

# Research on the thermo-characteristics of surface plasmon resonance spectrum

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Based on the configuration of surface plasmon resonance (SPR) sensor, the SPR sensor model is set up, and the thermo-properties of various parts in the model are discussed. The thermo-characteristics of SPR spectra in wavelength interrogation and angular interrogation are investigated. Results show that thermo-optic and dispersion effects in the model deteriorate the sensitivity of SPR sensor, especially the thermo-optic effects. Mathematical expression is established to describe the resonance wavelength or angle, which is dependent of temperature. It demonstrates that the thermo-property of sensing medium excites the fluctuation of resonance wavelength or angle more intensely than that of the substrate or metal film in 1–2 orders. Our theoretical research is consistent with the previous experimental results.

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Surface plasmon resonance (SPR) is a well known phenomenon of charge density oscillation, which exists at the boundary of metal-dielectric, and it can be excited by p-polarized light under specific condition. The SPR technique has great potential for detection and analysis of chemical and biochemical substances in many important areas, including medicine, environmental monitoring, biotechnology, drug, and food monitoring<sup>[1,2]</sup>. However, temperature has a pronounced impact on the performance of SPR sensor. Research on temperature characteristics of the SPR spectra in relation to attaining temperature compensation or regulation approaches in the SPR technique has gained increasing attention in recent years<sup>[3–5]</sup>.

Gentleman *et al.*<sup>[3]</sup> initially measured the drift in resonance wavelength of SPR sensor, which was used to detect KCl in solution; they suggested that the measurement results should be calibrated. However, they did not further investigate the relation between the resonance wavelength and temperature. In Ref. [4], measurement error caused by temperature has also been determined. Based on Drude mode, Chiang *et al.* had conducted primary research on the temperature property of the resonance angle in theory<sup>[6,7]</sup>. Recently, the sensitivity of SPR sensors that deteriorate with temperature has been investigated in Ref. [8]. However, they merely exploited temperature property of Au thin film-water configuration and did not set up any mathematical expression to describe the relation between resonance wavelength and temperature. As a result, it is not convenient to employ such a result in compensation.

In this letter, based on resonance principle, temperature-properties in various parts of the sensor have been discussed. Mathematical expression has also been established to describe the temperature-property of resonance wavelength or angular. Our theoretical research is consistent with previous experimental results and can be employed as theoretical guidance in temperature compensation or response regulation.

The SPR sensors have been developed into three types, namely, prism-coupled, integrated optical waveguide-coupled, and optical fiber-coupled sensors<sup>[9,10]</sup>. Based on discrepancy of analysis substances, the sensors can be classified as chemical and biochemical SPR sensors. For chemical SPR sensors, the sensing model can be expressed as a configuration of substrate-metal thin film-medium (Fig. 1). In biochemical sensors, a sensing-film for the binding affinity of bio-molecule is required, and its operating mechanism is shown as the model in Fig. 2.

Given that the thickness  $d_2$  of sensing-film is very weak, the resonance angle and full-width at half-maximum (FWHM) of the SPR spectrum both increase with the thickness  $d_2$  (Fig. 2). When thickness of the sensing-film is larger than a special value, the resonance angle and the FWHM are kept constant<sup>[11]</sup>, indicating that the wave vector of SPR is not influenced by the thickness.

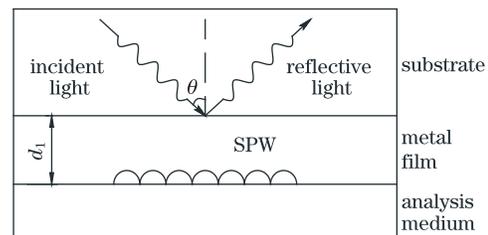


Fig. 1. Configuration of the chemical SPR sensor. SPW: surface plasmon wave.

