15 February 2001

ELSEVIER

Optics Communications 188 (2001) 283–289

OPTICS
COMMUNICATIONS

www.elsevier.com/locate/optcom

A theoretical model for the temperature-dependent sensitivity of the optical sensor based on surface plasmon resonance

H.-P. Chiang [a], Y.-C. Wang [a], P.T. Leung [b,*], W.S. Tse [c]

[a] *Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, Taiwan 20224, ROC*
[b] *Department of Physics, Portland State University, P.O. Box 751, Portland, OR 97207-0751, USA*
[c] *Institute of Physics, Academia Sinica, Taipei, Taiwan 11529, ROC*

Received 26 October 2000; received in revised form 29 November 2000; accepted 30 November 2000

Abstract

It is well established that the optical sensor based on the surface plasmon resonance at a metal–dielectric interface can provide very high sensitivity for many applications. It is also known that, however, this sensitivity is affected by the variation of temperature of the sensing environment, leading possibly to lower sensitivity at elevated temperatures. Here we provide a detailed theoretical model which can predict such variation of sensitivity with temperature. From the numerical results, we observe that the so-called "angular interrogation" approach seems to have the preferred stability against temperature variations. We also postulate that sensitivity gain can likely be achieved by operating the optical sensor at much lower temperatures. © 2001 Published by Elsevier Science B.V.

Keywords: Surface plasmon resonance; Optical sensor sensitivity; Temperature effects

---

1. Introduction

Optical excitation of surface plasmon resonance (SPR) at a metal–dielectric interface has been well known since the observation of Wood's anomaly from metallic gratings [1], and the later systematic development of the attenuated total reflection (ATR) technique by Otto [2] and Kretschmann [3,4]. Upon resonant excitation in the ATR approach, the incident light is strongly coupled to the collective oscillation of the free electrons at the interface, resulting in a dip in the reflectance curve at this characteristic angle of incidence [5]. Since this resonance condition is highly sensitive to the ambient conditions, and the reflectance curve can be very steep for noble metals at visible/IR frequencies, this SPR phenomenon has been actively employed in the application to optical sensor design in the past 20 years [6]. These applications have included, for example, gas and chemical sensing [7], biosensing [7,8], and real-time monitoring of laser-ablation processes [9].

Since the SPR mechanism relies on the collective oscillation of the free electrons at the metal surfaces, the effect will depend on many physical factors such as the dielectric properties of the metal and the geometry of the interface. Among these, the temperature of the metal is known to affect this SPR mechanism significantly. In fact, it has been proposed to utilize this effect to achieve

---

[*] Corresponding author. Tel.: +1-503-725-3818; fax: +1-503-725-3888.
E-mail address: hopl@odin.pdx.edu (P.T. Leung).

PII: S0030-4018(00)01175-5

real-time temperature sensing [9,10]. This is easily understood since the rise in temperature will lead to significant phonon–electron scattering, among other effects, which will seriously damp the oscillation of the free-electron plasma.

Although this dependence on temperature change of the SPR excitation can provide a means for monitoring the interfacial temperatures, the decrease in sensitivity (due to temperature rise) is often an unwanted feature for some other applications (e.g. biosensing). Thus, it will be valuable if one can have a model to simulate (and hence to understand) how such sensitivities will be affected as a function of the temperature of the sensor. It is the purpose of the present communication to provide such a model, and to apply it to study the temperature dependence of the sensitivity under different modes of operation of the SPR optical sensor.

2. Theoretical model

Let us refer to the Kretschmann geometry as depicted in Fig. 1. We shall assume a silver film of thickness d coated on a glass prism with incident light of wavelength λ according to the ATR geometry. As is well known, the simplest way to model the reflectivity (R) of the ATR multilayer system is to use the Fresnel equations. In this approach, the temperature dependence of R will depend mainly on the change of d and the metal dielectric function (ε) with the change of temperature (T). The variation of the optical constants with temperature for the glass prism is completely negligible in comparison with that for the metal film. Previously, we have adopted a free-electron model for ε in our study of the temperature-dependent effects on various phenomena, including the optical properties of composite materials and the surface-enhanced Raman scattering [11–13]. The model has gained reasonable agreement with experiments in the literature [14–16]. Here we give a brief account of that model and apply it to our present study of the SPR sensitivity problem in the following.

