Theoretical model of the oxide overlayer thickness influence on performance of surface plasmon fibre-optic sensor

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Abstract. Fibre-optic surface plasmon resonance (SPR) sensors have been proven to be useful tool in various measurement tasks where the miniaturization, compactness and low are the essential requirements. Recently, it has been shown that the sensitivity of SPR sensor can be improved if the metallic layer used for surface plasmon excitation is covered by a high refractive index overlayer (for example oxide or semiconductor). The semiconductor layer can protect the metal against the oxidation, but when it is exposed to the atmosphere, a thin oxide layer can be formed on its top surface. This fact leads to a general question, how an oxide layer (naturally or thermally grown) affects the sensing. The paper deals with the influence of the oxide layer on the sensor performance. The analyzed structure consists of thin gold film covered by partially oxidized silicon overlayer. The presented theoretical model of the fibre-optic SPR sensor is based on optics of multilayered media and optical dispersion of all involved media is taken into account. The influence of oxide layer thickness change on the sensor performance in wavelength domain is studied in detail. The computation of optical power transmitted through the sensing part of a multimode fibre is carried out in order to evaluate the response of the sensor in terms of sensitivity and detection accuracy.

Keywords: surface plasmon resonance, dispersion, optical fibre, fibre-optic sensor

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1. Introduction

The concept of optical sensing of various physical, chemical and biological quantities
based on surface plasmon resonance phenomenon [1, 2] has been proved to be very useful
during last four decades. Surface plasmons are electromagnetic excitations propagating
along the boundary between metal and dielectric material. Instead of metal, other
lossy media with sufficiently high density of free electrons can be considered. Such
waves can be excited only by p-polarized incident wave. Their electromagnetic fields
decay exponentially in the direction perpendicular to the boundary [3]. When a specific
resonance condition is fulfilled, maximum power of the incident wave can be coupled to
the surface plasma oscillations and the power carried by reflected wave drops down. The
resonance condition is sensitive to the value of surrounding medium (analyte) refractive
index. This mechanism gives the possibility to sense the properties of the surrounding
medium (usually liquid or gas) via the change of its refractive index, observing the shift
of the power reflectance minimum.

The early sensing setups were based on the use of optical prisms. The surface
plasmons were excited in the metallic film by attenuated total reflection (ATR)
mechanisms. The prism itself played the role of a coupling device between the evanescent
wave excited on its base and the surface plasmon under the condition that the light
beam incident angle exceeds its critical value $\theta_c$. The evanescent wave passes through
the thin metal film and the surface plasmons are excited at film lower boundary where
the metal is in contact with investigated analyte. The measurement is usually performed
in angular domain. Even if the devices based on prism coupling exhibit high sensitivity
and accuracy, they are rather bulky and expensive, so they are mostly used in laboratory
conditions. In order to overcome the mentioned disadvantages and push the SPR sensing
technology toward the industrial conditions, the use of mature optical fibre technology
is a natural choice. Sharing the same coupling mechanism based on internal total
reflection, the prism coupler can be replaced by a bare optical fibre core covered by a
thin metal layer. Because it is not possible to perform the detection in angular domain
as in the case of prism-based devices, the SPR fibre-optic sensors are operated in spectral
domain observing the resonance wavelength shift.

In the beginning, the first SPR sensing structures were based on silver or gold layers
mostly, because these metals exhibit sufficiently high free electron density essential for
effective excitation of surface plasmon. Beside this, the attempt to use other metals
as for example copper or aluminum were reported too [4]. Even if the structure based
on silver film is more sensitive, gold is still in favour because it offers better chemical
stability. The performance of the sensor using the other metals can be influenced by
unwanted oxide layer formed at the boundary exposed to the atmosphere. In order to
avoid such degradation, the metal layer has to be protected by some overlayer [5]. It
was proved that the introduction of an overlayer can extend the operational range of the
sensor [6, 7]. Recently, the usage of the Si overlayer deposited on top of the golden SPR
film was reported [8]. The influence of such a protection layer leads to considerable red
shift of the resonance wavelength. The sensitivity of the reported structure was increased as well. However, the outer boundary of the protection layer, which is in contact with the atmosphere or analyte, can be oxidized too. The growth of native oxide layers on silicon substrates has been thoroughly studied (as an unwanted effect mostly) for the purposes of semiconductor industry [9, 10]. Our contribution deals with the case when the protective silicon layer is the subject of naturally or thermally induced oxidation. The thickness of naturally formed oxide layer was reported to be smaller than 1 nm [11], thicker protection layers can be grown by thermal oxidation [12]. The influence of the oxide layer thickness on the performance of such sensing structure is numerically simulated and discussed.

