.1.2 Calibration of NanoSPR 6

After the simulation, we started the laboratory work. First, we assembled the elements of the NanoSPR 6 following the user’s manual. Secondly, we installed the affiliated software and connected the SPR device to the computer via the COM port. Thirdly, we set the key parameters such as the refractive index of the prism, etc.

After simulation and calibration, the NanoSPR 6 device should represent the SPR curve in absolute values of the incidence light angle, as shown in Fig. 3.6. The minimum of the SPR curve indicated that the incident angle is equal to the critical angle of the TIR.
Figure 3.6 The SPR curve of the air/gold film interface with K8-50 prism.

Fig. 3.6 is an original SPR curve obtained by NanoSPR 6, the x axis represents the absolute value of the incident angles in degree and the y axis represents the refraction intensity in the Relative Units. The reflection minimum of the curve occurs at 44.417°.

3.5.1.3 Preparation of the Thin Gold Films

Depending on the application, the SPR sensor chips are designed diversely. Taking a bio-sensing chip as an example, usually gold or silver is used as the thin metal layer of the slide due to their high sensitivity. Gold is more durable than silver, because of its inert chemical property. However, since gold is not easy to deposited to the glass
slide directly, a thin layer (2~5 nm) of chrome should be deposited between the slide and the gold layer. At this moment, a blank gold sensor chip is produced.

However, according to the properties of the undetected reactants, such as proteins, carbohydrates, nucleic acids and receptors, different ligands need to be deposited on the blank gold slide. Usually, there are four different assay formats of the SPR sensors, which are direct assay, sandwich assay, inhibition assay and surface competitive assay, as shown in Fig. 3.7 [3, 24]. The four different formats are basically classified by the molecular weight (MW) of the analyte. Direct assays and sandwich assays are suitable for macromolecular analyte (MW > 5000 Daltons).

In direct assays, the detecting molecules are attached to the sensor surface directly known as a ligand layer. When the sample is injected, the analyte will bind with the ligand layer. Then the concentrations and the reaction rate can be detected and analyzed with the help of a standard curve.

The sandwich assays are an extension of the direct assays. After the analyte are attached to the ligand layer, a secondary interactant which can enhance the signal of the SPR sensors is injected to bind to the analyte and amplify the binding response.

Inhibition arrays and surface competitive assays are suitable for low MW analyte (MW can be as small as 200 Daltons or less). Low MW molecules give a lower response than macromolecules for an equivalent molar concentration; therefore, an alternative indirect approach is needed in such cases which are generally recognized as competition assays.

The principle of competition assays is based on two analytes competing for the same recognition site at the sensor surface. One analyte is a high MW detecting molecule
and other is the sample analyte which we want to detect. Two commonly used competition assays are inhibition arrays and surface competitive assays. Inhibition arrays (also called solution competition) apply the analyte's ability of inhibition of the high MW detecting molecules to binding on the surface.

In an inhibition assay, the analyte or its derivative is usually attached to the surface as the ligand layer and the detecting macromolecule binds specifically to the analyte or its derivative. First, a constant amount of detecting macromolecule is added to the samples, the mixture is incubated to reach a chemical equilibrium with an antibody for the target analyte. Subsequently, the mixture is injected over the sensor surface and the amount of free detecting molecule (rest detecting molecule) can be measured. Then, the concentration of the target analyte can be calculated which is inversely related to the sensor response.

In a surface competitive assay, a binding partner of the analyte is attached to the sensor surface as a ligand layer, and a constant amount of detecting macromolecule which is analogue to the analyte (typically analyte conjugated to a carrier protein) is added to the sample. Therefore, the target analyte and the detecting macromolecule will compete to bind to the ligand and the binding of the detecting macromolecule and the ligand can be measured by the SPR signal. As a result, the response of the SPR signal is inversely related to the amount analyte in the sample [24].
Designs of the thin film slides include the chosen metal materials, number of layers, the thickness etc. The steps to manufacture it are as follows:

1. Clean the glass slides:

   (A) Select high quality, uniform glass slides, put the chosen slides into an ultrasonic cleaner in soapy water, clean for 20 minutes.

   (B) Carefully remove these slides from the cleaner, and put them into the ultrasonic cleaner in ethanol, washing for 20 minutes.
(C) Use ethanol to wash and carefully use nitrogen gas to dry them

2. The thin film coating process: We use the sputtering machine mentioned above. Bosch, Model VSC, Serial 8312106, in Room 2, Weyandt Hall IUP.

The 30 steps that need to be followed in the coating process are attached in Appendix 3.

When preparing the lab-made gold film, the gold is deposited on a glass slide directly and the thickness is set on 50 nm. The purchased slide has a 5nm chromium layer deposited on the glass slide first and then a 45 nm gold layer. To detect the properties of the lab-made gold film, we compared its SPR curve to the curve of the purchased gold films (see Fig. 3.8).

Fig. 3.8 shows that the dips of the SPR curves are different. The difference might result from the chromium layer and the properties of the glass slides. Fig. 3.8 also shows that the maximum of the reflective intensity of the lab-made gold film is only two-thirds of the purchased gold film, which indicates that the lab-made gold film should be thicker than 50 nm. The baseline of the purchased gold film is almost parallel to the x axis, which means that the thickness of the gold film slide is even but the baseline of the lab-made gold film is not parallel to the x axis, which means the thickness of the gold film is not even. Due to the inaccuracy of the thickness monitor gauge and the uneven gold film surface, the lab-made gold film is not suitable for the following experiments, therefore we decide to use the purchased gold films for the sequencing experiments.
3.5.1.4 The Measurement of Refractive Indices of air and water