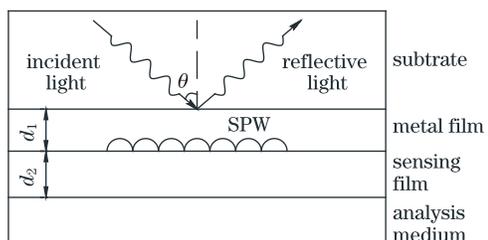


Fig. 2. Configuration of the biochemical SPR sensor.

Özdemir *et al.*<sup>[11]</sup> further declared that if the thickness of the sensing-film was larger than the surface plasmon wave (SPW) depth in the medium (about 110 nm), the wave momentum of the SPR became independent of the refractive index (RI) in ambience. In order to achieve the spectrum of SPR that is independent of sensor parameters, the thickness of sensing-film and analysis medium should be more than 110 nm. Under such a condition, chemical and biochemical sensing principles can be explained with the model in Fig. 1.

The wave vector of incident light in the substrate shown in the model in Fig. 1 can be expressed as

$$k_{\text{in}} = \frac{2\pi}{\lambda} \sqrt{\varepsilon_g} \sin \theta, \quad (1)$$

where  $\varepsilon_g$  is the permittivity of substrate, and  $\lambda$  and  $\theta$  are the wavelength and incident angle of incident light, respectively.

The wave vector of SPW in the inter-surface of substrate and metal film can be described as

$$k_{\text{SPW}} = k_0 \sqrt{\frac{\varepsilon_m \cdot \varepsilon_s}{\varepsilon_m + \varepsilon_s}}, \quad (2)$$

where  $\varepsilon_m$  and  $\varepsilon_s$  are the permittivities of metal film and analysis substances, respectively;  $k_0$  is a constant. The phenomena of SPR would occur in the inter-surface as equation  $k_{\text{in}} = k_{\text{SPW}}$  is satisfied. Based on Eqs. (1) and (2), we can obtain

$$\lambda_{\text{RES}} = 2\pi \sqrt{\varepsilon_g} \sin \theta \cdot \frac{1}{k_0} \sqrt{\frac{\varepsilon_m + \varepsilon_s}{\varepsilon_m \cdot \varepsilon_s}}. \quad (3)$$

In Eq. (3), given that permittivities  $\varepsilon_g$ ,  $\varepsilon_m$ , and  $\varepsilon_s$  are the functions of wavelength and temperature, respectively, they can be rewritten as

$$\varepsilon_g = \varepsilon_g(\lambda, T), \quad (4)$$

$$\varepsilon_m = \varepsilon_m(\lambda, T), \quad (5)$$

$$\varepsilon_s = \varepsilon_s(\lambda, T). \quad (6)$$

On wavelength interrogation, by derivating Eq. (3), the resonance wavelength can be expressed as

$$\begin{aligned} \frac{d\lambda_{\text{RES}}}{dT} = & \frac{2\pi^2}{\lambda_{\text{RES}} k_0^2} \sin^2 \theta \left[ \left( \frac{1}{\varepsilon_m} + \frac{1}{\varepsilon_s} \right) \frac{d\varepsilon_g}{dT} \right. \\ & \left. - \varepsilon_g \left( \frac{1}{\varepsilon_m^2} \cdot \frac{d\varepsilon_m}{dT} + \frac{1}{\varepsilon_s^2} \cdot \frac{d\varepsilon_s}{dT} \right) \right]. \quad (7) \end{aligned}$$

Given that the permittivity and wavelength are related with temperature, as shown in Eqs. (4)–(6), we can thus obtain

$$\frac{d\varepsilon_g}{dT} = \frac{\partial \varepsilon_g}{\partial \lambda} \cdot \frac{d\lambda}{dT} + \frac{\partial \varepsilon_g}{\partial T}, \quad (8)$$

$$\frac{d\varepsilon_m}{dT} = \frac{\partial \varepsilon_m}{\partial \lambda} \cdot \frac{d\lambda}{dT} + \frac{\partial \varepsilon_m}{\partial T}, \quad (9)$$

$$\frac{d\varepsilon_s}{dT} = \frac{\partial \varepsilon_s}{\partial \lambda} \cdot \frac{d\lambda}{dT} + \frac{\partial \varepsilon_s}{\partial T}. \quad (10)$$