2. Theoretical background

2.1. Principle of the sensing setup based on SPR

The schematic drawing of fibre-optic SPR sensor structure is depicted in the left part of figure 1. The sensing part consists of a five-layer system. The bare core of a multimode fibre (MMF) is covered by thin Au layer protected by high refractive index silicon overlayer. The Si layer is the subject of atmospheric or thermally induced oxidation causing the forming of a thin SiO$_2$ film. The outer boundary of that film is then in contact with the investigated analyte. In order to keep clear insight into the physics of the sensor, the real cylindrical structure is approximated by equivalent thin film system in Kretschmann’s configuration (see the right part of figure 1). The numerical simulation based on the mentioned approximation can be then performed in the frame of optics of layered media. The power carried by optical wave incident from within the fibre core can be coupled into the surface plasmon wave (SPW) if the tangential components of its wavevector $k_t$ matches the wavevector $k_{sp}$ of the SPW. The phase-matching condition

![Figure 1: Schematic drawing of an optical fibre SPR sensor (left), equivalent thin film structure (right) used for computation.](image-url)
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can be expressed as

\[ n_1(\lambda) \sin \theta = \text{Re} \left[ \sqrt{\frac{\varepsilon_2(\lambda)\varepsilon_3(\lambda)}{\varepsilon_2(\lambda) + \varepsilon_3(\lambda)}} \right], \]

(1)

where \( n_1 \) is the refractive index of the fibre core, \( \theta \) is the angle of incidence and \( \varepsilon_2, \varepsilon_3 \) are the relative permittivities of the metal layer and the Si overlayer. To calculate the power transmitted through the sensing part of the fibre, it is necessary to know how to compute the reflection coefficient for the wave incident from the fibre core on the multilayered sensing structure. One way is to use Airy’s formula [13] recursively in the computation process. At first, the complex reflection coefficient of the five-layer structure is represented by the expression obtained for a three-layer structure with 'effective' lower boundary

\[ r_{12345}(\lambda, \theta) = r_{12}(\lambda, \theta) + r_{\text{eff}}(\lambda, \theta) \exp\left[i2k_{z,2}(\lambda, \theta)t_2\right] \frac{1 + r_{12}(\lambda, \theta)r_{\text{eff}}(\lambda, \theta) \exp\left[i2k_{z,2}(\lambda, \theta)t_2\right]}{1 + r_{12}(\lambda, \theta)r_{\text{eff}}(\lambda, \theta) \exp\left[i2k_{z,2}(\lambda, \theta)t_2\right]}, \]

(2)

where \( r_{12} \) is the reflection coefficient (given by appropriate Fresnel formula) on the upper boundary of the gold layer, \( 2k_{z,2}(\lambda, \theta)t_2 \) represents the phase shift introduced during the propagation through the gold layer and \( r_{\text{eff}} \) is the reflection coefficient on lower 'effective' boundary of the layer represented by four-layer system Au-Si-SiO\(_2\)-analyte. That coefficient can by expressed using the coefficient \( r_{23} \), phase shift \( 2k_{3,z}(\lambda, \theta)t_3 \) and \( r_{345} \). The procedure is repeated, till the bottom of the structure is reached. An alternative way is to use a matrix formalism [13]. If the phase matching condition (1) is fulfilled, then the power reflectance \( R(\lambda, \theta) \), given as the squared modulus of a complex reflection coefficient according to equation (2), drops to its minimum value (dip). Because the SPR fibre-optic sensors are operated in spectral domain, the position of the dip at a specific resonance wavelength \( \lambda_r \) and its shift is observed. The dip position and its shape are very sensitive to the changes of refractive index of the investigated analyte.

2.2. Computation of power transfer

2.2.1. General considerations  As in the other cases of fibre-optic sensors, the change of the monitored quantity is finally converted into the change of the power transmitted through the fibre sensing part - see figure 1. The fibre-optic sensors constructed using single-mode fibres exhibit better characteristics than the ones based on MMFs [14], but the task of coupling or decoupling of the light into and out of the MMF-based sensor is easier. That is why the above described sensing scheme is based on MMF. The light from a polychromatic source is coupled into the input end of the fibre where typically a hundreds of modes are guided simultaneously, and the spectrum of the transmitted power \( P_t(\lambda) \) is recorded at the output end. Under such conditions, the surface plasmon resonance takes place for each of the modes separately [see the left-hand side of equation (1)], but at the output the overall transmitted power is detected. This fact has to be included into a correct calculation of the transferred power. In other
words, the angular distribution of the power among the guided modes has to be specified. The shape of it depends on the radiation properties of the used light source. Two cases are distinguished: excitation by a diffuse source and excitation by a collimated beam focused on the input end of the fibre using some type of launching optics (microscope objective for example). Considering the above described facts, it is more correct to use the position \( \lambda_D \) of the dip bottom in spectral domain than the commonly referred SPR resonance wavelength \( \lambda_r \) given by equation (1).