The refractive index of a substance is one fundamental property of this material, which is a measurement of the speed of light in this substance. According to Snell’s Law:

\[
\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1},
\]

where \( n_1 \) and \( \theta_1 \) are the refractive index and the incident angle from the material 1 (the known material) and \( n_2 \) and \( \theta_2 \) represent the refractive index and the incident angle from the material 2 (unknown material).
When the SPR is excited, the ATR condition must be reached. Therefore, \( \sin \theta_1 = 1, \theta_2 \) equals the incident angle \( \theta \), and \( \vec{k}_{\text{sprx}} = \vec{k}_{2x} \). \( \vec{k}_{\text{sprx}} \) is the wave vector of the SPs in the x direction, and \( \vec{k}_{2x} \) is the wave vector of the incident light in the metal at the x direction. (Details see Section 2.6.1.) Also,

\[
\vec{k}_{\text{sprx}} = k_x' = \frac{\omega}{c} \left( \frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2} \right)^{1/2},
\]

\[
\vec{k}_{2x} = k_{mx} = k_0 \sqrt{\varepsilon_0 \sin \theta} = \frac{\omega}{c} \sqrt{\varepsilon_0 \sin \theta};
\]

where, subscripts “0”, “1” and “2” represent the prism, the metal film and the unknown material respectively. Together with the definition that the square of the refractive index is the dielectric constant in a certain material, which is \( n^2 = \varepsilon \), we have the refractive index formula of the unknown material:

\[
n_2 = \sqrt{\left( \frac{(n_0 \sin \theta)^2 \varepsilon_1'}{(\varepsilon_1' - (n_0 \sin \theta)^2)} \right)}.
\]

Therefore, when the critical angle for the air/gold interface is detected by the NanoSPR 6, the refractive index can be calculated using Eq. (3.4).

For air at room temperature, as shown in Fig. 3.6 the minimum angle of the SPR curve is found to be 44.417\(^\circ\), and the refractive index of the prism [KB8-50 optical glass] for a gaseous sample is 1.51 [25]. We calculated the refractive index of air as \( n_2 = 1.0053 \) using the above formula, where the actual value is 1.000277 [26], resulting in an error percentage of 0.5\%.

For water at room temperature, the minimum value of the SPR curve is found to be 64.6611\(^\circ\) (see Fig. 3.8), and the refractive index of the prism [TF1-65 optical glass] for
a liquid sample is 1.60. Using Eq. (3.4), we calculated the refractive index of water which
is 1.3417, where the actual value of the refractive index is 1.333, resulting in an error
percentage of 0.6%. The program codes of the calculation of the refractive indices using
Mathematica are attached in Appendix 4.

![Reflection Intensity vs Incident Angle](image)

**Figure 3.9** The SPR curve of water at room temperature.

*The minimum value of the curve occurs at 64.661°*

In summary, from the data provided above, it is fair to say that the simulation
model fits well to the experimental data, and the NanoSPR 6 device is calibrated properly.
Therefore, we can start to detect the current effect on the SPR phenomenon in the next
chapter.
4.1 Introduction

The physical and chemical characteristics of materials are affected by electromagnetic fields [27]. On the molecular biological level, the only significant forces are electromagnetic, so that ultimately all living processes must be understood in terms of electromagnetic fields and forces. Therefore, the mechanisms of electrical activity in biological tissues and systems are worth studying carefully [27, 28]. Due to its high sensitivity and accuracy, the SPR sensing system may potentially serve as a bio-electromagnetic detecting device used in the in vitro bioelectric studies.

In this chapter, the SPR chip will be connected with a DC power supply to detect the electromagnetic effect on SPR phenomenon. The difference between the SPR curve with a current going through the gold film and the SPR curve without the current will be detected and analyzed.

As discussed before, though the resistance of the gold slide is small, the slide will still heat up when a current goes through it. Since the SPR curve will change with the elevation of temperature [29, 30], the temperature effects on the SPR phenomenon should be fully considered. The temperature effect on the SPR curve of air/gold interface is simulated in this chapter. This simulation will be compared to the experimental data and the electromagnetic effects on SPR will be summarized.
4.2 The Experimental Configuration

The equipment and materials used in this chapter were the same as previously tabulated in Chapter 3. The DC power supply connection is shown in Fig 4.1.
Figure 4.1 (A) A simple sketch of how the power source is connected. (B) A photograph of the NanoSPR 6 with a power supply. (C) A photograph of how the sensing chip is connected to a power supply.

As shown in Fig. 4.1, there are two thin copper foils attached to the ends of the gold layer using silver solder paste. The resistance of the gold film is around 0.03 Ω and 0.7 Ω of the loop. Therefore, the loop easily reaches the current limit of the power supply, 3 Amp, at a rather small voltage around 2.1 V.

For convenience of measurement, the current is fixed at 3 A in each measurement. That is because the mean collision time of electrons in a metal is around $10^{-7}$ second. When the power is turned off, the current will disappear in a very short time, which requires that we fix the voltage of the power supply allowing the experiment to be repeated quantitatively. Another thing worth mentioning is that the prism should be
cleaned by Isopropyl Alcohol and high quality lens tissue paper to avoid scratches on the prism, since the SPR is highly sensitive to the surface condition.

4.3 The Operation Steps of Electromagnetic Effect on the SPR Experiments

1) Turn on the laser for half an hour to make sure the intensity of the laser is stable. In case the laser heats up the slide, the laser beam needs to be covered by an opaque card.

2) After the laser is stable, take 10 measurements without current flowing, then switch on the power supply and take 10 measurements with the current on. Record the minimum value of the incident angle, the strength of the reflection intensity, and the temperature of the gold film at each measurement.

3) Repeat step 2 several times (at least 15 times). Save the experimental data for further analysis.

4.4 Results and Data Analysis

As discussed before, the current will heat up the gold film and the temperature of the gold film will increase, therefore the SPR curve will definitely shift with the changing temperature. So if the experimental data collected when the current is applied at a given temperature show different features to the experimental data collected when measurement is applied at the same temperature without current, the conclusion can be drawn that the electromagnetic current affects the SPR phenomenon. On the other hand, if the SPR curve plotted when the current going through the gold film shifts in the same direction of the SPR curve with the same temperature changes, then the quantitative differences of the electromagnetic current and the temperature effects must be calculated separately. Finally,
the differences of the two effects should be compared to each other and examine if there is an obvious deviation.

