Improving the performance of surface plasmon resonance sensors for liquid chemical detection

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Our research aims to study four layers surface resonance (SPR) structure containing amorphous As_2S_3 high refractivity index thin films. Calculations performed show that the SPR curves expressed different shift and sharpness, depending on the thin film thickness. The SPR resonance shift with optimized sensor's sensitivity is three times larger than the conventional three-layer configuration. However, the curve width is a bit higher also, so that the quality factor of four layers structure, parameter which finally determines the sensor's resolving power, is 2.2 times higher. Fuels and hydrocarbons can be identified successfully with SPR four-layers optical sensors.

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1. Introduction

Since the year Kretschman, Raether and Otto have proposed the method of evanescent waves as the method of coupling light with a polariton wave that forms at the metal-dielectric interface, the number of publications has grown exponentially, including several monographs [1]-[6]. Many specific properties of amorphous films compared to crystals make them interesting for photonic devices applications [7], [8].

The sensor based on the surface plasmon resonance is a universal label-free sensor that detects the changes of the surface index in the immediate vicinity of the surface, below ½ wavelength of light, about 250 nm. Thus, several variants of chemical sensors have been proposed. The application of SPR-based sensors to monitoring biomolecular interaction was first demonstrated in 1983. Currently, the most prominent example of a biosensor is the glucose sensor, reporting glucose concentration as an electronic signal, e.g. based on a selective enzymatic process. In the years following the introduction of the first commercial surface plasmon resonance instrument (SPR) (Biacore) in 1990, the number of publications including data collected from commercial biosensors increased to over 20,000 works by 2016. The number of channels or independent spots increased from four channels in 1990 (Biacore) to at least 192 streams monitored simultaneously, the sensitivity to the refractive index being up to 10^{-6}.

Wave confinement near the interface metal-dielectric is obtained when the light is directed on the prism at a resonance angle and is put in evidence by determining the angle of incidence of the light on the prism at which the resonance appears. An approach to determine the resonance angle is to solve Helmholtz wave equation, derived from Maxwell's equations [9]-[11]. The approach is effective when complex effective refractive index is required for a given wavelength.

This method can also be used when we are interested in knowledge of electric field distribution. The aim of this study is to determine the resonance peaks in plasmonic configuration containing amorphous As_2S_3 films for different combinations of metal and chalcogenide layer thicknesses over a wide wavelength range. The peak shift due to change of environment refractive index determines the sensitivity of chemical sensors. As we are only interested in the resonance peak shape the transfer matrix formalism approach was chosen.

2. SPR in three layers configuration: basic feature

The SPR configuration employs the total internal reflection of the light at prism base. The evanescent field extends through the thin metal film deposited on the base and it couples with the plasmon-polariton wave created at the external metal interface of metal film. The resonant coupling of the light occurs when the phase velocity of light parallel to surface is equal to the velocity of the plasmon so that surface plasmon polaritons (SPP) waves can propagate along the interface between the conductor and dielectric.

The Maxwell equations describing the SPP propagation reduces to a system of coupled Helmholtz wave equations when considering harmonic oscillations, one per each layer of the structure. They can be solved for different geometries [12]-[14]. In the case when the planar structure lies in xy plane which designates the interface of layers the equations correspond to the one-dimensional case. Every Helmholtz equation is still vectorial and, in the general case of an arbitrary polarization of the incident light, is a system of several equations. The number of equations correspond to the number of layers. The introduction of the concept of TM and TE mode allows reducing of the system to scalar equation. Finally, the following expression for the propagation constant was obtained [12]:

$$\beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad (1)$$

The conditions required for SPP waves coupling at the metal-dielectric interface are as follows [13]:

a) only TM polarization can trigger SPP waves. For this TM polarization, the electric field trigger oscillation of free electrons due to the electric field component perpendicular to the dielectric- metal interface.

b) the real permittivity of the metal (ε_{1r}) and dielectric (ε_2) are of opposite sign. They must satisfy the condition: Re $\{\varepsilon_{1r}\} < -\varepsilon_2$