We can calculate the fluctuation of resonance wavelength by combining the above with Eqs. (8)–(10), and by referring to Eq. (7). Given that the items  $\partial \varepsilon / \partial \lambda$  and  $\partial \varepsilon / \partial T$  in Eqs. (8)–(10) are involved with thermo-optic and dispersion effect, respectively, Eq. (7) shows that the fluctuation of resonance wavelength is determined by thermo-optic effect and dispersion effect in various parts of the sensor.

On angle interrogation, wavelength of incident light is kept constant. By derivating Eq. (3), the resonance angle can be expressed as

$$\begin{aligned} \frac{d\theta_{\text{RES}}}{dT} = & - \frac{2\pi^2}{k_0^2 \lambda^2 \sin^3 \theta \cos \theta} \left[ \left( \frac{1}{\varepsilon_m} + \frac{1}{\varepsilon_s} \right) \frac{d\varepsilon_g}{dT} \right. \\ & \left. - \varepsilon_g \left( \frac{1}{\varepsilon_m} \cdot \frac{d\varepsilon_m}{dT} + \frac{1}{\varepsilon_s} \cdot \frac{d\varepsilon_s}{dT} \right) \right], \quad (11) \end{aligned}$$

which shows that the resonance angle is a function of temperature. Given that permittivity is related to temperature, and independent of light wavelength, the temperature characteristics of the resonance angle is only influenced by the thermo-optic effect.

The ranges of various coefficients shown in the model in Fig. 1 are given in Table 1. Comparing the coefficient of metal thin-film with the substrate or sensing medium, we find that the former is larger than the latter in 1–2 orders.

In Eq. (8), the item  $\partial \varepsilon_g / \partial \lambda$  refers to light dispersion in the substrate, and we define the term  $\partial n_g / \partial \lambda$  as the coefficient of dispersion.

Upon comparison, we find that the values of the coefficients of light dispersion and thermo-optic effect in substrate are extremely less than those in metal film and sensing medium. Since  $d\lambda/dT$  is in  $10^{-2}$ – $10^{-1}$  nm/°C<sup>[8]</sup>, Eq. (8) can be further simplified as

$$\frac{d\varepsilon_g}{dT} \approx \frac{\partial \varepsilon_g}{\partial T}. \quad (12)$$

By discussing characteristics of the metal film and sensing medium, we obtain similar results as

$$\frac{d\varepsilon_m}{dT} \approx \frac{\partial \varepsilon_m}{\partial T}, \quad (13)$$

$$\frac{d\varepsilon_s}{dT} \approx \frac{\partial \varepsilon_s}{\partial T}. \quad (14)$$

Based on Eqs. (12)–(14), it can be seen that the thermo-optic property in the sensor plays a main role in influencing the characteristic of the SPR spectrum. Upon further investigation, we find that the influence of the substrate can be neglected and that the thermo-characteristics of resonance wavelength or angle are

**Table 1. Range of Thermo-optic Coefficient**

Thermo-optic Coefficient (/°C)	Substrate <sup>[8]</sup>	Metal Thin Film <sup>[8]</sup>	Sensing Medium <sup>[4]</sup>
$\partial \varepsilon / \partial T$	$10^{-5} - 10^{-6}$	$10^{-3}$	$-10^{-4}$

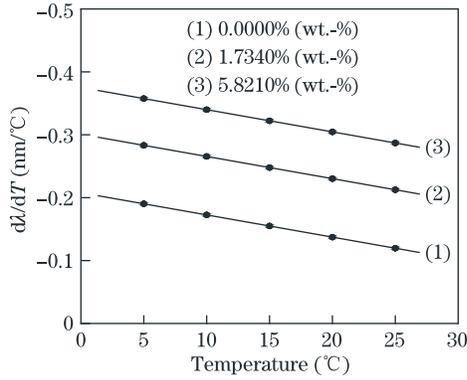


Fig. 3. Relation between the resonance wavelength and temperature.