4.4.1 The Temperature Effects Simulations

First, the temperature effects on the SPR curve need to be simulated to detect how the SPR curve shifts with the temperature effect. Chiang et al [29] studied the temperature effects on the dielectric function of a metal film, but they did not take the temperature effects on the prism and the sensing medium into account. Sharma et al [30] studied theoretically the effects of temperature on the sensitivity of an optical fiber based SPR sensor, but they did not study the prism coupling configuration. In this present research, we will discuss comprehensively the temperature dependence behavior of the SPR curve of a prism coupling configuration including both the refractive indices of the prism and the dielectric function of the metal layer.

4.4.1.1 Temperature Effect on the Prism

NanoSPR 6 is an angular detecting SPR sensor system that operates at a fixed wavelength; it detects the reflective intensity corresponding to different incident angles. According to the Sellmeier Relation, the refractive index of the prism at a certain temperature is a constant, when the wavelength of the incident light is monochromatic.

The temperature dependence of the prism’s refractive index can be described by the function of the thermo-optic coefficient \( \frac{dn_p(\lambda)}{dT} \) [31]:

\[
2n_p(\lambda)\frac{dn_p(\lambda)}{dT} = G \times R + H \times R^2
\]  

(4.1)
where G and H are constant for a specific material, which can be detected from experimental data,

\[ R = \frac{\lambda^2}{\lambda^2 - \lambda_{ig}^2} \]

\( \lambda_{ig} \) is the wavelength correlated with the optical forbidden gap,

\( n_p = 1.51 \) is the refractive index of the prism at room temperature (300 K);

In our case, the prism is made of silica, the wavelength is 650 nm, and the parameters used in Eq. (4.1) are given in Table 4.1 [31],

**Table 4.1 THE PARAMETERS OF SELLMEIER RELATION OF GOLD FILM AT 650 NM WAVELENGTH**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>G (the 1\textsuperscript{st} order coefficient)</td>
<td>(-1.6548 \times 10^{-6} / K)</td>
</tr>
<tr>
<td>H (the 2\textsuperscript{nd} order coefficient)</td>
<td>(31.7794 \times 10^{-6} / K)</td>
</tr>
<tr>
<td>(\lambda_{ig}) (wavelength correlated with the optical forbidden gap)</td>
<td>109 nm</td>
</tr>
<tr>
<td>(\lambda) (the wavelength of the incident light)</td>
<td>650 nm</td>
</tr>
<tr>
<td>R</td>
<td>0.0289344</td>
</tr>
</tbody>
</table>

Substitution of the parameters from Table 4.1 in Eq. (4.1), yields

\[ n_T^2 = n_{RT}^2 - 2.12749 \times 10^{-8} (T - R.T.) \]

(4.2)

where, R.T. represents room temperature.

This relationship indicates that \( n_T \approx n_{RT} \) when the change of temperature is not too large. In our case, the prism is made from BK-9 optical glass that is not sensitive to temperature changes, so the temperature effect on the prism in our experiment is negligible.
4.4.1.2 Temperature Effect on the Gold Film

Now, let us examine the temperature effects on the gold film. According to the Drude model, the dielectric function of any metal can be appropriately represented by Eq. (2.27), \( \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \).

For clarity, here I rewrite it as [4]:

\[ \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\omega_c)} ; \quad (4.3) \]

and

\[ \omega_p = \sqrt{\frac{4\pi \rho e^2}{m}} ; \quad (4.4) \]

where, \( \omega_p \) is the plasma frequency defined in section 2.5.1.

Here \( \gamma \) is rewritten as \( \omega_c \), which is the collision frequency.

The number of free electrons in the metal is a constant and does not change with temperature [16], but the volume of the metal will expand when the gold film is heated. Therefore, the temperature dependent plasma frequency can be written as [13]:

\[ \omega_p(T) = \omega_p(T_0)[1 + \gamma_e(T - T_0)]^{-\frac{1}{2}} ; \quad (4.5) \]

where \( T_0 \) represents the room temperature, which equals 300 K;

\( T \) represents the real-time temperature, where current goes through the gold film;

\( \omega_p(T_0) \) is the plasma frequency at room temperature, which equals \( 1.3754 \times 10^{16} \text{rad/s} \); 

\( \omega_p(T) \) is the plasma frequency at temperature \( T \);
and \( \gamma_e \) is the expansion coefficient of the gold film, which is equal to \( 1.42 \times 10^{-5} \) per K.

As mentioned in Ch. 2, the collision frequency means the chance of the collision between the free electrons. According to the Drude model, two factors affect the temperature behavior of the collision frequency \( \omega_c \), which are the phonon-electron scattering \( (\omega_{cp}) \) and the electron-electron scattering \( (\omega_{ce}) \) [30, 32]. Adding them together gives,

\[
\omega_c = \omega_{ce} + \omega_{cp} .
\]

(4.6)

The phonon-electron scattering can be simulated by the Hubbard-Holstein model of phonon-electron scattering [33]. The Holstein model is developed using the Debye model. Comparing the Fermi energy and the Debye energy level of a certain material, the Holstein model has two forms [30]. In our case, since the Fermi energy \( (E_F) \) of gold is much greater than \( K_B T \), the Holstein model has the following form

\[
\omega_{cp}(T) = \omega_0 [\frac{2}{5} + 4 \frac{T}{T_D} \int_0^{T_D/T} \frac{x^4}{e^x - 1} dx]
\]

(4.7)

where \( \omega_0 \) is a constant related to the electric conductivity of that metal. Its value is \( 2.0477 \times 10^{13} \) rad/s for gold [34].

The electron-electron scattering can be simulated by the Lawrence model [34],

\[
\omega_{ce}(T) = \frac{1}{6} \pi^4 \frac{\Gamma \Delta}{h E_F} [(K_B T)^2 + \left( \frac{\hbar \omega}{4\pi^2} \right)^2]
\]

(4.8)

where, \( \Gamma \) and \( \Delta \) are constants that represent the scattering probability on the Fermi surface and the fractional Umklapp scattering respectively. For gold, \( \Gamma \) is 0.55 and \( \Delta \) is 0.77.
Using Eqs. (4.3-4.8) together, we can fully describe the temperature dependent dielectric function of gold films. Fig. 4.2 shows the temperature dependent SPR curves at lower (300 K) temperature and higher temperature (400 K). The blue and red curves represent the SPR curve at lower and higher temperature respectively. The simulation codes are attached in Appendix 5. For simplicity, a three layered system is used in the simulation, but in Appendices 3, four and five layered systems have also been discussed. The three layers in this simulation are prism/gold film/air. From the discussion above, the refractive index of the prism hardly changes as the temperature changes. In addition, the refractive index of air hardly changes with temperature either. Therefore, temperature effect on the gold film dielectric function determines the change in the SPR curve. Figure 4.2 shows the SPR modeling curves at temperature 300 K (blue) and 400 K (red).

