

# Effect of temperature on the incident angle-dependence of the sensitivity for surface plasmon resonance spectroscopy

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## Abstract

The recent work reporting the observation of the increase in sensitivity for surface plasmon resonance (SPR) spectroscopy at smaller incident angles, is further studied with variation in the temperature of the SPR sensor. Using a simple theoretical model established previously, it is found that in spite of the increase in damping for the resonance at higher temperatures, the recent finding of the increase of sensitivity with decrease in incident angles remains valid.

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## 1. Introduction

The optical sensor based on surface plasmon resonance (SPR) at a metal–dielectric interface is known to have very high sensitivity, with analyte easily detected down to the nanomolar level under ambient conditions [1]. Moreover, this sensitivity is a function of many factors: depending on the geometrical and dielectric properties of the sensor materials, properties of the probing light, and the different modes of monitoring adopted in the sensing procedure. Over the years, there have been many studies—both theoretical and experimental—on various issues concerning the sensitivity of the SPR optical sensor [2–5].

Among the different modes of monitoring in actual SPR sensing, the angular interrogation (angular SPR) and wavelength interrogation (spectral SPR) are the most commonly adopted in practice. The sensitivity of each of these two modes depends on various factors, and has been studied in detail recently in the literature, including our previous work on the temperature dependence of these sensitivities [6]. Very recently, it has been reported, both theoretically [4] and experimentally [5], that the sensitivity in spectral SPR is also very sensitive

to the value of the incident angle—with higher sensitivity at smaller angle of incidence in the Kretschmann ATR geometry [7]. This is significant since spectral SPR is preferred in remote sensing using optical fibres [8,9] as discussed in Ref. [5].

However, in actual remote sensing, the sensor probe can likely be exposed to environments under abnormal conditions such as high temperatures. Even in laboratory experiments, fluctuation in environment temperatures can also occur from time to time. It is thus the purpose of the present work to further study this recent observation [5] on the increase of SPR sensor sensitivity with decrease in incident angles—extending to conditions when the sensor chip is situated in an environment of elevated temperatures. We shall apply the model from our previous work [6] to conclude that the recent report [5] remains valid even at elevated sensor temperatures. This information should be useful for sensors designed to be used in such environments.

## 2. Modeling and results

Let us refer to the Kretschmann geometry [10] for the SPR excitation in which a thin ( $\sim 50$  nm) film of noble metal is coated on a glass prism, and the incident light from the prism under the ATR condition is directed to excite the SPR at the metal/analyte interface. The

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details of the model we use here for the temperature dependence of the sensitivity of such a SPR sensor are presented previously [6,11,12]. Briefly, we have attributed the major temperature dependence to arise from the variation of the metal (e.g. Ag) dielectric function ( $\varepsilon$ ) with the change of temperature ( $T$ ), and the modeling of which is achieved by adopting a free-electron model for  $\varepsilon$ . Although, in principle, the refractive indices of all the other components of the sensor (e.g. the glass prism, analyte,...) also vary with temperature, these changes ( $\Delta n$ ) are completely insignificant compared to that of the dielectric properties of metal in our modeling (e.g. for an increase of  $T$  from 300 to 400 K,  $\Delta n$  for water is  $< 1.2\%$  and that for silver is  $\sim 10$  times larger).

Thus, starting with the Drude model for the metal film, we have:

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

where  $\omega_c$  is the collision frequency and  $\omega_p$  the plasma frequency given by:

$$\omega_p = \sqrt{\frac{4\pi N e^2}{m^*}}, \quad (2)$$

with  $N$  and  $m^*$  the density and effective mass of the electrons, respectively. The collision frequency will have contributions from both phonon–electron and electron–electron scattering:

$$\omega_c = \omega_{cp} + \omega_{ce}. \quad (3)$$

As reported previously [11,12], for a resonance phenomenon like SPR, one must account for the temperature variation of  $\omega_p$  besides that of  $\omega_c$ . Thus, as before,  $\omega_p$  will depend on  $T$  via volumetric effects as follows [6,11,12]:

$$\omega_p = \omega_{p0} (1 + \gamma(T - T_0))^{-1/2}, \quad (4)$$

where  $\gamma$  is the expansion coefficient of the metal, and  $T_0$  is a reference temperature taken to be the room temperature.  $\omega_c$  can then be modelled using the phonon–electron scattering model of Holstein and the electron–electron scattering model of Lawrence, respectively. We hence obtain [11,12]:

$$\omega_{cp}(T) = \omega_0 \left( \frac{2}{5} + 4 \left( \frac{T}{\theta} \right)^5 \int_0^{\theta/T} \frac{z^4 dz}{e^z - 1} \right), \quad (5)$$

