Highest Achievable Detection Range for SPR Based Sensors Using Gallium Phosphide (GaP) as a Substrate: a Theoretical Study

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Abstract: In the present study, we have theoretically modelled a surface plasmon resonance (SPR) based sensing chip utilizing a prism made up of gallium phosphidee. It has been found in the study that a large range of refractive index starting from the gaseous medium to highly concentrated liquids can be sensed by using a single chip in the visible region of the spectrum. The variation of the sensitivity as well as detection accuracy with sensing region refractive index has been analyzed in detail. The large value of the sensitivity along with the large dynamic range is the advantageous feature of the present sensing probe.

Keywords: Optical fiber sensors; evanescent waves; gallium phosphide; surface plasmon

1. Introduction

The surface plasmon resonance (SPR) technique is the most promising tool for the detection of various chemical and biological species [1−12]. At the present time, the SPR technique is being used not only in the biochemical species detection and gas sensing but also in imaging, terahertz plasmonics, artificially structured materials lithography, and many other areas [2−4]. In SPR based sensors, the famous Kretschmann-Reather configuration is utilized [1]. In this configuration, a thin layer of metal such as silver or gold is deposited onto the base of a prism as shown in Fig. 1. A p-polarized light is allowed to fall from the substrate side. The medium to be sensed is kept in contact with the metal layer.
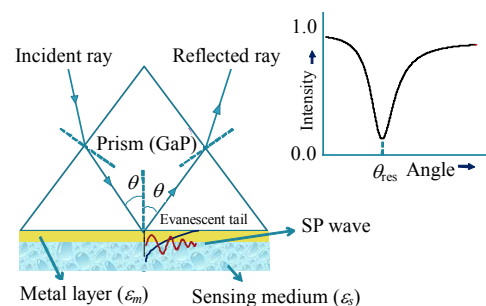

Fig. 1 Schematic diagram of the sensing probe.

Under the resonance condition, the reflected light beam causes a sharp dip into the intensity when the wavevector of the incident wave matches with the wave vector of the surface plasmon wave (Fig. 1 insight). If n_s and ε_m represent the refractive index and the dielectric function of the sensing medium and metal layer, respectively, the resonance condition can be written as

$$\frac{2\pi}{\lambda_o} n_{\text{substrate}} \sin\theta_{\text{SPR}} = \text{Re}\left[\frac{2\pi}{\lambda_o}\left(\frac{\varepsilon_m n_s^2}{\varepsilon_m + n_s^2}\right)^{1/2}\right]. \quad (1)$$

The expression on the left hand side represents the propagation constant (k) of the evanescent wave, and the right hand side represents the propagation constant of the surface plasmon wave existing at the gold sensing layer interface. θ_{SPR} is the resonance angle, i.e. the angle at which two wave vectors match. Here, λ_o is the wavelength of light being used.

In SPR based sensors, two interrogation schemes are generally used. One is called the angular interrogation, and the other is called the spectral interrogation. In the angular interrogation technique, we fix the wavelength of the incident light, i.e. we use a monochromatic light source and vary the angle of incidence from the critical angle to 90°. This change in the angle changes the propagation constant of the incident wave. At a particular value of the angle of incidence, this propagation constant becomes equal to the SPR propagation constant leading to the condition of the resonance. This resonance angle is quite sensitive to the changes in the sensing region environment. A slight change in the surrounding refractive index causes a corresponding change in the resonance angle. By measuring the change in the resonance angle, the change in the surrounding region refractive index can be measured.

In another scheme called the wavelength interrogation scheme, we use a polychromatic source of light and fix the angle of incidence to any particular value between θ_c and 90°. This again changes the value of the propagation constant of the incident beam. At a particular value of the incident wavelength, the propagation constant of the incident wave may become equal to the surface plasmon wave vector. This is called the resonance condition, and the wavelength at which this occurs is called the resonance wavelength. At this wavelength, the intensity of the reflected light shows the minimum.

For a change in the refractive index of the sensing medium, the resonance wavelength changes. By measuring the change in the resonance wavelength, the corresponding change in the refractive index of the medium can be measured. There are other techniques also for measuring changes in the refractive index such as the Mach-Zhander interferometer and Febry-Perot interferometer, however, SPR sensors are also getting progressed with the equal pace such as in the sensing of hydrogen gas using palladium [13−15].