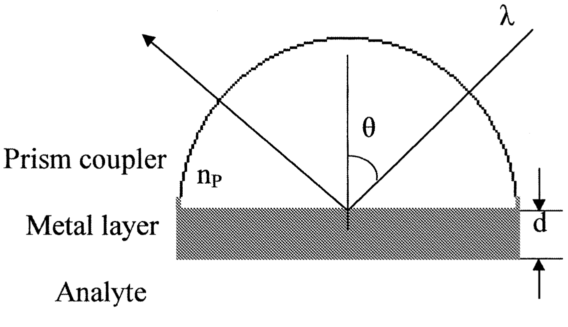

Fig. 1. Geometry of the ATR setup.

For simplicity, we start by adopting the Drude model

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

where ω_c is the collision frequency and ω_p the plasma frequency given by:

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

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:

$$\omega_c = \omega_{cp} + \omega_{ce}. \tag{3}$$

As reported previously [13], for a resonance phenomenon like SPR, one must account for the temperature (T) variation of ω_p besides that for ω_c. As before, ω_p will depend on T via volumetric effects as follows [12]:

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

where γ is the expansion coefficient of the metal, and T_0 is a reference temperature taken to be the room temperature. ω_c can then be modeled using the phonon–electron scattering model of Holstein [17,18] and the electron–electron scattering model of Lawrence [19], respectively. We thus obtain:

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

where θ is the Debye temperature and ω_0 is a constant to be determined from the static limit of the above expression together with the knowledge of the d.c. conductivity [11]. In addition, we have:

$$\omega_{\mathrm{ce}}(T) = \frac{1}{12}\pi^3 \frac{\Gamma\Delta}{\hbar E_{\mathrm{F}}}\left[(k_{\mathrm{B}}T)^2 + (\hbar\omega/2\pi)^2\right], \qquad (6)$$

where Γ and Δ are defined previously in Ref. [19]. 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 to note that, in the previous literature [10], a similar temperature-dependent Drude model has been mentioned in the modeling of transient thermoreflectance from silver surfaces measured using SPR in an ATR geometry. However, no details were given as to how the temperature dependence was modeled in this previous work [10].

Here our main interest is to apply the above model to study the variation of the sensitivity of the SPR sensor with temperature. Since there exist various definitions for the sensitivity (S) in the literature [20,21], depending mainly on what parameter is monitored in the sensing process, we shall here focus on three commonly practiced measurements in the sensor operation using the ATR geometry: (i) measurement in the change of the resonant angle (“angular interrogation” [21]); (ii) measurement in the change of reflectance at fixed incident angle [20]; and (iii) measurement in the change of resonant wavelength at fixed incident angle (“wavelength interrogation” [21]).

3. Numerical results and discussion

Fig. 2 shows how the SPR reflectance (R) curve varies with temperature at fixed incident wavelength ($\lambda = 820$ nm) and Ag film thickness ($d = 60$ nm at room temperature). We have accounted for the expansion of d using the Poisson number of Ag as done previously [10]. Two features are clear from this graph: (i) the resonance angle (θ_{m}) shifts to larger values, and (ii) the R curve broadens, implying the absolute value of the slope at any fixed θ becomes smaller as the temperature (T) increases. As far as the value of the minimum reflectance (R_{m}) at θ_{m} is concerned, it depends on the values of λ and d used. As an example, at $\lambda = 532$ nm, we have observed that R_{m} can become smaller (with $d = 50$ nm) or greater ($d = 60$ nm) as T increases. Next we perform our analysis of the temperature dependence of the various sensitivities according to different monitoring schemes with respect to the ATR geometry:

3.1. Angular interrogation

According to this scheme, λ is fixed and the shift of θ_{m} is monitored as change in the refractive index

