Surface plasmon resonance based refractive index sensor for liquids

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A surface plasmon resonance (SPR) refractive index sensor for liquids was fabricated and characterized. A thin silver (Ag) film (545Å) was deposited on a prism face and surface plasmon modes were excited along the interfaces of Ag and air, Ag and water and Ag and sugar solutions by prism-coupling using a He-Ne laser. The experimental SPR reflectance curves shifted continuously with increase in sugar concentration. Theoretical fitting of the SPR dip angles yielded the dielectric constant of Ag and refractive indices of water and sugar solutions. A maximum sensitivity of 1.4×10^{-4} R.I.U. (refractive index units) was achieved with SPR dip angle as variable parameter. With SPR reflectance as variable parameter at a fixed angle, the maximum sensitivity was 3.9×10^{-5} R.I.U. in a selected narrow range of refractive index.

Keywords: Surface plasmon resonance, Refractive index sensor, Optical characterization, Thin metal films

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1 Introduction

Surface plasmons (SPs) are electromagnetic waves guided along a metal-dielectric interface and can be excited by the method of attenuated total reflection (ATR). The surface plasmon (SPR) parameters are highly sensitive to the dielectric constant of the metal film and the surrounding medium and can be used to detect and study any changes occurring on or near the metal film surface. Surface plasmon resonance appears as a sharp minimum in the internal reflectance of a metal film deposited on the face of a prism. The excitation of surface plasmon oscillations is possible only in a certain metal film thickness range.

One of the major applications of SPs is in the field of gas, chemical and biological sensors. The principle of operation is that surface plasmons are very sensitive to any changes in the dielectric environment of the metal surface. Therefore, a slight change in the refractive index of the surrounding medium causes a large change in the SPR parameters. The variation in refractive index can be calibrated in terms of the concentration of gas or solute in solution, resulting in a highly sensitive sensor.

In this paper, a SPR based refractive index sensor has been developed using a prism-coupling technique and a He-Ne laser. The calibration has been done in the case of sugar solution as a convenient test sample, and the obtained maximum sensitivity was 3.9×10^{-5} R.I.U. (refractive index units).

2 Theory

The essential condition for the excitation of surface plasmon waves by the prism coupling technique is equivalence of the tangential component of incident wavevector with real part of surface plasmon wavevector i.e.

\[
\frac{2\pi}{\lambda} n_p \sin \theta_{ATR} = \text{Re}(k_p)
\]

or

\[
\frac{2\pi}{\lambda} n_p \sin \theta_{ATR} \approx \left( \frac{2\pi}{\lambda} \right) \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}^{1/2}
\]

where \( n_p \) is the prism refractive index, \( \theta_{ATR} \) is the SPR angle where a dip is observed in the intensity of light reflected internally from the film, and \( \varepsilon_0, \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric constants of the prism, metal film and dielectric medium, respectively. The reflectance of a structure comprising prism coated with a metal and a dielectric media on the metal surface is calculated by Fresnel’s relations. For \( p \)-polarized light travelling from the \( i \)th medium to the \( k \)th medium, the Fresnel’s reflection coefficient is given by

\[
r_{ik} = \left( \frac{k_{ni}}{\varepsilon_i} - \frac{k_{nk}}{\varepsilon_k} \right) \left/ \left( \frac{k_{ni}}{\varepsilon_i} + \frac{k_{nk}}{\varepsilon_k} \right) \right.
\]

where \( k_{ni} \) and \( k_{nk} \) are the wavevectors in the \( i \)th and \( k \)th medium, respectively.
with \( k_{zi} = \frac{2\pi}{\lambda} \left( \varepsilon_i - \varepsilon_0 \sin^2 \theta \right)^{1/2} \) \hspace{1cm} (3)

where \( \theta \) is the angle of incidence, \( k_{zi} \) and \( k_{zk} \) are the wavevectors while \( \varepsilon_i \) and \( \varepsilon_k \) are the dielectric constants for the \( i^{th} \) and \( k^{th} \) media, respectively. The reflectance of the prism-metal film-air system \( (\varepsilon_0-\varepsilon_1-\varepsilon_2) \), which consists of a single film separated by two semi-infinite media, is given by

\[
R_{012} = \left| \frac{r_{01} + r_{12} \exp(2ik_zd_1)}{1 + r_{01}r_{12} \exp(2ik_zd_1)} \right|^2 \hspace{1cm} (4)
\]

where subscripts 0, 1 and 2 refer to the prism, metal and air media, respectively, and \( d_1 \) is the thickness of the deposited metal film on prism.