In the present work, an angular interrogation technique is used to exploit the famous Krestchmann-Reather configuration. People have devised various sensing probes which are applicable either for the gas sensing or for the liquid medium. We here are proffering a sensing chip which can detect various gases as well as highly concentrated liquid in the visible region of the spectrum thereby producing a large dynamic range of the sensing medium refractive index. This could be possibly realized by utilizing the sensor chip which can be fabricated by depositing a thin layer of gold layer (50 nm) onto the base of a prism made up of a semiconducting material called gallium phosphide. Gallium phosphide is a transparent semiconducting material having refractive index around 3.3 in the visible range of the spectrum. Also it is a wide band gap material. The detailed theoretical analysis is carried out in terms of the sensitivity and detection accuracy. The most advantageous feature of having large detection range has been addressed.

In order to realize the practical design of the sensor, consider a GaP prism coated with a gold layer of about 50 nm as shown in Fig. 1. For coating the gold layer, any vacuum deposition technique such as thermal evaporation, sputtering or electron beam deposition can be used. The chemical or the gaseous medium which is to be sensed is kept in contact with the gold layer. A p-polarized light with the intensity I and wavelength 632 nm from He-Ne laser is allowed to fall on the substrate. The intensity

of the reflected light is measured with respect to the angle of incidence. A sharp dip is observed at a particular value of the angle of the incidence. This will be the resonance angle. A slight change in the sensing region will reflect in terms of the corresponding change in the resonance angle.

In mathematical modelling, we require the value of the dielectric constant of the metal layer for the He-Ne laser wavelength which can be calculated from the Drude formula [6]:

$$\varepsilon_m(\lambda) = \varepsilon_{mr} + i\varepsilon_{mi} = 1 - \frac{\lambda^2 \lambda_c}{\lambda_p^2(\lambda_c + i\lambda)} \tag{2}$$

where ε_{mr} and ε_{mi} are the real and imaginary parts of the dielectric constants of the gold layer. Also λ_p and λ_c are the plasma and collision frequencies of the gold layer. Their values are 1.6826×10^{-7} m and 8.9342×10^{-6} m, respectively.

To get a feel of the refractive index variation, one should note that most of the gases possess the refractive index close to unity whereas highly concentrated liquid chemicals such as solutions of $C_7H_6Cl_2$ have their refractive index values around 1.6 to 1.7 [11]. For the calculation of the reflected light beam intensity, one should be very precise because it is the resonance angle which decides the sensitivity of the sensor. In the present case, we have used a N-layer matrix method for the calculation of the reflection coefficient. The first medium is the GaP prism, the second medium is the gold layer, and the third medium is the sensing region itself which is to be sensed. These layers are assumed to be stacked along the z axis as shown in Fig. 2.
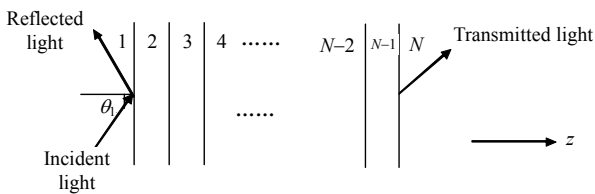

Fig. 2 Stack of N-layers arranged along the z axis.

The arbitrary medium layer has the thickness d_i, the dialectic constant ε_i, and the permeability μ_i. The relationship between the tangential electric field and

magnetic field at $z=z_1=0$ and at $z=z_{N-1}$ are related by

$$\begin{bmatrix} E_1 \\ H_1 \end{bmatrix} = \mathbf{M} \begin{bmatrix} E_{N-1} \\ H_{N-1} \end{bmatrix} \tag{3}$$

where E_1 and H_1 are the tangential electric and magnetic fields at the first boundary. E_{N-1} and H_{N-1} are the similar fields at the Nth layer. M is called the characteristic matrix of the combined structure and is given by

$$\mathbf{M} = \prod_{i=2}^{N-1} M_i = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \tag{4}$$

where

$$q_i = \left(\frac{\mu_i}{\varepsilon_i}\right)^{1/2} \cos\theta_i = \frac{\left(\varepsilon_i - n_1^2 \sin^2\theta_1\right)^{1/2}}{\varepsilon_i} \tag{5}$$

and

$$\beta_i = \frac{2\pi}{\lambda} n_i \cos\theta_i (z_i - z_{i-1}) = \frac{2\pi d_i}{\lambda}\left(\varepsilon_i - n_1^2 \sin^2\theta_1\right)^{1/2}. \tag{6}$$