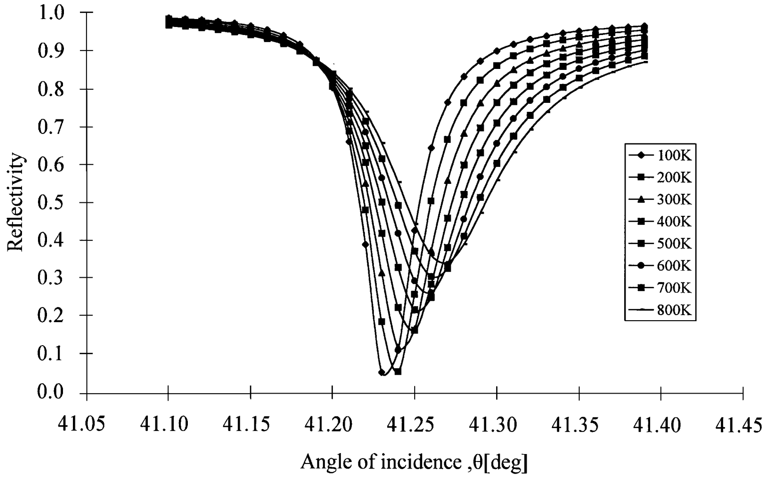

Fig. 2. SPR reflectance curve as a function of the temperature of the Ag film. Thickness of film at room temperature is fixed at 60 nm and incident wavelength at 820 nm.

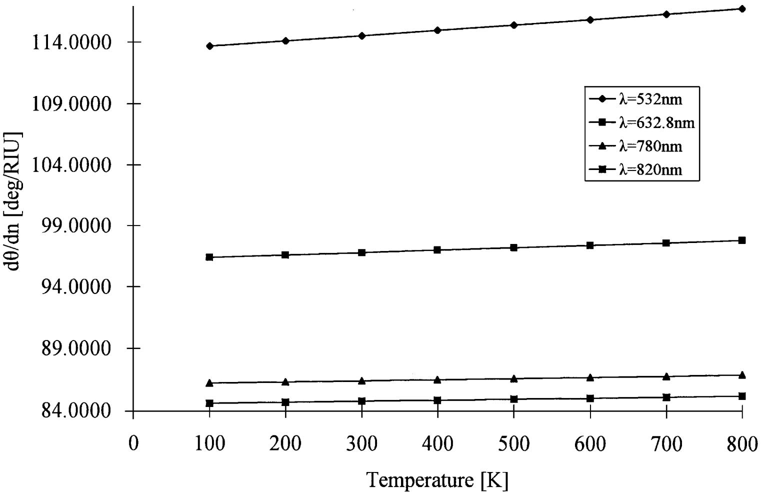

Fig. 3. Sensitivity according to the "angular interrogation" approach as a function of temperature at different incident wavelengths with $n_a = 1.32$ and $n_p = 1.54$.

(n_a) of the "analyte" occurs during the sensing process. By differentiating the resonance condition for the SPR excitation, Homola et al. [21] obtained the following expression for the sensitivity of the ATR geometry as follows:

$$S_\theta = \frac{d\theta_m}{dn_a} = \frac{\varepsilon_{mr}\sqrt{-\varepsilon_{mr}}}{(\varepsilon_{mr} + n_a^2)\sqrt{\varepsilon_{mr}(n_a^2 - n_p^2) - n_p^2 n_a^2}}, \quad (7)$$

where n_p is the index of the glass of the prism, and the real part of the dielectric function of the metal ε_{mr} is negative for SPR to take place. Assuming only ε_{mr} varies significantly with T, we have studied the variation of S_θ as a function of T using Eqs. (1)–(7). Fig. 3 shows the results for a Ag film at various incident wavelengths. As is clear from the results, we find that the sensitivity in this monitoring mode is *very stable* with the change of temperature! This is due to the well-established fact that ε_{mr} varies relatively insignificantly with T compared to the imaginary part of the dielectric function for metals [22].