The amount of the power transmitted through the sensing part of the fibre is influenced by the number of reflections \( N_{\text{ref}} \) the rays undergo in that region. When an optical beam is focused on the centre of an optical fibre core and its axis coincides with the axis of the fibre, the number of reflections can be expressed as

\[
N_{\text{ref}} = \frac{L}{D \tan \theta},
\]

where \( L \) is the length of the sensing region (see figure 1), \( D \) is the fibre core diameter and \( \theta \) is the angle of incidence within the fibre core. Under the mentioned conditions, only the meridional rays are excited. For the sake of clarity, we treat this case in subsequent computation. The power \( P_t \) transmitted through the sensing part can be then given as

\[
P_t \propto (R)^{N_{\text{ref}}},
\]

where \( R \) is the power reflectance. In the case of optical fibre, the minimum value for \( \theta \) equals to the critical angle \( \theta_c \) given by the refractive indices of the core and cladding materials.

### 2.2.2. Excitation by focused beam

In order to keep clear insight into the physics of the sensing scheme only the meridional rays are included into the analysis although the case when the skew rays are involved can be addressed in the frame of planar optics as well [15]. Commonly used MMFs support a vast number of guided modes, so it is reasonable to treat them as mode ‘continuum’. Then the distribution carried power among the guided modes can be considered in the frame of planar optics approach as a continuous function depending on the angle of incidence. Using this approach, the power contribution \( dP \) related to the angular interval \( (\theta, \theta + d\theta) \) can be expressed as [16]

\[
dP \propto \frac{n_1^2 \sin \theta \cos \theta}{(1 - n_1^2 \cos^2 \theta)^2} d\theta.
\]

If the power transfer through the sensing fibre core is to be correctly computed using the planar optics approach, not only the p-polarized component, but the s-polarized component contributes to the transmitted power too and its contribution should be taken into account. That is because of the cylindrical geometry of the fibre core. Finally, when the centrosymmetric focused beam is launched into the fibre under the condition that only the meridional rays are excited, the expression for the normalized power \( P_{\text{in}} \) at a specific wavelength \( \lambda \) at the end of the fibre sensing part is written in following
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The theoretical model of oxide layer influence on SPR sensor is given by the following equation:

\[
P_{\text{in}}(\lambda) = \frac{\int_{\theta_c(\lambda)}^{\pi/2} \frac{1}{2} [R_P^{\text{ref}}(\theta, \lambda) + R_S^{\text{ref}}(\theta, \lambda)] \frac{n_1^2(\lambda) \sin \theta \cos \theta}{(1 - n_1^2(\lambda) \cos^2 \theta)^2} d\theta}{\int_{\theta_c(\lambda)}^{\pi/2} \frac{n_1^2(\lambda) \sin \theta \cos \theta}{(1 - n_1^2(\lambda) \cos^2 \theta)^2} d\theta}.
\]

(6)

The numerator is related to the power carried by the outgoing modes at the output end of the sensing part (see the left part of figure 1), and the denominator represents the total incoming power at the beginning of the sensing part. The reflectances \( R_s \) and \( R_p \) are related to both polarization components, though only the p-polarized component is influenced by SPR phenomenon. The equation (6) plays key role in our computations.

2.3. Dispersion of materials

Because the fibre-optic SPR sensors are operated in spectral domain, the knowledge of dispersion of all materials involved in the model computations has to be taken into account.

2.3.1. The fibre core

The presented sensing structure scheme is based on the optical fibre whose core is made of pure silica. The dispersion properties of pure silica are described by well-known three-term Sellmeier formula

\[
n_1^2(\lambda) = 1 + \sum_{i=1}^{3} \frac{A_i \lambda^2}{\lambda^2 - B_i},
\]

(7)

where \( \lambda \) is the wavelength in \( \mu \text{m} \) and \( A_i, B_i \) are the Sellmeier coefficients. Their values according [17] are: \( A_1 = 0.6961663, A_2 = 0.4079426, A_3 = 0.8974794, B_1 = 0.0684043, B_2 = 0.1162414 \) and \( B_3 = 9.896161 \).