In the present case, there are three media and two layers $N=2$. Therefore, n_1 is the refractive index of the substrate, $n_2 = \sqrt{\varepsilon_m}$ is the refractive index of the metal layer (gold), n_3 is the refractive index of the sensing medium, and d_2 will be the thickness of the gold layer which is 50 nm in the present case. If θ_1 is the angle of incidence and λ_o is the wavelength of light in the free space which is 632 nm for He-Ne laser, the amplitude reflection coefficient r_p for the p-polarized incident wave is given as

$$r_p = \frac{(M_{11} + M_{12}q_N)q_1 - (M_{21} + M_{22}q_N)}{(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)}. \tag{7}$$

All the M_{11}, M_{12}, M_{21}, and M_{24} are the four matrix coefficients of the matrix in (4). This will be a complex number. The reflection coefficient is the absolute square of r_p as

$$R_p = |r_p|^2. \tag{8}$$

We shall evaluate the performance of the sensor in terms of the two parameters:

Sensitivity: if the refractive index of the sensing medium is altered by δn_s, the resonance angle will also change, and if the change in the corresponding angle is $\delta\theta_{res}$, we define the sensitivity as

$$S_n = \frac{\delta\theta_{\text{SPR}}}{\delta n_s}. \qquad (8)$$

Detection accuracy: for each SPR curve, we have to determine the exact location of the SPR angle which will be more correct if the SPR curve is sharp. So we define a parameter called the detection accuracy which is just the reciprocal of the full width at half maximum (FWHM) of an SPR curve:

$$DA = \frac{1}{\Delta\theta_{\text{FWHM}}}. \qquad (10)$$

In this particular section of the article, we shall present various theoretical results obtained from the theory discussed above.

Now since we are using here the technique of angular interrogation, so we shall check first the possibility of the SP wave excitation by incident light. For this, we have plotted in Fig. 3 the propagation constant of the surface plasmon wave with the angle of incidence along with the propagation constant of the incident wave from glass as well as from the GaP substrate.
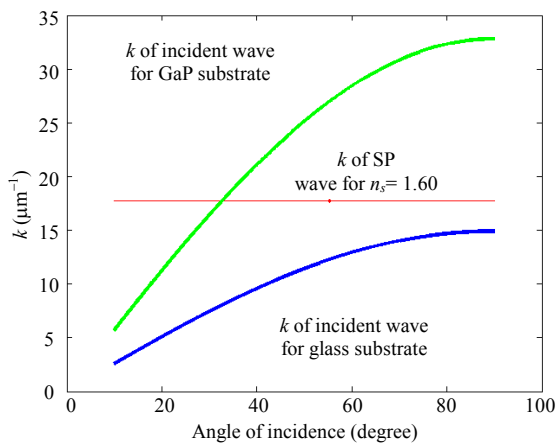

Fig. 3 Variation of propagation constants (k) with angles.

As it is quite clear from (1) that the surface plasmon wave vector is independent of the angle of incidence, hence the curve comes out to a straight line parallel to the angle axis as shown in Fig. 3. The surface plasmon wave vector is plotted for n_s=1.62. In the same graph, we have also plotted the propagation constant of the direct light, i.e. light in the glass prism, i.e. the evanescent wave and also the propagation constant of the wave in the GaP

prism. It is quite obvious from the figure that the propagation constant of light through the glass prism does not intersect the SP wave propagation constant which indicates that the SP wave cannot be excited for these waves. However, the SP dispersion curve intersects the light wave for GaP showing the possibility that the SP can be excited by these waves at a particular angle of incidence called the resonance angle. Thus, it is clear that the SP wave at the gold and high refractive index medium interface can be excited by using a GaP substrate. Now we shall calculate the reflection coefficient.