3.2. Reflectance monitoring

One widely used method in the application of the SPR sensor is to monitor the change of the reflectance R at a fixed incident (and reflection) angle θ as the binding of the analyte occurs [20]. To investigate how the sensitivity of this process will be affected with the change of temperature, we first study how the slope of the reflectance curve at a fixed θ (e.g., at $\theta < \theta_m$ at FWHM) varies with T. Fig. 4a shows how this quantity ($dR/d\theta$) decreases with T at various film thicknesses d. It is clear that this behavior (decreasing with T) is of general validity from Fig. 2, irrespective of what θ value is fixed and what wavelength is used. To confirm further, Fig. 4b shows this decreasing behavior at different wavelengths for d fixed at 60 nm. Hence one can obtain an estimate for (dR/dn_a) as a function of T by plotting the product of the results in Fig. 3 and those in Fig. 4b. Note that in practical sensing, the change of n_a is very small (e.g., $\Delta n_a \sim 10^{-5}$), so that $\Delta\theta$ is small and of the same order of magnitude at any incident angle θ. This justifies the above estimate process for (dR/dn_a) at an angle $\theta \neq \theta_m$. Since Fig. 3 shows that ($d\theta_m/dn_a$) is relatively insensitive to temperature change, one expects (dR/dn_a) will decrease significantly as T rises. This is illustrated in Fig. 5, with results presented both for different film thicknesses and for different incident wavelengths.

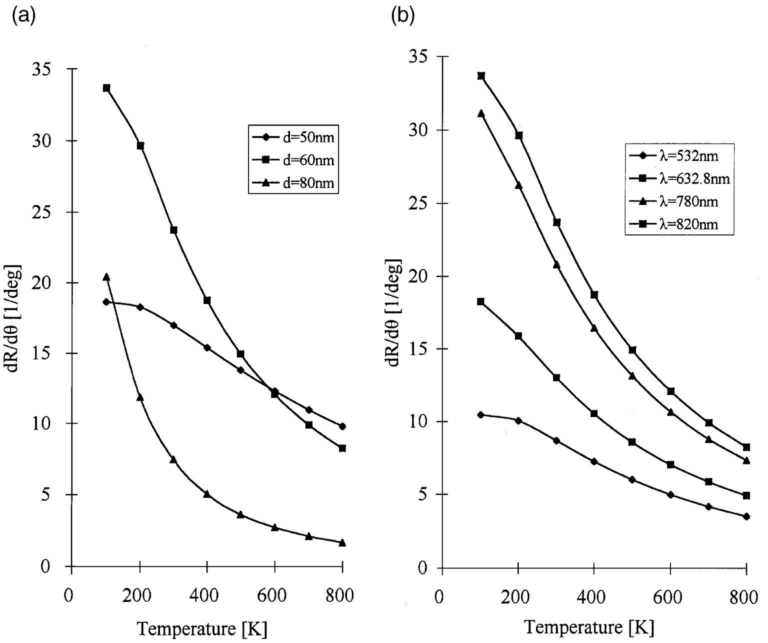

Fig. 4. Slope of the SPR reflectance curve (absolute values) at the FWHM angle of incidence as a function of temperature for (a) various film thickness at fixed incident wavelength of 820 nm, and (b) various incident wavelengths with film thickness fixed at 60 nm.