2.3.2. The metal SPR layer

As to the metal layer used for excitation of SPR, gold is the favoured material, so a thin golden film it was considered in our model. Usually the dielectric function of the gold is expressed by a Drude model only. In order to obtain more exact results, an analytical Kramers-Kronning consistent model based on the critical point analysis, was used [18]. The frequency-dependent optical properties of gold are described by a three-term analytic formula. Besides the Drude term, there are two additional terms related to interband transition. The wavelength-dependent complex dielectric function of gold is then expressed by following equation

\[
\varepsilon_{\text{Au}}(\lambda) = \varepsilon_{\infty} - \frac{1}{\lambda^2 (1/\lambda^2 + i/\gamma_p \lambda)} + \sum_{j=1}^{2} \frac{A_j}{\lambda_j} \left[ \frac{e^{i\phi_j}}{1/\lambda_j - 1/\lambda - i/\gamma_j} + \frac{e^{-i\phi_j}}{1/\lambda_j + 1/\lambda + i/\gamma_j} \right].
\]

(8)

The parametric fit of this equation was performed to the most often used data set for the optical properties of gold coming from a paper by Johnson and Christy [19]. The parameters obtained from that fit [18] are summarized in table 1, where the wavelength is considered in nanometers. The equation (8) describes the dispersion of Au optical


Table 1: Parameters for computation of dielectric function of Au from [18].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
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<tr>
<td>$\varepsilon_\infty$</td>
<td>—</td>
<td>1.53</td>
<td>$A_1$</td>
<td>—</td>
<td>0.94</td>
<td>$A_2$</td>
<td>—</td>
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</tr>
<tr>
<td>$\lambda_p$</td>
<td>nm</td>
<td>145.0</td>
<td>$\lambda_1$</td>
<td>nm</td>
<td>468.0</td>
<td>$\lambda_2$</td>
<td>nm</td>
<td>331.0</td>
</tr>
<tr>
<td>$\gamma_p$</td>
<td>nm</td>
<td>17000.0</td>
<td>$\gamma_1$</td>
<td>nm</td>
<td>2300.0</td>
<td>$\gamma_2$</td>
<td>nm</td>
<td>940.0</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>rad</td>
<td>—</td>
<td>$\phi_2$</td>
<td>rad</td>
<td>$-\pi/4$</td>
<td>$\phi_2$</td>
<td>rad</td>
<td>$-\pi/4$</td>
</tr>
</tbody>
</table>

Table 2: The coefficients for computation of optical properties of poly-Si.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_n$</td>
<td>$-0.0665012$</td>
<td>$A_k$</td>
<td>$-0.0526153$</td>
</tr>
<tr>
<td>$B_n$</td>
<td>$3.5793596$</td>
<td>$B_k$</td>
<td>$0.1706010$</td>
</tr>
<tr>
<td>$C_n$</td>
<td>$-0.0552960$</td>
<td>$C_k$</td>
<td>$-0.1879841$</td>
</tr>
<tr>
<td>$D_n$</td>
<td>$0.1073835$</td>
<td>$D_k$</td>
<td>$0.0859321$</td>
</tr>
<tr>
<td>$E_n$</td>
<td>$-0.0204809$</td>
<td>$E_k$</td>
<td>$-0.0143556$</td>
</tr>
<tr>
<td>$F_n$</td>
<td>$0.0019208$</td>
<td>$F_k$</td>
<td>$0.0010763$</td>
</tr>
</tbody>
</table>

parameters with accuracy suitable for model computation within the spectral range from 300 to 1000 nm and it was used for the extrapolation toward the longer wavelengths.

2.3.3. High-index dielectric layer  In order to increase the sensitivity of the proposed setup, the structure contains an overlayer with high value of refractive index covering the SPR gold layer. In [8] the Si layer prepared by sputtering process was reported. In presented model, the polycrystalline character of such a layer is supposed. Because no suitable dispersion formula for polysilicon was found, the data from http://www.refractiveindex.info (SOPRA:polysilicon 2) were used and a parametric fit to modified Cauchy’s dispersion equation was performed. The dispersion equations for the real and imaginary part of refractive index of poly-Si (based on Laurent series) are expressed as

$$n(\lambda) = A_n \lambda^2 + B_n + \frac{C_n}{\lambda^2} + \frac{D_n}{\lambda^4} + \frac{E_n}{\lambda^6} + \frac{F_n}{\lambda^8}$$

$$k(\lambda) = A_k \lambda^2 + B_k + \frac{C_k}{\lambda^2} + \frac{D_k}{\lambda^4} + \frac{E_k}{\lambda^6} + \frac{F_k}{\lambda^8}.$$  \hspace{1cm} (9)