### 3 Experimental Details

A thin Ag film of thickness 545Å was deposited on the hypotenuse face of a flint glass prism \( (n_p = 1.714) \) by thermal evaporation at the rate of 5Å/s in a vacuum of \( 7\times10^{-6} \) Torr. The purity of the Ag used was 99.99%. A quartz crystal thickness monitor was used to monitor the film thickness. A specially designed glass sample cell, into which a liquid solution can be poured, was fixed to the silver coated face of the prism with Canada balsam. Fig. 1 shows the experimental SPR set-up developed and used for fabricating the sensor.

A \( p \)-polarized He-Ne laser was used to excite surface plasmon waves by the prism-coupling technique. The prism was placed on a XYZθ rotating stage with a resolution of 0.01°. The intensity of light reflected internally from the metal film was measured with the laser power detector of resolution of 0.01 mW with air, water or different concentrations of sugar solution in the sample cell at different incident angles near the corresponding SPR dip angles. The measured reflected intensity was divided by the incident intensity of the laser beam to get the reflectance.

### 4 Results and Discussion

The excitation of surface plasmon waves in the silver metal-air interface was examined, and a dip in reflected intensity was observed at an incident angle of 37.02°. A slight increase in the SPR dip angle (37.06°) was observed in a period of two days required for drying the Canada balsam adhesive used for fixing the sample cell, and also resulted in a slight broadening of the curve due to reaction of silver with atmospheric \( \text{H}_2\text{S} \). The measured SPR reflectance curve is shown in Fig. 2. The obtained SPR reflectance curve for the Ag-air mode was theoretically fitted by using Fresnel’s relation (4) with \( \varepsilon_2 = 1 \) (for air). A good agreement between the experimental and theoretical curves was obtained, as shown in Fig. 2, with \( \varepsilon_1 = -16.3+0.51i \), and \( d_1 = 545\)Å as the fitting parameters. The SPR dip angle is dependent on the real part of the dielectric constant of the silver film, whereas the imaginary part of the dielectric constant and the metal film thickness influence the half-width and dip reflectance of the SPR reflectance curve

Thereafter, distilled water was poured into the sample cell through its opening at the top. A SPR reflectance dip was now observed at an incident angle...
of 55.63° (instead of 37.06° observed in case of Ag-air interface) due to surface plasmon waves (SPWs) excited at the Ag-water interface and the corresponding SPR reflectance curve is shown in Fig. 3. The experimental reflectance curve with $\theta_{\text{ATR}} = 55.63^\circ$ for Ag-H$_2$O SPR mode was fitted with Fresnel’s Eq. (4), with fitting parameters $\varepsilon_2 = (1.3343)^2$ while keeping $\varepsilon_1 (= -16.3+0.51i)$ and $d_1 (= 545\text{Å})$ as same as determined from Ag-air SPR mode. The normalized theoretical curve is also included in Fig. 3 for comparison and is found to be in well agreement with the experimental curve. The determined value of refractive index of water is $n_w = 1.3343$ and this is close to the reported values$^7$.

The performance of SPR refractive index sensor was investigated by using sugar solutions of varying concentrations. The different number of sugar cubes (each weighing 4.17 g) were added to 100 ml of distilled water to prepare the test solutions ranging from 0.0417 to 0.209 g/ml, which were poured into the sample cell one at a time. The reflectance values near the SPR dip angles were noted for the different concentrations. Figure 4 shows the normalized SPR reflectance curves for modes excited at the interface of the Ag film and the sugar solutions of different concentrations. It is noted that the SPR reflectance curve shifts by nearly 0.3° for every 0.4 g/ml increase in sugar concentration. The magnitude of reflectance at dip angle is not observed to change much with increase in sugar concentration, and the curves become only slightly broader, indicating that the solution is not highly absorbing in nature.