![SPR Curve](image)

**Figure 4.2** The simulation curves at 300 K (blue line) and 400 K (red line).
Figure 4.2 shows at least three features:

(1) As the temperature increases, the intensity minimum of the SPR curve will shift to the right hand side;

(2) The reflection intensity over the angular range of the SPR decreases

(3) The full width at half minimum increases.

These three features show the similar patterns in the modeling of silver thin film by Chiang et al [29, 35] and Sharma et al [30].

4.4.1.3 The Experimental Data of Temperature Effects on SPR

The next step is to compare the experimental data to the simulation model in order to check if the shift of the SPR curve is reasonable. The data of the SPR at three different temperatures is shown in Fig. 4.3 A and Fig. 4.3 B.
Figure 4.3 (A) The experimental data collected at three different temperatures (30.048 °C, 40.238 °C and 58.474 °C). (B) Enlargement of Fig. 4.3 A near the dips of SPR curves.

From Fig. 4.3 A, we find that the difference of the SPR curves at 30.048 °C and 40.238 °C, which essentially overlap as shown, is much less than the difference between the curves at 40.238 °C and 58.474 °C. Fig. 4.3 B is the enlargement of these SPR curves near minima shown in Fig. 4.3 A. Fig. 4.3 B shows that the critical angles increase with the temperature and the reflection intensity at minimum of the SPR curves increase with temperature too. These two features are expected by the temperature modeling, but the increases of the full width at half minimum increases are not obvious. A possible explanation might be that the temperature difference in the experiment is much smaller than the temperature difference of the modeling assumption. Therefore, it is fair to say that the simulations of the temperature effect correspond to the experimental data and it is a proper model. Additionally, the correct difference is -1.66 degree of incident angles in
our case. The difference comes from the reflection of the light at the back surface of the glasses slide (see reference [36]).

Using the incident angles of the minima reflection intensity (the critical angles) and the temperatures of the corresponding SPR curves, we plotted the “critical angles vs. temperatures” in Fig. 4.4 using Origin 8.

![Graph showing critical angles vs. temperature](image)

**Figure 4.4** The critical angles at the minimum reflection intensity vs. the increasing temperatures.

From Fig. 4.4, it appears that the “critical angles” is an exponential function of the temperatures. Using Origin 8 [37], we find the best fit of the experimental data as shown in Fig. 4.5, which is:

\[
\theta = 44.38971 + 4.039 \times 10^{-5}\text{Exp}(-9.57871 \cdot t)
\]
where, $\theta$ represents the critical angle and $t$ represents the temperature. The standard error is around $10^{-4} \sim 10^{-5}$ and the detailed report is attached in Appendix 6. This equation provides a numerical description between the incident angle and the temperature.

Figure 4.5 The best fit of the critical angles at the minimum reflection intensity vs. the increasing temperatures.

4.4.2 The Experiment of the Electromagnetic Current Effects

After analyzing the temperature effect on the SPR curves, we apply an electromagnetic current on the gold film to examine changes on the SPR curves. The steps of the experiment are as follows:
1) First, turn on the laser for about 30 minutes until the laser is stable.

2) After the laser is stable, turn on the power switch, so the current will pass through the metal film. Take 10 measurements, and then record the temperature, the angle corresponding to the minimum reflection, and the SPR curves.

3) After the 10 measurements, turn off the power, and then take another 10 measurements, recording the temperatures and the critical angles.

4) Repeat Steps 2) and 3) at least 10 times. Group the 3 continuous measurements of switching on and off the current. The first and second measurements are with current going through the gold film, and the third measurement is the first measurement after the power is turned off. Then put them into Origin 8 as shown in Fig. 4.6 A and enlarge the minima in Fig. 4.6 B.

5) After inputting the data into excel and comparing to the data from previous articles to check if the data makes sense, calculate the difference between two continuous curves.

6) Input the data into Origin 8 to obtain a fitting function to describe the current effects.

Sometimes, the time taken to finish a full measurement is not stable. This may cause by the computer’s performance or mechanical issues of the instrument. Sometimes the rotation platform of the instrument may go quickly and sometimes it goes slowly, so the data needs to be examined carefully.
Figure 4.6 (A) SPR curves of three continuous measurements: the first two measurements with current and the third one without current. (B) Enlargement of the SPR curves dips of three continuous measurements.
Fig. 4.6 A. shows the SPR curves of a group of three continuous measurements. The vital parameters are listed in the following table.

### Table 4.2 THE VITAL PARAMETERS OF THE SPR CURVES

<table>
<thead>
<tr>
<th>Number of measurement</th>
<th>Minimum angle(°)</th>
<th>Temperature(°C )</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>44.333</td>
<td>70.090</td>
<td>Yes</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>44.333</td>
<td>73.043</td>
<td>Yes</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>44.319</td>
<td>71.718</td>
<td>No</td>
</tr>
</tbody>
</table>

Fig. 4.6 B magnifies the minima of the SPR curves in Fig. 4.6 A. When the power is turned off, the current on the slide disappears instantly. The SPR measurement 3 shifts in the positive x direction. Curve 1 and 2 essentially overlap with each other as shown in Fig. 4.6, and a possible reason is that the temperature difference between the two SPR curves is rather small. Therefore, the temperature effect between these two continuous measurements is insignificant, which is because the time between the two continuous measurements is small (2 seconds).