where $\lambda$ is assumed to be the wavelength in µm. The values of the coefficients obtained from the fit are summarized in table 2. The proposed formulae represent well the mentioned data sets and they can be used within the wavelength range from 400 nm to 1200 nm.
2.3.4. Oxide layer  The metal layer used for excitation of surface plasmons can be covered by an overlayer in order to prevent the unwanted interaction with the surrounding media. After the protection layer is deposited, the outer boundary of that protective layer is exposed to the atmosphere and the thin oxide film can be formed by natural oxidation process [11, 20]. Thicker protection oxide layers can be formed by thermal oxidation [12, 21]. The presence of the oxide layer inevitably influences the response of the fibre-optic sensing structure, so it is necessary to know the dispersion of SiO$_2$. The refractive index of this material can be approximated by simplified Sellmeier formula [22]

$$n^2(\lambda) = 1 + \frac{A\lambda^2}{\lambda^2 - B^2},$$

(10)

where the coefficients take the values $A = 1.1336$ and $B = 9.261 \times 10^{-2}$. The wavelength is expressed in micrometers. The formula (10) was suggested for the description of refractive index dispersion in the range from 230 nm to 840 nm and its use was extended up to 950 nm.

2.3.5. Dispersion of the analyte  The dispersion of the analyte naturally depends on its composition. As to the presented model computation, a binary mixture of miscible liquids is considered. In such a case, the refractive index $n(\lambda)$ of the mixture can be obtained using Lorentz-Lorenz [23] equation

$$\frac{n^2(\lambda) - 1}{n^2(\lambda) + 2} = \left(\frac{n_a^2(\lambda) - 1}{n_a^2(\lambda) + 2}\right) \frac{\varrho_a}{\varrho} w_a + \left(\frac{n_b^2(\lambda) - 1}{n_b^2(\lambda) + 2}\right) \frac{\varrho_b}{\varrho} w_b.$$

(11)

The symbols $n_a(\lambda), n_b(\lambda)$ denote the refractive indices and $\varrho_a, \varrho_b$ are the densities of both components, $\varrho$ refers to the density of the mixture. The contents of both compounds are expressed using their appropriate mass fractions $w_a$ and $w_b$. The mass fractions obey the condition $w_a + w_b = 1$. As a model case of an analyte, the aqueous solution of ethanol [24] was considered in following computations.

Pure ethanol was considered to be the solute. According to [25], its refractive index wavelength dependence can be expressed by Cauchy’s dispersion equation

$$n(\lambda) = C_1 + \frac{C_2}{\lambda^2} + \frac{C_3}{\lambda^4},$$

(12)

where $\lambda$ is the wavelength expressed in micrometers. The coefficient values are: $C_1 = 1.35265$, $C_2 = 0.00306$ and $C_3 = 0.00002$. The suggested formula describes the refractive index spectral dependence of ethanol in a range from 400 nm to 800 nm at the temperature of 20°C and it was used for extrapolation to longer wavelengths when necessary. At that temperature, the density of ethanol used in computation was $\varrho_a = 0.7893 \text{ g/cm}^3$[26].

Distilled water was chosen to be the solvent. Various model functions describing its dispersion can be found in the literature, in our computations four-term Sellmeier relation [27] was used

$$n^2(\lambda) = 1 + \sum_{i=1}^{4} \frac{A_i\lambda^2}{\lambda^2 - C_i},$$

(13)
where the coefficients are: $A_1 = 5.684027565 \times 10^{-1}$, $A_2 = 1.726177391 \times 10^{-1}$, $A_3 = 2.086189578 \times 10^{-2}$, $A_4 = 1.130748688 \times 10^{-1}$, $C_1 = 5.101829712 \times 10^{-3}$, $C_2 = 1.821153936 \times 10^{-2}$, $C_3 = 2.62072293 \times 10^{-2}$ and $C_4 = 10.69792721$. The wavelength is in $\mu$m. The formula can be used for $\lambda \in (0.182, 1.129) \mu$m, the values of the coefficients were obtained for the temperature of $20^\circ$C. At that temperature, the appropriate density of water used in computation was $\varrho_b = 0.9982$ g/cm$^3$ [26].