In Fig. 4, we have plotted the variation of reflected light intensity with the angle of incidence. As it is obvious, the intensity shows a sharp dip at a particular value of the angle of incidence. For n_s=1.30, the resonance angle comes out to be 24.9788°. As we increase the value of n_s from 1.30 to 1.50, i.e. δn_s=0.2, the SPR dip shifts to the higher value of angle of incidence θ_{SPR}= 29.9641° giving rise to a shift of $\delta\theta$= 4.9853°. The larger the value of shift is, the greater the sensitivity is. This cannot be compared for the Si based prism as the SPR can not be excited for such a high value of sensing region refractive index. In the same figure, we have also plotted the SPR curve for n_s= 1.7 and 1.9, and the four curves are well depict the quite high value of the sensitivity separately.
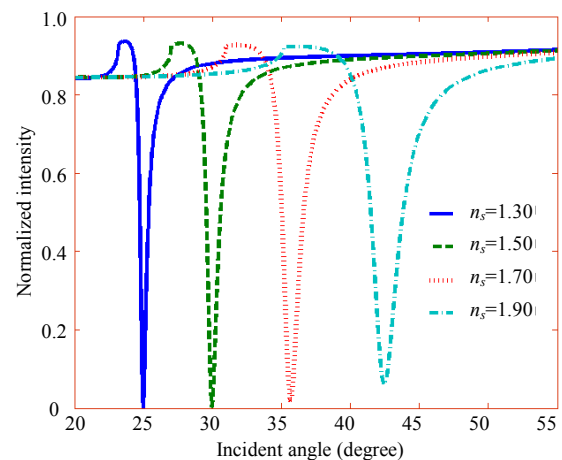

Fig. 4 Variation of normalized intensity with the angle of incidence (SPR curves).

To check the variation of sensitivity with the sensing region refractive index, we have calculated the resonance angle for a large range of refractive index starting from the gaseous medium to highly concentrated liquids.

The curve between the sensitivity and sensing region refractive index is shown in Fig. 5. The sensitivity increases with an increase in the sensing region refractive index as for higher concentrations the resonance condition will be satisfied at higher values of SPR angles. One more parameter is the detection accuracy. For the calculation of the detection accuracy, first we have calculated the full width at half maximum FWHM of each SPR curve, and then the DA is evaluated as per the definition given in (10).
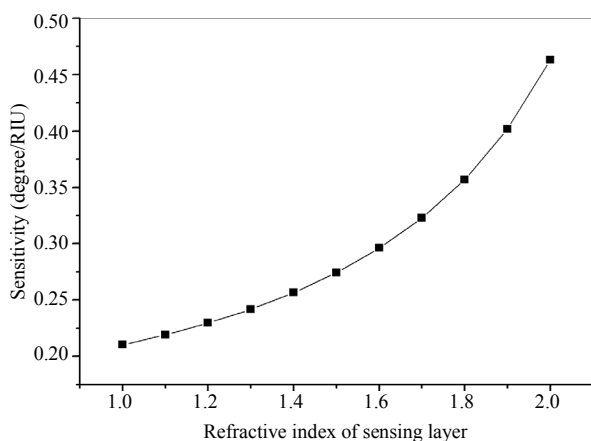

Fig. 5 Sensitivity variation with sensing region refractive index.

It is visible from the SPR curves that with an increase in the sensing region the refractive index, the SPR curves get broadened giving rise to poor detection accuracy. However, the broadening in SPR curves as given in Fig. 4 is not too much so that it may affect θ_{SPR}. The variation of detection accuracy with refractive index of the sensing layer is plotted in Fig. 6.

More importantly, we are using the visible light source, i.e. a He-Ne laser with the wavelength 632 nm, and we are able to sense a large spectrum of the sensing region refractive index. The sensor reported till now either uses the infra red (IR) source

or uses a buffer layer to bring the SPR dip in the visible region, but in the present case, we have modelled a single sensing chip which can be used to sense the gases as well as the liquid medium in the visible region of the spectrum. The large range of n_s is the most advantageous feature of the present study. The theoretical study given in the current study has already been verified experimentally by Motogaito *et al.* [11]. However, a detailed theoretical analysis in terms of detection accuracy and sensitivity is missing. The current study provides a material to fill that gap.
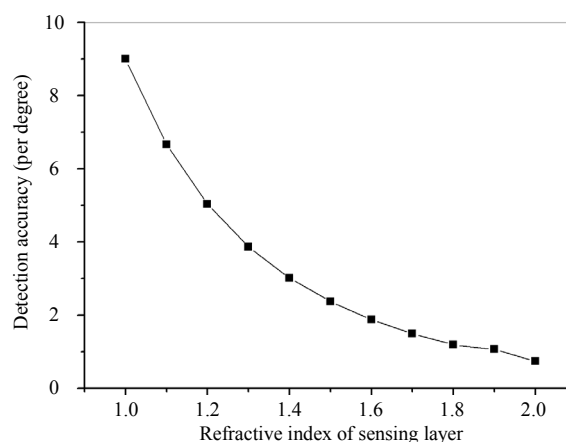

Fig. 6 Variation of detection accuracy with sensing region refractive index.