Then, calculate the differences between each 2 continuous measurements and plot the difference with the incident angle as shown in the Fig. 4.7. The red curve in Fig. 4.7 is the difference between the first two measurements (curve 2 minus curve 1); therefore, it represents \( \Delta R(\theta, T) \). The blue curve is the difference between the second and the third measurement (curve 2 minus curve 3), which represents \( \Delta R(\theta, T, I) \), where \( \theta \) represents the incident angle, \( T \) represents the temperature, and \( I \) represents the current on the gold thin film.
Figure 4.7 Differences between two continuous measurements vs. incident angle respectively.

Fig. 4.7 shows that the red curve has negligible variation of the reflective intensity, which means that the temperature effect on the two continuous measurements is essentially negligible. However, the difference in a small range around the critical angle is a little larger, because the SPR phenomenon is more sensitive around the critical angle.

On the other hand, the blue curve that represents the difference of SPR curves between the cases “with current” and “without current” is rather noticeable around the dip of the SPR curve and the curve decreases by 20 more refractive intensity units compared to the noise line. Therefore, we can draw a conclusion that, the current effects are much stronger than the temperature effects.

Using Origin 8.0 software, we can find out the best fit of the blue curve:

First, use the “fit multiple peaks” command, and then measure the vital parameters of the 2 peaks, and use the “nonlinear fit” command to obtain the best fit.
curve that represents the blue curve as shown in Fig. 4.8. The report of the curve fitting is attached in Appendix 5.

Figure 4.8 The best fit of the reflection intensity difference between measurement 2 and measurement 3.

The fitting function of the blue curve is the summation of two Lorentzian functions:

\[ y = y_0 + \sum_i^2 \left( \frac{2Al}{\pi} \frac{W_i}{4(x-x_{ci})^2 + W_i^2} \right) \]  

(4.9)

where, \( y \) represents the reflection intensity difference, and \( x \) represents the incident angle.

The vital parameters for this Lorentzian function are tabulated in Table 4.3.
Table 4.3 THE PARAMETERS OF THE FUNCTION OF THE BLUE CURVE IN FIG. 4.7

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_0$</td>
<td>19.28692171</td>
<td>0.638936417</td>
</tr>
<tr>
<td>$x_{c1}$</td>
<td>44.24763551</td>
<td>0.070407709</td>
</tr>
<tr>
<td>$w_1$</td>
<td>0.737710775</td>
<td>0.07901786</td>
</tr>
<tr>
<td>$A_1$</td>
<td>228.1539045</td>
<td>191.8488296</td>
</tr>
<tr>
<td>$x_{c2}$</td>
<td>44.45135511</td>
<td>0.116930387</td>
</tr>
<tr>
<td>$w_2$</td>
<td>0.803332477</td>
<td>0.061882622</td>
</tr>
<tr>
<td>$A_2$</td>
<td>180.8991706</td>
<td>193.322209</td>
</tr>
</tbody>
</table>

With the parameters provided in Table 4.3, Eq. 4.9 gives the value of the current effects on the SPR curve. Therefore, we have $y = \Delta R(\theta, T, I)$ and $x = \theta$.

As a result, the SPR curves with and without current can be calculated by the empirical formula. Using this empirical formula we can find a theoretical explanation of the electromagnetic current effects on the SPR sensors in a future study.
CHAPTER 5

CONCLUSIONS AND DISCUSSIONS

5.1 Summary and Conclusions

The development of the SPR sensors and the detail of the SPR theories were reviewed in Chapters 1 and 2. Further, an economical and practical SPR sensing reflectometer, NanoSPR 6, was presented, including the preparation of the gold sensing films and the measurement of the refractive indices of the analytes.

In Chapter 3, simulations of the multiple layered system SPR curves and waveguide coupling SPR curves were developed. Using the simulations, we found that the refractive indices of air and water at room temperature to be 1.0053 and 1.3417 respectively. We also presented the equipment and materials used in this project and discussed four formats of SPR bio-sensor chips.

Chapter 4 discussed the current effect of the SPR curve. A integrated simulation of the temperature effects on a Kretschmann coupling configuration was modeled by Mathematica. Both the temperature effect of the layers and the prism system were considered in this model. With a temperature increase of 100 degree, the model showed that the value of the critical angle of the SPR curve should increase by ~0.08 degree; the minimum reflective intensity of the SPR will increase by ~ 3%, and the full width at half minimum increased by almost 1.5 degree. Furthermore, we showed that the current applied through the gold film also shifted the SPR curve to the right as shown in Fig. 4.6. The electromagnetic current altered the SPR curve by an amount of 4.0 times (at least) greater than the temperature alters it. According to the experimental data, an empirical
formula of the electromagnetic current effect was obtained using the Origin software. The Reduced Chi-Square is $1.022 \times 10^{-6}$ and the probability distribution of the formula is 0.9826, which shows that the empirical formula fitted the data very well.

5.2 Discussions

5.2.1 Improvement of the accuracy of the modeling

In the present thesis, two models about the SPR curves have been developed. However, to build a more accurate model, we not only need to apply the proper theoretical functions but also the reasonable parameters. Therefore, the sources of the parameters used in the simulations are very important and need to be double checked including the dielectric constants, the depth of each layer, the thermo-optic coefficient, refractive indices, etc.

Sometimes, even using the proper theoretical functions and reasonable parameters, the theoretical data still may not overlap the experimental data well due to the device’s features. There is a possibility that the standard parameters of each device are slightly different. Therefore, correction coefficients or correction differences should be determinated to improve the accuracy of the device.

5.3 Suggestion of Further Research Directions

As presented above, this thesis has successfully shown that the electromagnetic effect will alter the SPR curves and originally obtained an empirical formula to describe this effect. The next step for this research is to build a theoretical model of the electromagnetic effects. There are two physical concepts that can be used for reference. One is the classical Drude model, another is the quantum collection theory of plasma.
The proposed ideas are to add an extra-electromagnetic field to each model, however the temperature and the size effects of the metal thin film should also be taken into account. There may be an extra field term needed in the kinetic function, Eq. (2.26), to calculate the dielectric function of the gold film.