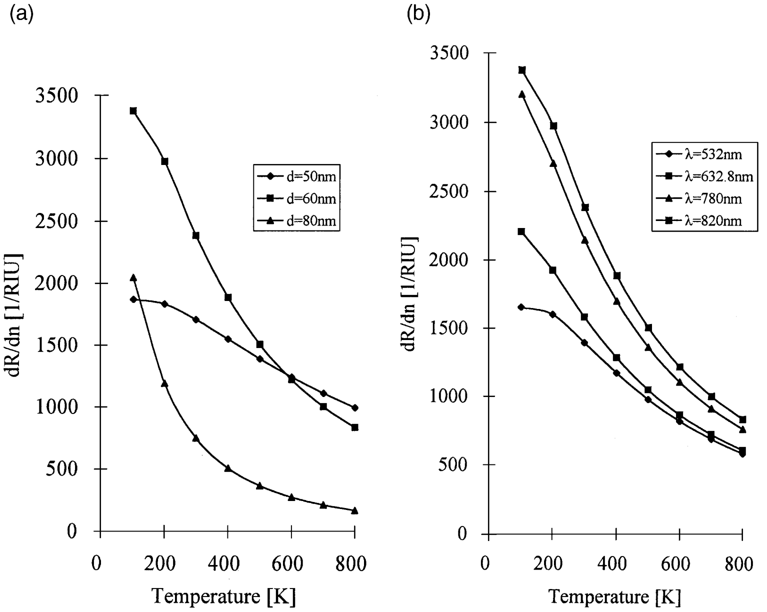

Fig. 5. The product of results in Figs. (3) and (4) yielding an estimate for the variation of the reflectance with analyte as a function of the sensor temperature for (a) various film thickness at fixed incident wavelength of 820 nm, and (b) various incident wavelengths with film thickness fixed at 60 nm.

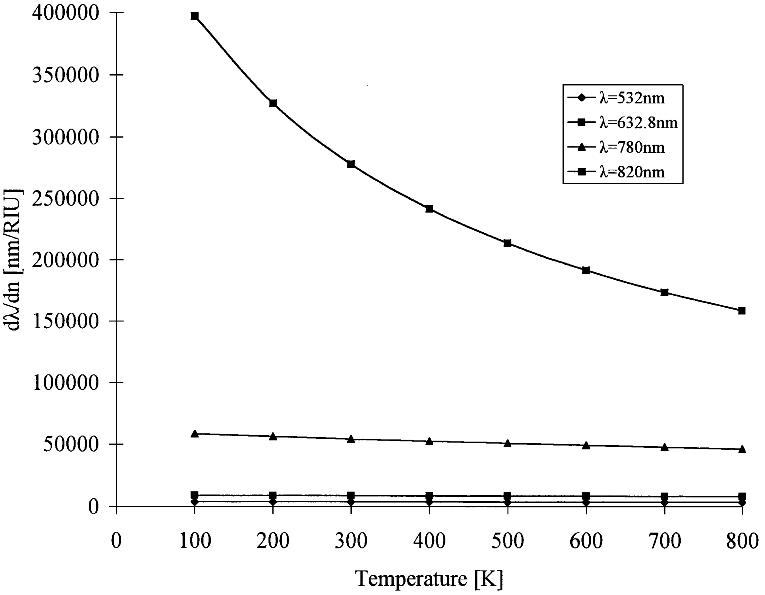

Fig. 6. Sensitivity according to the "wavelength interrogation" approach as a function of temperature at different incident wavelengths with $n_a = 1.32$ and $n_p = 1.54$.

3.3. Wavelength interrogation

We have also studied the temperature dependence of the sensitivity when the resonant wavelength is monitored at fixed θ. As reported by Homola et al. [21], the sensitivity in this case can be obtained as follows for the ATR geometry:

$$S_\lambda = \frac{d\lambda}{dn_a} = \frac{\varepsilon_{mr}^2}{\frac{n_a^3}{2}\left|\frac{d\varepsilon_{mr}}{d\lambda}\right| + (\varepsilon_{mr} + n_a^2)\varepsilon_{mr}\frac{dn_p}{d\lambda}\frac{n_a}{n_p}}, \quad (8)$$

where the dispersion for glass in the visible region is small and $(dn_p/d\lambda)$ is of the order of -10^{-4}. 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_λ as a function of temperature using Eqs. (1)–(6). Fig. 6 shows the results for $S_\lambda(T)$ for a Ag film for several incident wavelengths. We observe that except for 820 nm, $S_\lambda(T)$ stays relatively constant for shorter incident wavelengths. Moreover, the values for $S_\lambda(T)$ at these shorter wavelengths are relatively much smaller than those at 820 nm.