References

[1] R. C. Jorgenson and S. S. Yee, "A fiber-optic chemical sensor based on surface plasmon resonance," *Sensors and Actuators B: Chemical*, 1993, 12(3): 213−220.

[2] O. Esteban, R. Alonso, C. Navarrete, and C. A. G. Cano, "Surface plasmon excitation in fiber-optic sensors: a novel theoretical approach," *Journal of Lightwave Technology*, 2002, 20(3): 448−453.

[3] L. K. Chau, Y. F. Lin, S. F. Cheng, and T. J. Lin, "Fiber-optic chemical and biochemical probes based

on localized surface plasmon resonance," *Sensors and Actuators B: Chemical*, 2006, 113(1): 100−105.

[4] X. Chen, R. R.Wei, M. Shen, Z. F. Zhang, and C. F. Li, "Bistable and negative lateral shifts of the reflected light beam from Kretschmann configuration with nonlinear left handed metamaterials," *Applied Physics B*, 2010, 101(1): 283−289.

[5] S. A. Zynio, A. V. Samoylov, E. R. Surovtseva, V. M. Mirsky, and Y. M. Shirsov, "Bimetallic layers increase sensitivity of affinity sensors based on surface plasmon resonance," *Sensors*, 2002, 2(2): 62−70.

[6] R. K. Verma and B. D. Gupta, "Surface plasmon resonance based fiber optic senor for IR region using conductin metal oxide," *Journal of the Optical Society of America A*, 2010, 27(4): 846−851.

[7] G. G. Nenninger, P. Tobiska, J. Homola, and S. S. Yee, "Long range surface plasmons for high resolution surface plasmon resonance sensors," *Sensors and Actuators B: Chemical*, 2001, 74(1−3): 145−151.

[8] Rajan, A. K. Sharma, and B. D. Gupta, "Fiber optic sensor based on long range surface plasmon resonance," *Journal of Optics A: Pure and Applied Optics*, 2007, 9(7): 682.

[9] A. K. Sharma, Rajan, and B. D. Gupta, "Influence of dopants on the performance of a fiber optic surface plasmon resonance sensor," *Optics Communications*, 2007, 274(2): 320−326.

[10] S. K. Mishra and B. D. Gupta, "Surface plasmon resonance based fiber optic pH sensor utilizing Ag/ITO/Al/hydrogel layers," *Analyst*, 2013, 138(9): 2640−2646.

[11] A. Motogaito, S. Nakamura, J. Miyazaki, H. Miyake, and K. Hiramatsu,"Using surface plasmon polariton at GaP-Au interface in order to detect chemical species in high refractive index media," *Optics Communications*, 2015, 341: 64−68.

[12] S. Singh, S. K. Mishra, and B. D. Gupta, "SPR based fibre optic biosensor for phenolic compounds using immobilization of tyrosinase in polyacrylamide gel," *Sensors and Actuators B: Chemical*, 2013, 186: 388−395.

[13] J. Zhou, Y. Wang, C. Liao, B. Sun, J. He, G. Yin, *et al*., "Intensity modulated refractive index sensor based on optical fiber Michelson interferometer," *Sensors and Actuators B: Chemical*, 2015, 208: 315−319.

[14] M. Deng, C. P. Tang, T. Zhu, Y. J. Rao, L. C. Xu, and M. Han, "Refractive index measurement using photonic crystal fiber-based Fabry-Perot interferometer," *Applied Optics*, 2013, 49(9): 1593−1598.

[15] P. Tobiska, O. Hugon, A. Trouillet, and H. Gagnaire, "An integrated optic hydrogen sensor based on SPR on palladium," *Sensors and Actuators B: Chemical*, 2001, 74(1−3): 168−172.