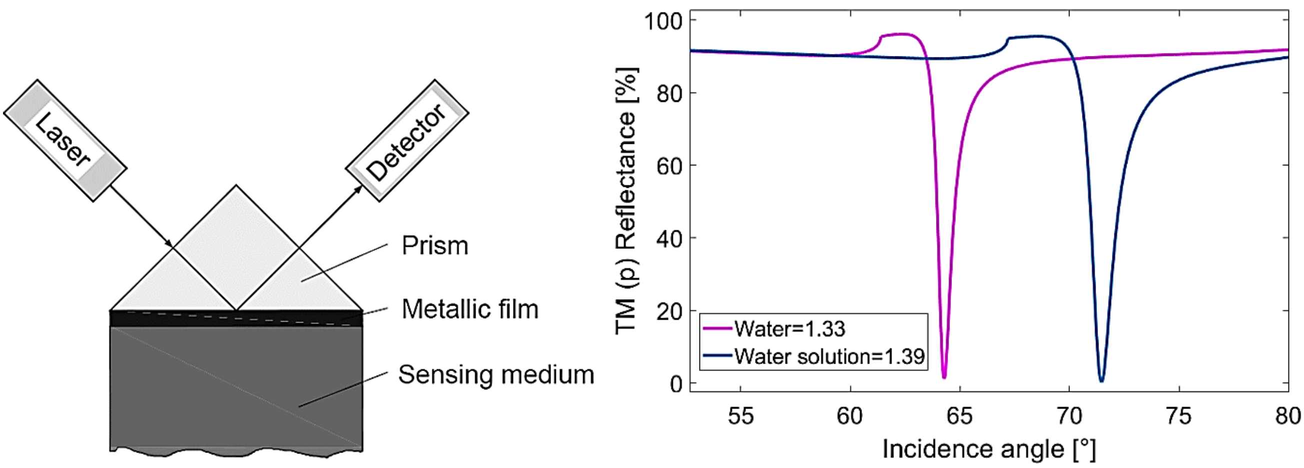
The electromagnetic fields decrease exponentially with distance from both interfaces. The depth of penetration is on the order of 250–300 nm in dielectrics (half of the wavelength approximate). In the metals the field penetration is on the order of 10–15 nm due to high absorption. So, a coupled state of plasmon-polariton and electromagnetic waves propagate along the metal-dielectric interface. The relative permittivity is generally calculated from the optical constants *n* and *k* as $\varepsilon(\omega) = (n - ik)^2$. Tabulated values for the optical constants are given in Handbook of Palik [15], [16]. From this data the dielectric constants, which are complex one, can be calculated.

The analyses concept presented above lead to the formula for plasmon propagation constant β. To excite the SPP waves, the phase-matching conditions for energy and momentum must be fulfilled. Since the propagation constant β is greater than the wave vector k of the light in the dielectric, the realization of phase-matching conditions is not a trivial problem. Kretschmann and Raether [1] demonstrated that phase-matching conditions can be achieved by using a thin metal film in a three-layer configuration. In this configuration, the top semi-infinite medium is made of a dielectric with the refractive index higher than the bottom one and SPP wave can be excited at the bottom metal interface via the evanescent waves. Fig.1(a) presents a three layers structure with BK7 glass with refractive index 1.51 (the coupling prism) at the top, and water or water solutions. The water refractive index as ambient medium was considered equal to 1.33. Other chemicals dissolved in water can only lead to an increase in the refractive index.

The resonance conditions require that the propagation constant β (Equation (1)) must be equal to the propagation constant of light tangential to surface:

$$k_0 n \sin\theta = \beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad (2)$$

The incidence angle θ is measured against normal to interface. The angle of incidence calculated with respect to the normal of the structure is very high, around 70-75 degrees (see Fig. 1b) if the ambient medium is water. In the case of contact with air, the angle is smaller, but still exceeds 45^0. Due to phenomenon of refraction, it is necessary to use a symmetrical prism with the base angle chosen so that the laser beam falls approximately normal to the side surface. The experimental curves correspond very well to the calculated ones.



(a) (b)

Fig. 1. Three-layers SPR configuration (a) and (b the calculated resonance curves. Gold of 50 nm thickness was used as metallic film. Interrogation wavelength was chosen to be 940 nm.

3. Multilayer SPR structures: the calculation procedure in short

For multilayers configuration it is not possible to obtain explicit solution for the reflectivity. The reflectivity can be obtained for the general *N*-layer case in terms of characteristic transfer matrices. Following [17] we can write:

$$\begin{bmatrix} H_0 \\ E_0 \end{bmatrix} = M1 \cdot M_2 \cdot M_3 \cdots M_N \cdot \begin{bmatrix} H_N \\ EV_N \end{bmatrix} \quad (3)$$

Calculations may be performed for both p and s polarizations. The following notations are used:

$$\beta_{pj} = \left(\frac{2\pi \cdot d_j}{\lambda}\right) \cdot \sqrt{e_{pj} - \left(n_{p1} \cdot \sin\theta\right)^2}$$

$$\beta_{sj} = \left(\frac{2\pi \cdot d_j}{\lambda}\right) \cdot \sqrt{e_{sj} - \left(n_{s1} \cdot \sin\theta\right)^2} \quad (4)$$