The basic use of the NanoSPR 6 is to measure the refractive indices. Based on sensing the change of the refractive indices, it can monitor the dynamic change of an analyte, such as the concentration and both chemical and biological interactions.
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APPENDIX

Appendix 1 Programs for the Dispersion Relations of Photons and SPs

The code for Fig. 2.6 the dispersion relations of photons (light wave) and SPs (electron wave) in Mathemtica7.0

```
The dispersion relationship
where \( x = kx / kx0 \)
\( y = w / wp \)

\[
x[y_] := \sqrt{\frac{y^2 (y^2 - 1)}{2y^2 - 1}}
\]

\[
xlist = Table[x[y], {y, 0, 1.5, 0.01}];
ylist = Table[y, {y, 0, 1.5, 0.01}];
y2list = Table[i, {i, 0, 1.5}];
x2list = Table[j, {j, 0, 1.5}];
plot1 = ListLinePlot[Transpose[{xlist, ylist}]];
plot2 = Plot[{x, 1, 0.71}, {x, 0, 1.7}, PlotStyle -> {Automatic, Dashed, Dashed}];
Show[plot1, plot2]
```
Appendix 2 Programs of The Multiple layer SPR Curves

The parameters of this model are tabulated as follows. These parameters are provided by the NanoSPR Company.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thickness (nm)</th>
<th>Dielectric constant (e1=n1^2) real part</th>
<th>Dielectric constant (e2=n2^2) image part</th>
</tr>
</thead>
<tbody>
<tr>
<td>prism</td>
<td>0</td>
<td>2.29</td>
<td></td>
</tr>
<tr>
<td>Immersion oil</td>
<td>100</td>
<td>1.61^2 = 2.5921</td>
<td></td>
</tr>
<tr>
<td>Glass slide</td>
<td>0</td>
<td>1.513^2=2.28917</td>
<td></td>
</tr>
<tr>
<td>Gold layer</td>
<td>50</td>
<td>-12.93749</td>
<td>1.0799i</td>
</tr>
<tr>
<td>Air</td>
<td>0</td>
<td>1.000277</td>
<td></td>
</tr>
</tbody>
</table>

% the reflection intensity of multiple layers

n0=1.51; % reflective index of the prism
e0=n0^2; % dielectric constant of the prism

n1=1.61; % the refractive index of the immersion oil
e1=n1^2; % dielectric function of the immersion oil

e2=-12.93749 + 1.0799i % { y -> 1.08, x -> -12.94 calculated by Mathematica}
n3=1.513; % the reflective constant of the slide
e3=n3^2;

n4=1.0; % the analyte's refractive index
e4=n4^2;

lamta=650.00; % wavelength of the laser

theta_degree=linspace(40,50,100); % the range of the angle
theta_deg=pi/180*theta_degree; % the angle in degree

for number=1:100;
    theta=theta_deg(number);
    kz0=2*pi/lamta*sqrt(e0-e0*sin(theta)^2);
    kz1=2*pi/lamta*sqrt(e1-e0*sin(theta)^2);
    kz2=2*pi/lamta*sqrt(e2-e0*sin(theta)^2);
    kz3=2*pi/lamta*sqrt(e3-e0*sin(theta)^2);
kz4=2*pi/lambda*sqrt(e4-e0*sin(theta)^2);

zeta0=e0/kz0;
zeta1=e1/kz1;
zeta2=e2/kz2;
zeta3=e3/kz3;
zeta4=e4/kz4;

r34=(zeta4-zeta3)/(zeta4+zeta3);
r23=(zeta3-zeta2)/(zeta3+zeta2);
r12=(zeta2-zeta1)/(zeta2+zeta1);
r01=(zeta1-zeta0)/(zeta1+zeta0);

d1=100; \% the depth of the oil
d2=50; \% thickness of the gold film
d3=0; \% thickness of the slide

r24=(r23+r34*exp(2*i*d3*kz3))/(1+r23*r34*exp(2*i*d3*kz3));
r14=(r12+r24*exp(2*i*d2*kz2))/(1+r12*r24*exp(2*i*d2*kz2));
r04=(r01+r14*exp(2*i*d1*kz1))/(1+r01*r14*exp(2*i*d1*kz1));

r=abs(r04)^2;

R(number)=r; \% total reflection intensity

end

plot(theta_degree,R,'r')
Appendix 3 The Steps of the Coating Procedure

The Coating Procedure

Get Ready

1. Note down on the logbook your coating task.
2. Check the Argon gas flow. Set up the pressure at 20 (psi).
3. Check the cooling water in the chiller system, including the water level, the pressure range and the temperature (60 F). Note the water should be the DI water, and you can leave the chiller system on.
4. If the sputtering machine is not on, switch off the cyro pump driver first. Then turn on the sputtering machine power switch on the wall.

Unload and Load the Sample

5. Make sure all vents are closed. Open the vent valve to vent the chamber.
6. Hold the two “Up/Down” switches up to lift the chamber cover.
7. Check the target source position using the special tool and rotate the stage right below the target. Put the samples under the source.
8. Hold the two “Up/Down” switches down to close the chamber cover. May need to clean and grease the area the cover will sit on.

Rough Pump

9. Make sure the HIVAC valve is closed.
10. First, switch on the Roughing Pump by pressing the green button behind the coating machine. Then using the keys on the operation panel to move the cursor to the Rough Valve and press the F2 key to open it.
11. Move the cursor to the Foreline Valve and press the F2 key to open it.
12. When the values of the Cham TC and Pump TC drop from 999 to around 50 mTorr, then you close the roughing valve and foreline valve.

Cyro Pump

13. Make sure the cyro pump drive is on by turning on two switches (compressor and cold head) manually.

14. Monitor the Cyro Pump temperature. It should drop from room temperature 298K to 11K within 2-3 hours if it starts from room temperature. The ION Gauge should read ~5.5x10^-6 Torr.

15. After the cyro pump reaches 11~12K, reopen the rough valve to rough pump the chamber again to get the 50 mTorr reading. Then switch off the rough pump.

16. Move the cursor to open HIVAC VALE (cryopump). The ion gauge will go back to 10^-4 Torr. About 5 minutes later, the ion gauge will drop down to 10^-6 Torr again.