The refractive indices of the sugar solutions $[n_s = (\varepsilon_2)^{1/2}]$ with varying concentrations were estimated by fitting the observed SPR dip angles by using Eq. (4) and the values of measured $\theta_{\text{ATR}}$ and the estimated parameters $[\varepsilon_1 = -16.3+0.51i$ and $d_1 = 545\text{Å}]$ determined from Ag-air SPR mode. Fig. 5 shows the plot of estimated values of refractive indices as a function of measured SPR dip angles (for different sugar solutions). It is observed that the values of refractive indices increases linearly with SPR dip angle over the entire measured range. Therefore, the sensitivity of refractive index sensor, ratio of the change in the refractive index with the SPR dip angle, remains same over the entire range of varying concentration of sugar solution. The value of estimated sensitivity is found to be about $1.37\times10^{-4}$ R.I.U after considering the resolution of 0.01° of the measuring apparatus used in the present study. The value of refractive in-

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**Fig. 3**—Experimental and theoretical SPR reflectance curves for surface plasmon modes excited along the Ag film (545Å)—water interface

**Fig. 4**—Experimental SPR reflectance curves for surface plasmon modes excited along the interface of Ag film (545Å) and sugar solutions of different concentrations

**Fig. 5**—SPR dip angle ($\theta_{\text{ATR}}$) versus refractive index of sugar solution ($n_s$)
The refractive index was also found to increase with increase in the concentration of sugar solution as shown in Fig. 6. The best fit for this curve is linear having a slope of about 0.125 R.I.U./g/ml. The maximum sensitivity of detecting the variation in concentration of sugar solution using this set-up in this way (i.e., using SPR dip angle as variable parameter) is also estimated from the slope of the curve in Fig. 6, and is found to be \((1.1 \times 10^{-3})\) g/ml.

Alternatively, the variation in the concentration of the sugar solution could also be detected more precisely after measuring the values of reflectance at a fixed angle of incidence in the vicinity of the dip angle. Therefore, the incident angle was fixed at a value \((55.40^\circ)\) in the vicinity of the SPR dip angle for water (i.e., for zero concentration of sugar solution) and the obtained values of reflectance for different concentration of sugar solution were obtained from Fig. 4. The obtained values of reflectance were plotted as a function of refractive index in Fig. 7. It may be noted that the value of reflectance initially increases almost linearly and tends to saturate thereafter to a value one. The sensitivity of the refractive index sensor was obtained to be about \(3.9 \times 10^{-5}\) R.I.U. from the linear portion of the curve and using the resolution of the set-up \((0.01\text{mW})\) used in the present work. The obtained sensitivity is one order higher as compared to that estimated in the previous procedure, i.e., when SPR dip angle was considered as the variable parameter. It is important to note that the high sensitivity is obtained over a limited range of refractive index. The limited refractive index range of the sensor corresponds to the selection of a particular value of fixed incident angle (in this case, it is \(55.40^\circ\)), and could be shifted over the entire range of refractive indices by varying the fixed incident angle. The value of sensitivity for the detection of concentration of sugar solution is also estimated and is found to be \(3.1 \times 10^{-4}\) g/ml, which is one order higher as compared to the sensitivity obtained in the previous procedure.

The maximum sensitivity \(3.9 \times 10^{-5}\) R.I.U. achieved in the present work is close to those reported by other researchers for SPR chemical and biological sensors\(^2,4\). Melendez et al.\(^2\) have reported a sensitivity of \(10^{-5}\) R.I.U. for their SPR sensor and Kunz et al.\(^4\) have reported a sensitivity of \(4.3 \times 10^{-5}\) R.I.U. for the fibre-optic SPR biosensor developed by them. The indigenous SPR set-up developed in the present case is suitable for biosensing applications.

5 Conclusions
SPR refractive index sensor has been developed and used for detecting the variation in the concentration of sugar solution. A high sensitivity of \(3.9 \times 10^{-5}\) R.I.U. has been achieved which is appropriate and sufficient for the development of sensitive SPR biosensing devices. It is inferred that if the SPR dip angle in the reflectance is used as a basis for the detection of variation in concentration of a solution, a reasonably high sensitivity is achieved over a wide range of refractive index measurements. On the other side, if SPR reflectance value is considered as a variable parameter, it yields a higher sensitivity, but requires a proper selection of the fixed incident angle for a desired refractive index range.

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