where  $\theta$  is the Debye temperature and  $\omega_0$  is a constant to be determined from the static limit of the above

expression together with the knowledge of the d.c. conductivity. In addition, we have:

$$\omega_{ce}(T) = \frac{1}{12} \pi^3 \frac{\Gamma \Delta}{\hbar E_F} [(k_B T)^2 + (\hbar \omega / 2\pi)^2], \quad (6)$$

where  $\Gamma$  and  $\Delta$  are defined previously in Refs. [11,12]. Thus, Eqs. (1)–(6) together with the Fresnel equations, provide a complete model for the simulation of the SPR sensor response with the variation of the temperature of the sensing environment. We have also accounted for the expansion of the film thickness ( $d$ ) using the Poisson number of the metal [13]. This model, though relatively oversimplified, has nevertheless been accessed with reasonable accuracy in various applications previously in Ref. [14].

We next apply the above model to a four-layer (analyte–metal–glass (prism)–air) system with reference to the Kretschmann geometry [6]. To make correlation with the recent report on the effect of the incident angle, we will focus on the ‘wavelength interrogation mode’ of operation by referring to the ‘spectral SPR’ sensing [5]. In this mode of operation, it has been shown that the sensitivity (defined as the variation of the SPR resonant wavelength with the change of the analyte refractive index  $n_a$ ) can be calculated as follows [3]:

$$S_\lambda = \frac{d\lambda}{dn_a} = \frac{\varepsilon_{mr}^2}{\frac{n_a^3}{2} \left| \frac{d\varepsilon_{mr}}{d\lambda} \right| + (\varepsilon_{mr} + n_a^2) \varepsilon_{mr} \frac{dn_p}{d\lambda} \frac{n_a}{n_p}}, \quad (7)$$

where  $\varepsilon_{mr}$  is the real part of the dielectric function of the metal which is negative, and the dispersion for the glass prism in the visible region is small and ( $dn_p/d\lambda < 0$ ) is of the order of  $10^{-4}$ . Eq. (7) is accurate as long as the metal film thickness is not too small ( $> 45$  nm, [3]). Note that the second term in the denominator is negative under the SPR condition. Since ( $d\varepsilon_{mr}/d\lambda$ ) can be calculated from Eq. (1), hence we can obtain  $S_\lambda$  as a function of temperature. Note that the data obtained in Fig. 5 of Ref. [5] can, in principle, be obtained via integration of Eq. (7) by converting the change in analyte concentration to that in the analyte refractive index.

To demonstrate numerically the temperature effects, we have considered a Ag film of thickness 50 nm at room temperature as our SP generator. Fig. 1 shows the result of the resonant wavelength vs. the incident angle at various temperatures which agrees qualitatively with that obtained in Fig. 3 of Ref. [5]. We also notice that the temperature change has relatively minor effects on these results. Note that we have here considered a wide range of temperatures (300–700 K) which may not be realistic for biosensor operations. However, it is possible for other applications of the SPR sensor to operate at

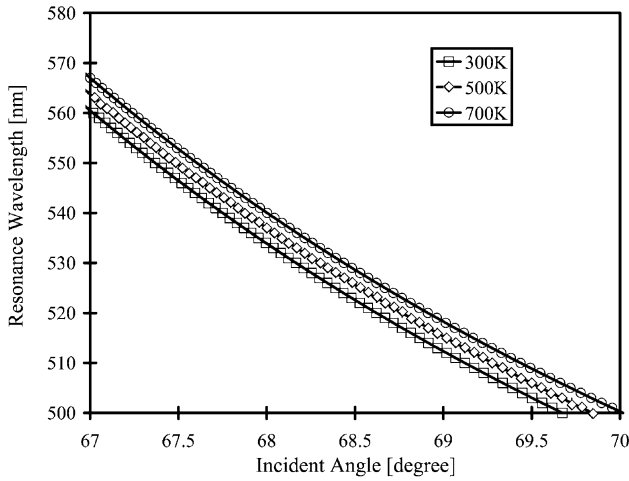


Fig. 1. SPR resonant wavelength as a function of angle of incidence at different temperatures for Ag film with  $n_a=1.333$  and  $n_p=1.540$ . Thickness of film at room temperature is fixed at 50 nm.

highly elevated temperatures, such as in the case of a gas/chemical sensor. Fig. 2 shows the change of the spectral SPR sensitivity with temperature at various values of incident angles. It is seen that by decreasing the incident angle from  $68^\circ$  to approximately  $62^\circ$ , the sensitivity can be enhanced by several order of magnitudes. Most dramatically, a small decrease in the angle from  $62.8$  to  $62.5^\circ$  can amount to almost an order of magnitude increase in sensitivity. It is also noted that this sharp increase in sensitivity prevails to highly elevated sensor temperatures, in spite of the fact that a small decrease in sensitivity occurs as temperature rises (most obviously seen for the case with the incident angle equal to  $62.5^\circ$ ). Fig. 3 shows the variation of the sensitivity with incident angles at two temperatures. It shows clearly that, although the sensitivities are lower at elevated sensor temperatures, the fact that higher sensitivities are achieved by decreasing the angle of incidence remains to be valid—as confirmed recently in Ref. [5] for the case of room temperature operation of the sensor. We have also computed all these results (Figs. 1–3) for the case of a gold film and have obtained very similar results as those for a silver film.