RF Etching

17. Manually switch on the RF power.

Coating

18. Open the two switches that control Ar gas flow.

19. Highlight the last 3 items on the left side of the control panel (MKS Open, GRIFICE Close and ARGON FLOW ON).

20. The Ar gas should run into the chamber and the CHAM TC gauge should show 10~11 mTorr.
21. Manually turn on the power supply on the bottom right corner.

22. Select the right material corresponding to the source selected. Zero the thickness reading on the IFICON display window.

23. Move the cursor to select the right source (e.g. 1, 2 or 3).

24. Open the shutter corresponding to the source (e.g. 1, 2 and 3).

25. Move the cursor to select Power “enable” and Source Power “on”.

26. Look at the thickness monitor. When it reaches the value you want, close the shutter, and switch off the power.

27. Close everything, including all the valves and Ar gas flow.

28. After the coating, always close the valve of the Ar gas bottle. Then close the valves on the panel.

29. Unload/load the sample.

30. Complete your logbook before you leave.
Appendix 4 Program of the Calculation of the Refractive Indices

(* the calculation of the refractive index of the Air or water/gold interface in Mathematica 7.0 *)

\[ \sqrt{\frac{e_1 + (n_0 \ast b)^2}{e_1 - (n_0 \ast b)^2}} \]

\[
\text{Calculate for the refractive index of air at room temperature the min. of the angle is 44.417}
\]

\[
\text{The real part of the dielectric function is } e_1 = -12.94
\]

\[
e_1 = -12.94;
\]
\[
n_0 = 1.51;
\]
\[
a = 44.417;
\]
\[
b = \text{Sin}[a \ast \text{Pi} / 180];
\]

\[
\text{Out[215]= 1.00535}
\]

\[
\text{Error}
\]

\[
\text{ln[216]} = (1.00535 - 1.000277) / 1.000277
\]

\[
\text{Out[216]= 0.0050716}
\]

\[ \sqrt{\frac{e_1 + (n_0 \ast b)^2}{e_1 - (n_0 \ast b)^2}} \]

\[
\text{Calculate for the refractive index of water the min. of the angle is 64.6611}
\]

\[
\text{ln[230]} = n_0 = 1.60;
\]
\[
a = 64.6611;
\]
\[
b = \text{Sin}[a \ast \text{Pi} / 180];
\]

\[
\text{Out[233]= 1.34171}
\]

\[
\text{Error}
\]

\[
\text{ln[234]} = (1.34171 - 1.3330) / 1.333
\]

\[
\text{Out[234]= 0.00653413}
\]
Appendix 5 Simulation Codes of the Temperature Effects

(*The simulation of the temperature effects for (Fig. 4.2) Computer Code Using Mathematica7.0*)

\begin{verbatim}
(*temperature effect*)
(* wp[T_] := wp0*(1 + ye* (T - 300))^(1/2) (4.5)*)
Clear["Global`*"]
wp0 = 1.3754 * 10^16 (* rad/s *);
ye = 1.42 * 10^-5 (* per k *);
wp[T_] := wp0 * (1 + ye * (T - 273))^(1/2);
wp[300] (*for test*)
(*Wce*)
\[Gamma] = 0.55;
\[Delta] = 0.77;
Ef = 5.53;
Rb = 8.617343 * 10^-5; (*ev*)
h = 4.13566733 * 10^-15; (*ev*)
c = 2.99 * 10^8;
wavelength = 550.0 * 10^-9; (*wavelegth*)
\omega = 2 * Pi * c / wavelength;
Wce[T_] := 1 / 6 * Pi^4 * (\[Gamma] * \[Delta]) / (h * Ef) * ((Rb * T)^(1/2) - ((h * \omega) / (4 * Pi^2))^(1/2)); (*Equ, 4.8*)
(*Wcp*)
Wo = 2.0477 * 10^13; (*the constant related to the electric conductivity*)
\[Theta]gold = 170; (*Debye temperature of gold*)
Wcp[T_] := Wo * (2 / 5 + 4 (T / \[Theta]gold)^(5/3)) * \[Integral]((t)^(4 / (E^t - 1)), (t, 0, \[Theta]gold / \[CapitalDelta]));
(*Equ, 4.7*)
Wc[T_] := Wcp[T] + Wce[T]; (*4.6*)
Wc300 = Wce[300] + Wcp[300] (*test for room temperature*)
1.37514 * 10^16
6.45388 * 10^13

(*Dielectric Function*)
\[Epsilon](\omega) = 1 - \omega_p^2 / (\omega(\omega + i \omega_c))
\[Epsilon][T_] := 1 - \[Im]wp[T] / (\omega(\omega + i * Wc[T]));
\[Epsilon][300]
\[Epsilon][350]
\[Epsilon][400]
\[Epsilon][450]
-21.62557739570996` + 0.5052227135176403` \[Im]
\[Im][\[Epsilon][T]], {T, 300, 500}, PlotRange -> ((300, 500), \{-21.75, -21, 55\}), Frame -> True]
x = Plot[Re[\[Epsilon][T]], {T, 300, 500}, PlotRange -> ((300, 500), \{0.5, 0.7\}), Frame -> True]
Show[x, xx]
\end{verbatim}
n0 = 1.51; (* prism*)
e0 = n0^2;

e1 = ε[300]
n2 = 1.00027;
e2 = n2^2;
λ = 650 (*wavelength*)
d1 = 50;
θ = Range[42.5, 43, 0.01];
θdegree = Pi / 180 * θ;
Count[θ, Except[θ]];
kz0 = (2 * Pi / λ) * √[ε0 - e0 * Sin[θdegree]^2];
kz1 = (2 * Pi / λ) * √[ε1 - e0 * Sin[θdegree]^2];
kz2 = (2 * Pi / λ) * √[ε2 - e0 * Sin[θdegree]^2];
Length[θ];
(*zeta=ε(λ)*kiz*)
zeta0 = e0 / kz0;
zeta1 = e1 / kz1;
zeta2 = e2 / kz2;
(*refractive coefficient*)
r01 = (zeta1 - zeta0) / (zeta1 + zeta0);
r12 = (zeta2 - zeta1) / (zeta2 + zeta1);
(* r3[θ_]:=(zeta3[θ]-zeta2[θ])/(zeta3[θ]+zeta2[θ]); r4[θ_]:=(zeta4[θ]-zeta3[θ])/(zeta4[θ]+zeta3[θ]);*)
r012 = r01 + r12 * Exp[2 * I * d1 * kz1];
rr = (Abs[r012])^2;
(* ListLinePlot[rr,Frame→True,PlotRange→{(0,10000),(0,1)}]*)
rrr = Table[{θ[[i]], rr[[i]]}, {i, 1, Length[θ]}];
s = ListLinePlot[rr, Frame → True, PlotRange → {{42.5, 43}, {0, 1}}]
n0 = 1.51; (* prism *)
e0 = n0^2;