4. Conclusion

We have presented a self-contained model which enables one to model the temperature dependence of the sensitivity of the SPR optical sensor. All the three common modes of monitoring, namely: the resonant-angle, reflectance, and resonant-wavelength monitoring have been studied. Although we have limited ourselves to the ATR geometry, other geometries such as the grating approach can also be studied in a similar fashion [21]. The main possible over-simplification in our approach is the use of the Drude model for idealized free electrons in the metal. Though it is known that the interband transitions from the s and d electrons will be significant for the description of the surface plasmon [23], it has nevertheless been found that the Drude model does have reasonable accuracy in the modeling of SPR-related phenomena [10,15,16]. In addition, the simplicity of the Drude model makes the modeling of the temperature dependence feasible on a purely theoretical basis. Within the results we obtained, it seems that the resonant-angle interrogation approach has a sensitivity which is most stable against the variation of temperature, and is thus preferable in this aspect. In addition, for the other approaches, especially for the monitoring of the SPR reflectance at a fixed incident angle, we propose that it might be possible to achieve higher sensitivity by operating the sensor at temperatures much lower than room temperature. Of course, in practical sensing, other factors have also to be considered such as the effect of temperature on the binding rate of the analyte. In any case, systematic experimental studies on how the various sensitivities depend on temperature will be of value, and comparison with the above theoretical modeling results will be of interest.

Acknowledgements

This research is supported in part by the grant NSC89-2112-M-019-007 of Taiwan, and by the Faculty Development Funding of Portland State University.

References

[1] R.W. Wood, Phil. Magn. 4 (1902) 396.
[2] A. Otto, Z. Physik 216 (1968) 398.
[3] E. Kretschmann, H. Raether, Z. Naturforsch 23A (1968) 2135.
[4] E. Kretschmann, Z. Physik 241 (1971) 313.
[5] H. Raether, Surface Plasmons on Smooth and Rough Surfaces and on Gratings, Springer, Berlin, 1988.
[6] J. Homola, S.S. Yee, G. Gauglitz, Sensors and Actuators B 54 (1999) 3.
[7] B.L. Liedberg, C. Nylander, I. Lundström, Sensors and Actuators 4 (1983) 299.
[8] S. Lofas, M. Malmqvist, I. Ronnberg, E. Stenberg, B. Liedberg, I. Lundström, Sensors and Actuators B 5 (1991) 79.
[9] S. Herminghaus, P. Leiderer, Appl. Phys. Lett. 58 (1991) 352.
[10] S. Herminghaus, P. Leiderer, Appl. Phys. A 51 (1990) 350.
[11] H.P. Chiang, P.T. Leung, W.S. Tse, Solid State Commun. 101 (1997) 45.
[12] H.P. Chiang, P.T. Leung, W.S. Tse, J. Chem. Phys. 108 (1998) 2659.
[13] H.P. Chiang, P.T. Leung, W.S. Tse, J. Phys. Chem. B 104 (2000) 2348.
[14] B. Pettinger, X. Boa, I.C. Wilcock, M. Muhler, G. Ertl, Phys. Rev. Lett. 72 (1994) 1561.
[15] Y.S. Pang, H.J. Hwang, M.S. Kim, J. Phys. Chem. B 102 (1998) 7203.
[16] C.H. Kwon, D.W. Boo, H.J. Hwang, M.S. Kim, J. Phys. Chem. B 103 (1999) 9610.
[17] T. Holstein, Phys. Rev. 96 (1954) 535.
[18] T. Holstein, Ann. Phys. (NY) 29 (1964) 410.
[19] W.E. Lawrence, Phys. Rev. B 13 (1976) 5316.
[20] R.P.H. Kooyman, H. Kolkman, J. van Gent, J. Greve, Anal. Chim. Acta 213 (1988) 35.
[21] J. Homola, I. Koudela, S.S. Yee, Sensors and Actuators B 54 (1999) 16.
[22] P.T. Leung, M.H. Hider, E.J. Sanchez, Phys. Rev. B 53 (1996) 12659.
[23] A. Liebsch, Phys. Rev. B 48 (1993) 11317.