### 3. Discussion and conclusion

As shown in Fig. 1, it is well-known that there is a one–one correspondence between the resonant wavelength and the angle of incidence given by the following resonance condition for the excitation of surface plasmon (accurate as long as the loss is small in the metal and the film thickness is greater than  $\sim 45$  nm) [3]:

$$n_p \sin \theta = \sqrt{\frac{\epsilon_{mr}(\omega)n_a^2}{\epsilon_{mr}(\omega) + n_a^2}} \quad (8)$$

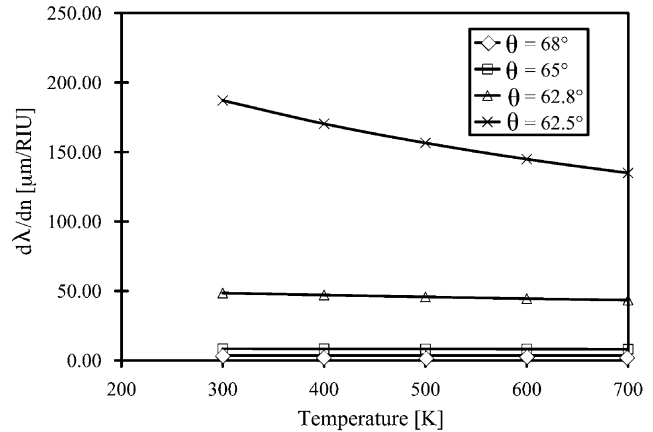


Fig. 2. Sensitivity as a function of sensor temperatures for different values of incident angles with  $n_a=1.333$  and  $n_p=1.540$ . Note that RIU stands for ‘refractive index unit’.

It is based on this condition that Eq. (7) was derived. Also from Eq. (8), one can show that smaller incident angle  $\theta$  will lead to longer resonant wavelength  $\lambda$ , which also depends on the analyte concentration through  $n_a$ . Since  $\epsilon_{mr}(\omega)$  varies with temperature, this dependence of  $\lambda$  on  $n_a$  also varies with temperatures. What we have demonstrated in the present work is that the very sensitive variation of  $\lambda$  with  $n_a$  at large values of  $\lambda$  prevails at high temperatures, in spite of the increase in damping of the surface plasmon at such temperatures. Although environments with highly elevated temperature is rarely encountered in some applications such as biosensors operating in the laboratory, temperature fluctuation does occur from time to time during the sensing process. Our modeling results imply that the recent observation of Akimoto et al. [5] should remain valid even when such temperature fluctuation is taking place

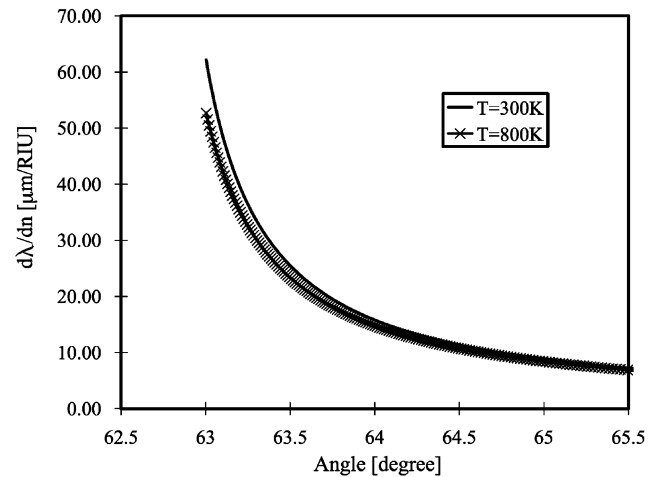


Fig. 3. Sensitivity as a function of incident angles at two different temperatures with  $n_a=1.333$  and  $n_p=1.540$ .

during the operation of the sensor. This thus guarantees the preferred choice of smaller incident angles in spectral SPR sensors, and should provide useful guidelines in the design of such sensors—especially in the application of these sensors to remote sensing using optical fibres [8].

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