3. Results and discussion

Numerical simulations were carried out for the model case of a fibre-optic SPR sensing structure based on a step-index multimode fibre. The low-OH optical fibre (Thorlabs, BFL22-200) with numerical aperture $NA = 0.22$ was considered. The proposed sensing structure is comprised of pure silica bare fibre core covered by thin layer of gold with the high-refractive index layer consisting of Si on the top of it. The outer boundary of the silicon protective layer can become the subject of either natural [11, 20] or controlled [12] oxidation process, therefore a realistic model of such a sensor has to be based on five-layer thin-film structure (see the right part of figure 1). The length of the sensing part was chosen as $L = 1$ cm and the fibre diameter was $D = 200 \mu$m. For this fibre, the normalized frequency (the $V$ parameter - see [28]) in the case of the ‘worst’ considered wavelength $950$ nm is $\approx 146$. That leads to approximately $8500$ modes in the fibre. Such a number of modes approves the usage of equation (6) for the computation of normalized power transfer.

The analysis of SPR fibre-optic sensor response is usually performed with respect to the analyte refractive index change. To push the simulations toward more realistic conditions, ethanol-water mixture was chosen as the analyte because ethanol is an important ingredient either in food or chemical industry, or in application where it is considered as an alternative fuel. Whereas in the beverage industry it is necessary to monitor the appropriate concentration of ethanol in water [24], the fuel production requires detection of low water content in the ethanol [29]. In our computation, variable mass content of ethanol was used to control the refractive index of the mixture. The ethanol concentration is expressed by its mass concentration $c_{Eth} = 100 \times w_{Eth}$ in mass%, where $w_{Eth}$ is the appropriate mass fraction used in equation (11) for mixture refractive index calculation. The necessary information about the density of the analyte depending on the ethanol mass concentration in water was taken from the data set freely available at http://us.mt.com. In order to achieve sufficient accuracy in the refractive index computation using equation (11), the 6-th degree approximation polynomial has to be used. The normalized power transferred through the sensing part of the fibre was computed using equation (6).
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Figure 2: Optimization of Au layer thickness $t_2$, silicon layer thicknesses $t_3 = 5, 7, \text{ and } 10 \, \text{nm}$, no oxide layer.

Figure 3: Parameters used for description of SPR spectral dip shape and definition of detection accuracy.

3.1. SPR layer thickness optimization

At first the optimization of gold layer thickness was performed for the case when no oxide layer was present. The computation was carried out for the values of silicon protective overlayer thickness $t_3 = 5, 7 \text{ and } 10 \, \text{nm}$. The aim was to find the value $t_2$ related to the lowest $P_{tn}(\lambda_D)$ at the dip bottom position. Because the shape and the position of the dip depends on the ethanol concentration in the mixture, the optimization was performed for its two limiting values defining the operational range of the sensor: $c_{\text{Eth}} = 0$ (pure water), and $c_{\text{Eth}} = 75 \, \text{mass}\%$.

Concerning the ethanol-water mixture, both liquids are completely miscible from the macroscopic point of view. Nevertheless, evident signs of non-miscibility having their origin in microscopic scale interactions have been reported [30]. The results is that the refractive index of the mixture increases with the increasing ethanol concentration at first, exceeding even the refractive index of pure ethanol, and then it decreases to the pure ethanol refractive index [31]. Such a behaviour can be explained as the manifestation of intermolecular interactions as molecular segregation and cluster formation [32], and it influences the density of the mixture. Subsequently the refractive index of the mixture calculated using equation (11) is affected via the density behaviour. The maximum of mixture refractive index appears at about $c_{\text{Eth}} \approx 78 \, \text{mass}\%$ [32], so the upper concentration limit used for the optimization of gold layer thickness was chosen as the mentioned $c_{\text{Eth}} = 75 \, \text{mass}\%$.

The computation of $P_{tn}(\lambda_D)$ curves with respect to the gold layer thickness $t_2$ for all combination of the mentioned thicknesses $t_3$ and $c_{\text{Eth}}$ limiting values revealed that the positions of $P_{tn}(t_2, \lambda_D)$ minima are scattered over the interval from 0 to 22 nm when $t_2 < 25 \, \text{nm}$. It means, that for Au layer thicknesses smaller than 25 nm the optimization
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is reasonable only for individual values of \( t_3 \). Moreover, the positions of minima are sensitive to the ethanol concentration too. In order to find one suitable value of \( t_2 \) and thus keep clear insight into the physics of the model, the optimization was performed for \( t_2 \in (30, 50) \) nm. The resulting curves are depicted in figure 2 together with appropriate minimum values (marked by \( \circ \)). It is clearly seen, that except for two cases related to pure water \( (t_3 = 5 \) and \( 7 \) nm), the other values of \( t_2 \) minimizing \( P_{tn}(\lambda_D) \) fall into the vicinity of 40 nm. Based on this result, the value of \( t_2 = 40 \) nm was chosen to be the optimum thickness of the Au layer. This value seems to be good trade-off fulfilling the mentioned criterion and it was used in all subsequent simulations.