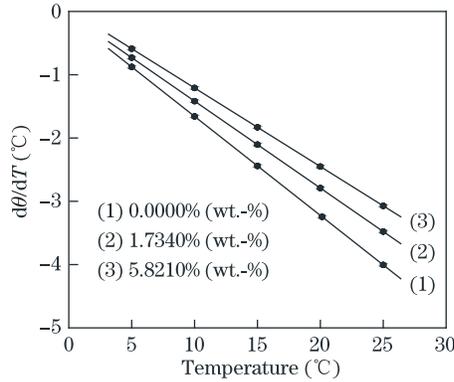


Fig. 4. Relation between the resonance angle and temperature.

mainly determined by thermo-optic effects in the metal film and medium. Equations (7) and (11) may be further simplified as

$$\frac{d\lambda_{\text{RES}}}{dT} = -\frac{2\pi^2\varepsilon_g}{\lambda_{\text{RES}}k_0^2} \sin^2\theta \left( \frac{1}{\varepsilon_m^2} \cdot \frac{d\varepsilon_m}{dT} + \frac{1}{\varepsilon_s^2} \cdot \frac{d\varepsilon_s}{dT} \right), \quad (15)$$

$$\frac{d\theta_{\text{RES}}}{dT} = \frac{2\pi^2\varepsilon_g}{k_0^2\lambda^2 \sin^3\theta \cos\theta} \left( \frac{1}{\varepsilon_m^2} \cdot \frac{d\varepsilon_m}{dT} + \frac{1}{\varepsilon_s^2} \cdot \frac{d\varepsilon_s}{dT} \right). \quad (16)$$

We can achieve temperature compensation to the response of SPR sensor since the RI of the sample medium is dependent of its ingredient and temperature; this is also based on its expression and Eqs. (15) and (16).

For the chemical SPR sensor, the RI of the sample is dependent of its ingredient and temperature. The RI of the analysis sample can be described as<sup>[4]</sup>

$$n(s, T) = n_0 + \sum_{i=1}^{+\infty} A_i s^i - (BT - CTs), \quad (17)$$

where  $n_0$  is the RI of distilled water at  $T = 0$  °C,  $A_i$  is a constant for certain  $i$ ,  $B = 5.84 \times 10^{-5}/\text{°C}$ , and  $C = 6.27 \times 10^{-5}/(\text{s} \cdot \text{°C})$ .

Given that the SPR sensor is utilized to detect salinity in sample, based on Eqs. (15) and (17), the thermo-property of resonance wavelength is shown in Fig. 3. As can be seen, the resonance wavelength is affected by temperature in the order of 0.1 nm/°C. Thus, our theoretical conclusion is consistent with previous experimental results<sup>[4]</sup>. Furthermore, Eq. (15) presents descriptions of the characteristics of resonance wavelength influenced with temperature. In angular interrogation, the property of the resonance angle is given in Fig. 4. As temperature changes, the ratio of the resonance angle is in the order of  $1 \times 10^{-4}/\text{°C}$ . Such a result is satisfied with experiment data given in a previous study in Ref. [8].

In conclusion, the characteristics of the SPR spectrum are affected by thermo-optic and light-dispersion effects in the configuration of the sensor, especially by thermo-optic effects. In angular interrogation, the thermo-optic effect exists solely in the sensor. It shows that the thermo-optic property of sensing medium stimulates the fluctuation of resonance wavelength more intensively than that of the substrate or metal film. Our research can be employed as theoretical guidance on temperature compensation or regulation for SPR sensors.

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