e1 = ε[500]
n2 = 1.00027;
e2 = n2^2;
λ = 650 (* wavelength *)
d1 = 50;
θ = Range[42.5, 43, 0.01];
θdegree = Pi / 180 * θ;
Count[θ, Except[θ]];

kz0 = (2 * Pi / λ) * √(e0 - e0 * Sin[θdegree]^2);
kz1 = (2 * Pi / λ) * √(e1 - e0 * Sin[θdegree]^2);
kz2 = (2 * Pi / λ) * √(e2 - e0 * Sin[θdegree]^2);

Length[θ]
(* zeta=ε(λ)*kz*)
zeta0 = e0 / kz0;
zeta1 = e1 / kz1;
zeta2 = e2 / kz2;

(* refractive coefficient *)
r01 = (zeta1 - zeta0) / (zeta1 + zeta0);
r12 = (zeta2 - zeta1) / (zeta2 + zeta1);

(* r34[θ]=: (zeta3[θ]-zeta2[θ])/(zeta3[θ]+zeta2[θ]);
r34[θ]=: (zeta4[θ]-zeta3[θ])/(zeta4[θ]+zeta3[θ]); *)

r01 + r12 * Exp[2 * I * d1 * kz1]

rr = (Abs[r012])^2;
(* ListLinePlot[rr, Frame->True, PlotRange->((0,10000),(0,1))] *)
rrr = Table[{θ[i], rr[[i]]}, {i, 1, Length[θ]}];
ss = ListLinePlot[rrr, Frame -> True, PlotRange -> {{42.5, 43}, {0, 1}}, PlotStyle -> Red]
Show[s, ss]
Appendix 6 Curving Fitting Report of the Curve in Fig. 4.5

**Nonlinear Curve Fit (ExpDec1) (2011-6-7 18:51:06)**

**Parameters**

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>y0</td>
<td>44.39099</td>
<td>4.48018E-4</td>
</tr>
<tr>
<td>A1</td>
<td>6.50563E-6</td>
<td>3.76754E-6</td>
</tr>
<tr>
<td>t1</td>
<td>-7.38685</td>
<td>0.52176</td>
</tr>
</tbody>
</table>

Iterations Performed = 94
Total Iterations in Session = 94
Fit converged - tolerance criterion satisfied.
Some input data points are missing.

**Statistics**

<table>
<thead>
<tr>
<th></th>
<th>angle(10as)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Points</td>
<td>188</td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>185</td>
</tr>
<tr>
<td>Reduced Chi-Sqr</td>
<td>1.02298E-6</td>
</tr>
<tr>
<td>Residual Sum of Squares</td>
<td>1.8925E-4</td>
</tr>
<tr>
<td>Adj. R-Square</td>
<td>0.96553</td>
</tr>
<tr>
<td>Fit Status</td>
<td>Succeeded(100)</td>
</tr>
</tbody>
</table>

Fit Status Code :
100 : Fit converged

<table>
<thead>
<tr>
<th></th>
<th>y0</th>
<th>A1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>Standard Error</td>
<td>Value</td>
</tr>
<tr>
<td>angle(10as)</td>
<td>44.39099</td>
<td>4.48018E-4</td>
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**ANOVA**

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<td>Regression</td>
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<td>370710.23502</td>
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<tr>
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</tr>
<tr>
<td>Corrected Total</td>
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Appendix 7 Curving Fitting Report of the Blue Curve in Fig. 4.7

The report of fitting function of the electromagnetic current effect shown as the blue curve in Fig. 4.7

### Multipeaks Fit (2011-6-13 05:27:27)

**Notes**
- X-Function: fitPeaks
- User Name: Shengming Zhang
- Time: 2011-6-13 05:27:27

**Input Data**

<table>
<thead>
<tr>
<th>Input X Data Source</th>
<th>Input Y Data Source</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>chann.1 [Book1]Sheet1angle(10as)</td>
<td>[Book1]Sheet1chann.1</td>
<td>[1:68]</td>
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</tbody>
</table>

**Parameters**

<table>
<thead>
<tr>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>y0</td>
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</tr>
<tr>
<td>xc1</td>
<td>44.24764</td>
</tr>
<tr>
<td>w1</td>
<td>0.73771</td>
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<tr>
<td>A1</td>
<td>228.1539</td>
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<tr>
<td>xc2</td>
<td>44.45136</td>
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<tr>
<td>w2</td>
<td>0.80333</td>
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<tr>
<td>A2</td>
<td>-180.89917</td>
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</tbody>
</table>

**Peaks**

<table>
<thead>
<tr>
<th>Area</th>
<th>Center</th>
<th>Width</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>228.1539</td>
<td>44.24764</td>
<td>0.73771</td>
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<tr>
<td>2</td>
<td>-180.89917</td>
<td>44.45136</td>
<td>0.80333</td>
</tr>
</tbody>
</table>

**Statistics**

- DF: 61
- COD (R^2): 0.974
- ReducedChiSq: 13.7712

<table>
<thead>
<tr>
<th>Standard Error</th>
<th>Value</th>
<th>Standard Error</th>
<th>Reduced Chi-Sqr</th>
<th>Adj. R-Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.76754E-6</td>
<td>-7.38686</td>
<td>0.52176</td>
<td>1.02298E-6</td>
<td>0.96553</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob&gt;F</th>
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</thead>
<tbody>
<tr>
<td>123570.07834</td>
<td>1.20795E11</td>
<td>0</td>
</tr>
<tr>
<td>1.02298E-6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>