3.2. Sensitivity, detection accuracy and figure of merit definition

The performance of the SPR sensors operated in spectral domain is usually evaluated in terms of sensitivity and detection accuracy. As for the sensitivity, this quantity is often defined with respect to the change of analyte refractive index expressed in refractive index units (RIU). However, when the dispersion of the analyte is taken into account, such definition seems to be questionable and the sensitivity definition related to the analyte composition is more proper. In our case, the sensitivity is expressed with respect to the change of the ethanol concentration \( c_{Eth} \) in the mixture

\[
S = \left| \frac{\delta \lambda_D}{\delta c_{Eth}} \right|, \quad (14)
\]

where \( \lambda_D \) is the position of the dip in the wavelength domain. Thus the sensitivity is the slope of the \( \lambda_D(c_{Eth}) \) curve and it is expressed in nm/mass\% instead of commonly used nm/RIU.

The other important parameter is the detection accuracy \( DA \). It is related to the shape of the SPR dip. As a measure of the dip width, the spectral width \( \Delta \lambda_{0.5} \) of the sensor response at 0.5 level of \( P_{tn}(\lambda) \) is often used [33]. The detection accuracy is then defined as \( DA = 1/\Delta \lambda_{0.5} \). However, numerical simulation revealed broad and shallow dips, where in some cases the 0.5 level of \( P_{tn}(\lambda) \) was not even reached. Therefore slightly different criterion was suggested and instead of \( \delta \lambda_{0.5} \) we introduced the spectral width \( \delta \lambda_{10} \) taken at \( 1.1 \times P_{tn}(\lambda_D) \) - see figure 3. The new detection accuracy \( DA_{10} = 1/\Delta \lambda_{10} \) is used in the rest of the paper.

The addition of the thin dielectric protective layer with high refractive index on top of the metal layer helped to improve the sensitivity [8], but the broadening of the dip leading to the detection accuracy decrease was reported as well. That is why the other parameter denoted as figure of merit (FOM) was introduced [34]. It combines the both above defined parameters and it is defined as the ratio between the sensitivity and the dip width

\[
FOM = \frac{S}{\Delta \lambda_{10}} = S DA_{10}, \quad (15)
\]

and it will be used as an additional parameter for evaluation of the performance of our proposed fibre-optic sensor.
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3.3. The influence of oxide layer thickness on sensor performance

The main objective of the work was to find out the influence of oxide layer formed on the top of Si overlayer on the performance of the SPR sensing structure. The computation was performed for three initial values of Si overlayer thickness $t_{3,\text{in}} = 5, 7, \text{and } 10 \text{ nm}$. The dependencies of various sensor parameters with respect to the increasing mass concentration of ethanol $c_{\text{eth}}$ were obtained for increasing thickness of the oxide layer.

The mechanism of oxide layer formation on the silicon surface has been thoroughly studied because of its importance in semiconductor industry [11, 12]. When the outer boundary of the silicon overlayer is exposed to the oxidation atmosphere, the growth of the oxide layer is accomplished by its thickness expansion with respect to the thickness of the silicon layer consumed in the process. This phenomenon can be described by the expansion factor $K = 100/44$ (44 nm of silicon consumed in the oxidation process yield 100 nm of oxide) - see [21]. In order to be able to compare the results related to different values of initial silicon layer thicknesses $t_{3,\text{in}}$, a dimensionless parameter $x = t_4/(t_3 + t_4)$ called relative oxide layer thickness was introduced. The appropriate layer thickness can be then obtained using the expressions

$$t_3(x) = \frac{K(1-x)t_{3,\text{in}}}{K + (1-K)x} \quad t_4(x) = \frac{Kt_{3,\text{in}}x}{K + (1-K)x} \quad \text{(16)}$$

At first, the parameters of the sensor with the thinnest initial silicon overlayer $t_{3,\text{in}} = 5 \text{ nm}$ were computed. The results are depicted in figure 4. The coverage of the golden SPR layer by silicon protective film results in the shift of the dip position $\lambda_D$ toward the red end of the spectra (see the dotted curve in figure 4a related to $x = 0$) with respect to the system without the overlayer where only Au film is present (solid curve in figure 4a). The formation of the oxide layer on the top of the overlayer leads to the blue shift of $\lambda_D(c_{\text{eth}})$ curves. This shift monotonically increases with the increase of relative oxide layer thickness $x$, as it is clearly seen in figure 4a, where the arrow direction denotes the growth of $x$ parameter values. In the same time the sensitivity $S(c_{\text{eth}})$ of the sensor is enhanced in comparison with the structure with Au layer only - see figure 4b. The growth of the oxide layer on expenses of the initial silicon layer thickness reduces the sensitivity. On the other hand, the thin film system related to $x = 0$ (without the oxide layer) exhibits the broadening of the SPR spectral dip resulting in the detection accuracy decrease. Here the trend is reversed - the thicker oxide layer, the higher detection accuracy (see figure 4c). For the ethanol content lower than 15% the detection accuracy is even better than the one related to the system with Au layer only. As to the $c_{\text{eth}} > 30\%$, the simple Au layer exhibits better values of detection accuracy. The overall performance of the sensing system described by figure of merit is depicted in figure 4d. It is clearly seen that the $FOM(c_{\text{eth}})$ curves shift monotonically with increasing $x$ parameter to the curve obtained for simple Au layer.