In the above notations *s, p* designates the polarization, while *j* is the layer's number. For each layer number *j*, the transfer matrices M_{pj} and M_{sj} are calculated:

$$M_{pj} = \begin{bmatrix} \cos\left(\beta_{pj}\right) & -i \cdot \sin\left(\beta_{pj}\right) / q_{pj} \\ -i \cdot \sin\left(\beta_{pj}\right) \cdot q_{pj} & \cos\left(\beta_{pj}\right) \end{bmatrix}$$

$$M_{sj} = \begin{bmatrix} \cos\left(\beta_{sj}\right) & -i \cdot \sin\left(\beta_{sj}\right) / q_{sj} \\ -i \cdot \sin\left(\beta_{sj}\right) \cdot q_{sj} & \cos\left(\beta_{sj}\right) \end{bmatrix} \quad (5)$$

The matrix for the first layer has the form: $M_{p0}=M_{s0} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$

Next, the full transfer matrices T_p and T_s are calculated:

$$T_p = \prod_{j=0}^{N} M_{pj} \, , T_s = \prod_{j=0}^{N} M_{sj} \quad (6)$$

By following these transformations, the reflectance R_p and R_s then can be calculated as:

$$R_p = \left| \frac{\left(T_p(0,1) \cdot q_{pN} + T_p(0,0)\right) \cdot q_{p1} - \left(T_p(1,1) \cdot q_{pN} + T_p(1,0)\right)}{\left(T_p(0,1) \cdot q_{pN} + T_p(0,0)\right) \cdot q_{p1} + \left(T_p(1,1) \cdot q_{pN} + T_p(1,0)\right)} \right|$$

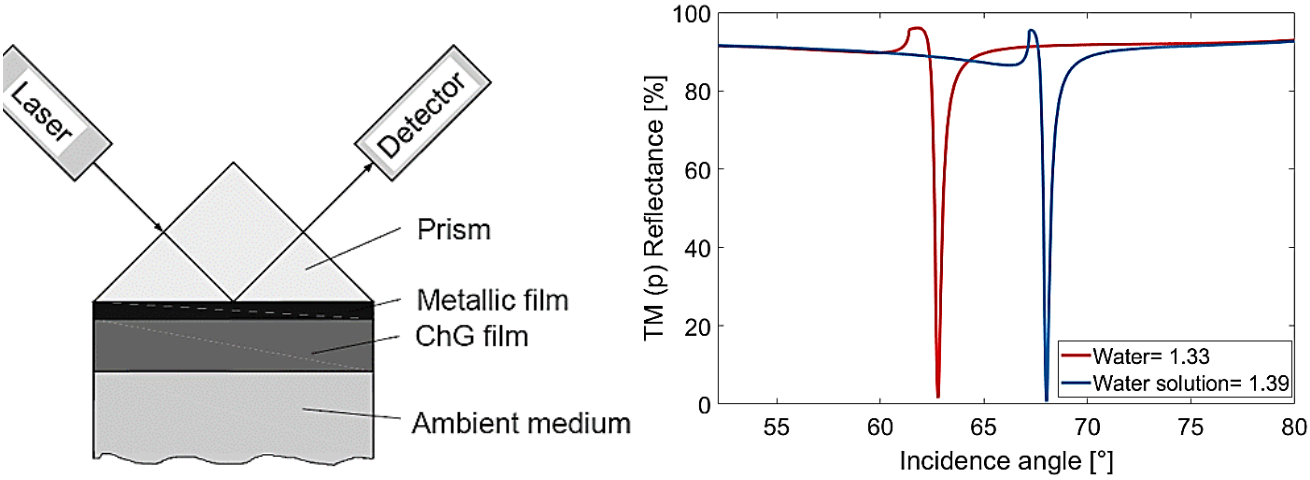
$$R_s = \left| \frac{\left(T_s(0,1) \cdot q_{sN} + T_s(0,0)\right) \cdot q_{s1} - \left(T_s(1,1) \cdot q_{sN} + T_s(1,0)\right)}{\left(T_s(0,1) \cdot q_{sN} + T_s(0,0)\right) \cdot q_{s1} + \left(T_s(1,1) \cdot q_{sN} + T_s(1,0)\right)} \right| \quad (7)$$

Computations for SPR reflectance curves were realized by using scripts developed in MATLAB.

4. Four layers SPR configuration features

The plasmonic resonance structure proposed by Kretschmann was developed and found applications as newest photonic devices. Several companies have realized and commercialized successful optical sensors based on SPR. These conventional schemes basically represent a three-layer configuration: a) the semi-infinite prism made of oxide glass; b) gold film with a thickness of 40-50 nm; (c) the ambient environment, which represents solutions of various chemicals in water.