The increase of initial silicon layer thickness $t_{\text{Si,\text{in}}} = 7 \text{ nm}$ leads to higher values of the mentioned red shift, as can be observed in figure 5a. The trend of blue shift of dip position curves connected with $x$ value increase is now more pronounced. The sensitivity
Figure 4: Parameters of the sensor vs ethanol concentration in ethanol-water mixture for initial silicon layer thickness $t_{3,\text{in}} = 5 \text{ nm}$, the arrow direction denotes the relative oxide thickness increase. (a) dip position, (b) sensitivity, (c) detection accuracy, (d) figure of merit.

curves in figure 5b exhibit the same trend as in the previous case of $t_{3,\text{in}} = 5 \text{ nm}$, but the sensitivity is more enhanced. As in the previous case, the detection accuracy is reduced (see figure 5c), but it can be improved by the oxide layer growth. The overall performance of the sensing system is more or less the same, but it is not so sensitive to the growth of parameter $x$ now - compare the curves in figures 4d and 5d.

The highest values of the red shift of $\lambda_D(c_{\text{Eth}})$ curves were obtained for the thickest silicon protective overlayer whose initial thickness was $t_{3,\text{in}} = 10 \text{ nm}$. The results are depicted in figure 6a. The dip position is shifted by approximately 200 nm for pure water with respect the value related to single Au layer. The shift increases with the ethanol...
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Figure 5: Parameters of the sensor vs ethanol concentration in ethanol-water mixture for initial silicon layer thickness $t_{3,\text{in}} = 7$ nm, the arrow direction denotes the relative oxide thickness increase. (a) dip position, (b) sensitivity, (c) detection accuracy, (d) figure of merit.

content in the structure. Such a trend, observed for all values of $t_{3,\text{in}}$, has its origin in the increase of analyte refractive index growing with ethanol content in the mixture in the range of $c_{\text{EtOH}} \in (0, 75\%)$. The sensitivity enhancement is further pronounced comparing to the previously analysed cases (compare the appropriate curves in figure 4b, 5b and 6b). The highest sensitivity is obtained for the thin-film system without any oxidation layer ($x = 0$). The growth of the oxide layer deteriorates the sensitivity - see figure 6b. On the other hand, the detection accuracy exhibit a reverse trend, as can be seen in figure 6c. The overall sensor performance, depicted in figure 6d looks almost insensitive to the relative oxide thickness (at least for $x < 0.75$). It means that the sensitivity
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Figure 6: Parameters of the sensor vs ethanol concentration in ethanol-water mixture for initial silicon layer thickness $t_{3,\text{in}} = 10$ nm, the arrow direction denotes the relative oxide thickness increase. (a) dip position, (b) sensitivity, (c) detection accuracy, (d) figure of merit.

decrease of the studied system is compensated by increase of detection accuracy. Thus the spectral operational range of the sensor can be tuned without notable loss of the overall performance of the system expressed by figure of merit.

4. Conclusion

The numerical simulation of surface plasmon resonance fibre-optic sensor operate in spectral domain was performed in order to study the effect of the oxidation of the silicon protective layer on the performance of the sensing scheme. The model computations
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were carried out in frame of planar optics using approximative five-layer structure. The results revealed that the formation of the low-refractive index (silicon oxide) growing on the outer boundary at the expense of silicon overlayer reduces the red shift of dip position, originally introduced by the presence of silicon overlayer. The oxide layer reduces the sensitivity as well. On the other hand, the detection accuracy is enhanced. Overall performance of the sensing structure described by the figure of merit is not much affected, especially in the case of the thickest protection overlayer ($t_{3,in} = 10\,\text{nm}$). Thus the proper adjustment of the oxide layer thickness can be used to shift the spectral operational range of the proposed sensing structure toward the required spectral range and to keep the reasonable values of the sensitivity and detection accuracy.

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