The properties of a plasmonic resonant structure can change drastically if a thin film of high refractive index is deposited on the metallic film. The structure is transformed into a four-layer configuration, which contains a transparent dielectric film as a waveguide (Fig. 2(a)). It consists of Prism glass - gold film - chalcogenide film - ambient medium. The refractive indices and film thicknesses are parameters that ultimately determine the sensitivity of sensors. The shape of resonance curves with amorphous chalcogenide films of thickness 450 nm is presented in Fig. 2 (b). The curves are sharper than those obtained in conventional structures without a chalcogenide film. Amorphous chalcogenide materials are good candidate for this purpose because they can be deposited on a wide range of substrates. In addition, the nonlinear effects and the photoinduced change of refractive index known in these materials may lead to the development of new photonic devices [18-20]. The incorporation of these materials in any resonant structure, but also SPR, leads to considerable amplification of the effects of interaction with light.



(a) *(b)*

Fig. 2. Four layers SPR for sensing the ambient medium. a) SPR structure; b) The shift of the resonance curve for 0.5% of water refractive index change with amorphous As_2S_3 thin film of thickness 450 nm. Interrogation wavelength is 940 nm. Gold thin film of thicknesses 40 nm was used as metal

The influence of salinity on the refractive index can be deduced from the following data found in [20]. The following refractive indices as function of salinity were founded: 1.3184 (salinity 0%); 1.3205 (salinity 10%); 1.3224 (salinity 20%); 1.3244 (salinity 30%); 1.3263 (salinity 40%). Data are on 18^0C and extrapolated at 940 nm. The calculated resonances are shown in Fig. 3.

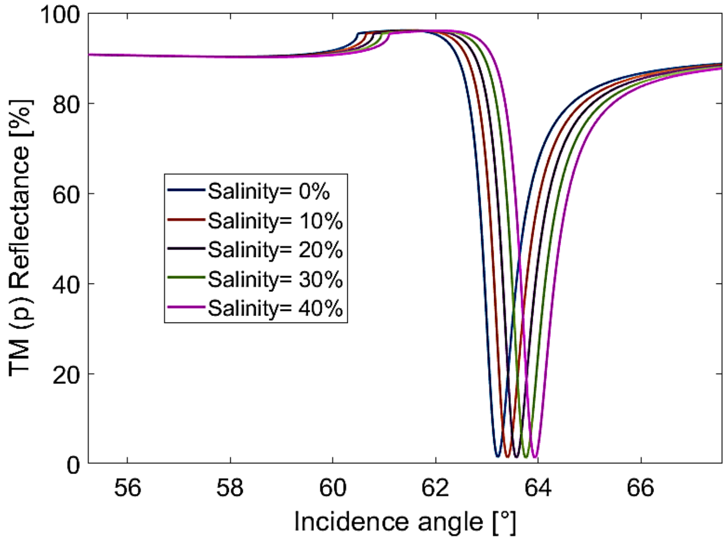


Fig. 3. Four layers SPR configuration. The SPR resonance curves for water solutions of different salinity. The As_2S_3 thin film was of thickness 450 nm and 940 nm probe beam.

Sensitivity S can be defined as the shift of the resonance angle Θ *vs* ambient media refractive index changes ΔN: $S=\Delta\Theta/\Delta N$. Sensitivity can be measured in Degree/Refractive index units (RIU). The resonance curve halfwidth influences also the sensor's capacity to distinguish the analyzed ambient media. So, the measure of $S/\delta = Q$ serves as sensor's quality factor. The data are presented in the Table 1.

Table 1. Comparative characteristics of SPR optical sensors

No.	SPR configuration	Sensitivity S, deg/RIU	Q-factor
1.	Conventional 3-layers SPR	15.5	0.28
2.	SPR with amorphous As_2S_3 thin film, thickness of 800 nm. Probe beam was of 940 nm.	4.07	0.27
3.	SPR with amorphous As_2S_3 thin film, thickness of 450 nm. Probe beam was of 940 nm.	5.94	0.59

5. Conclusions

The resolving power depends generally on registration schematic and usually 0.1% intensity changes is achieved in the differential set up measurements. With this admittance, we estimate the sensitivity to the refractive index of 10^{-4}-10^{-5}. The parameters of three-layers conventional SPR sensor depend on the metal optical constants. In the four-layers configuration the sensor's parameters depend also on the thin film thickness and can be improved (to see Table 1). The studied SPR configuration opens up new opportunities to realize label-free optical chemical sensors.

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