Sensitivity Features of Double-Resonance Plasmonic Sensor

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Abstract. The paper presents the results of a model investigation about the temporal dynamics of changes in the resonance excitation conditions of surface plasmon-polariton waves in a double-resonance plasmonic sensor at different thicknesses of the sensitive ligand layer. It was shown that the maximum sensor reaction rate to the emergence of analyte is observed at a ligand layer with 40–50 nm thickness. When the ligand layer thickness is less than 40 nm, the sensitivity of the sensor decreases sharply, and when the ligand thickness is increase over 60 nm, a delay in the sensor reaction is observed which due to the limited diffusion rate of the analyte into the ligand. The most effective mode of a plasmon sensor operation is the mode in which the angle of the exciting beam incidence is somewhat different from the resonance angle at condition when the analyte is absent.

1. Introduction
Plasmonic sensors and biosensors based on surface plasmon-polariton resonance (SPPR) have been increasingly used at recently [1–6]. This popularity is due to the high sensitivity of plasmonic sensors, which can achieve $10^{-5} - 10^{-6}$ RIU (refractive index units) [1, 2]. In addition, the using of biological markers (ligands) deposited on the sensitive plasmonic layer surface allows to create a selective sensor aimed at detecting one specific agent (analyte) [1–3, 5, 6].

A particular problem in the design of plasmonic biosensors is the choice of the ligand layer thickness [7–9]. For increasing of the sensor sensitivity, the ligand layer must be thick enough, this will lead to a more significant shift of the resonance. However, when the ligand interacts with the analyte, the change in its dielectric constant $\varepsilon_{Lg}$ does not occur immediately over the entire volume of the layer, but $\varepsilon_{Lg}$ changes with time from the surface into the layer volume during the diffusion of analyte into the ligand [10, 11]. Its leads to a delay in the response of the sensor to the analyte emergence. On the contrary, a decrease in the ligand layer thickness leads to an increase in the response rate of the sensor, but its sensitivity will decrease.

Thus, the aim of this work is to investigate the temporal dependence of the plasmonic sensor signal at various thicknesses of the ligand layer, with account the diffusion profile of the analyte distribution in the ligand layer. It was selected a double-resonance plasmonic sensor which was developed and synthesized by the authors of this article as a research object [12].

2. Double-resonance plasmonic excitation
There are two classical schemes of prismatic excitation of surface plasmon-polariton waves: the Kretschmann scheme and the Otto scheme [13]. The structure that allows combining Kretschmann and Otto schemes in one device has been developed by the authors of this article (in article [6] presented an alternative scheme of double-resonance plasmon excitation based on optic fiber). A feature of this structure is that between the prism and the plasmonic metal film an additional (buffer) layer of a transparent dielectric is presents and it has a refractive index less than that of the prism, but bigger than...
that of the environment. So, at small angles of the light beam incidence, the effect of total internal reflection (TIR) occurs at the interface of the dielectric layer and the environment, and a plasmon-polariton wave is excited on the external surface of the plasmonic film according to the Kretschmann scheme. At large angles of the light beam incidence, the TIR effect is observed at the interface between the prism and the dielectric layer, and a plasmon-polariton wave is excited on the internal surface of the plasmonic film according to the Otto scheme.

For the described structure, two resonances (according to Kretschmann and Otto) will be observed on the angular reflectometry curve. In this case, the condition of resonance by Kretschmann and the appropriate resonant angle will significantly depend on the dielectric properties of the environment. This makes it possible to realize a sensor system for detecting changes in the properties of this environment. Otto resonance, on the other hand, depends mainly on the properties of the dielectric buffer layer and will change weakly. Such resonant peak can be used as a standard peak when compared with a change in the position of the Kretschmann peak, which will improve the accuracy and stability of the double-resonance scheme in the sensory application compared to a single-resonance scheme.

The developed double-resonance scheme is realized on the basis of a structure including a rectangular prism from a single crystal of gadolinium gallium garnet Gd$_3$Ga$_5$O$_{12}$ (GGG prism) with a high refractive index $n = 1.960$ for $\lambda = 632.8$ nm, on which a dielectric buffer layer with a refractive index less than that of the prism and more than that of the environment (quartz SiO$_2$, $n = 1.456$ for $\lambda = 632.8$ nm) is deposited. An Au plasmonic metal film with a purity of no worse than 99.95% is deposited over the buffer layer (figure 1a).

The numerical modeling of the structure of the double-resonance SPPR sensor, and also the optimization of its structural parameters and operating regimes were carried out using the WinSpall software [14]. A double-resonance structure GGG$_{\text{prism}}$/SiO$_2$(grad $h$)/Au(50) was synthesized with a gold layer thickness of 50 nm and a gradient of the thickness of buffer layer $h_{\text{SiO}_2}$. On figure 1b the resonance curve which obtained on the range with 220 nm thickness of buffer layer is presented.

3. Model features

The double-resonance plasmonic sensor model is based on a triangular prism of total internal reflection (angles 90, 45 and 45 deg). The dielectric constant of the prism is $\varepsilon_{\text{GGG}} = 3.842$, which corresponds to a single crystal of garnet Gd$_3$Ga$_5$O$_{12}$ at a wavelength of $\lambda = 632.8$ nm (the imaginary part of $\varepsilon_{\text{GGG}}$ in the model is omitted, since we neglect the optical loss in the prism). Parameters of the buffer layer: $\varepsilon_{\text{SiO}_2} = 2.122 + 0.0001i$ (quartz SiO2), thickness $h_{\text{SiO}_2} = 220$ nm. Parameters of the plasmonic layer (gold film): $\varepsilon_{\text{Au}} = -11.647 + 1.263i$, thickness $h_{\text{Au}} = 50$ nm (figure 2a).

Figure 1. Double-resonance scheme for SPPR excitation: a – structure of double-resonance scheme, b – resonance curve (circles – experimental data, line – modelling curve).

At a buffer layer thickness $h_{\text{SiO}_2} = 220$ nm a clear peak of plasmon-polariton resonance by Otto scheme is observed at an incidence angle 64 deg of the exciting beam. The resonant angle of the peak by Kretschmann is 19.5 deg. The results which presented on figure 1b clearly demonstrate good agreement between the experimental data and modelling calculations.
A sensitive ligand layer is located on the surface of the Au plasmon layer. The thickness of the ligand layer varies in the range of 20 - 100 nm for investigation the features of the temporal dynamics of the sensor reaction to the emergence of the analyte. The dielectric constant of the ligand in the model varies from 1.7 - 1.8, while $\varepsilon_{Lg} = 1.7$ corresponds to the null analyte content in the ligand, and $\varepsilon_{Lg} = 1.8$ corresponds to the maximum ligand reaction to the presence of analyte.

The penetration of the analyte into the ligand layer is calculated based on the standard diffusion model where the diffusion equation is solved numerically by of finite-differences time-domain (FDTD) method [15, 16]. For this, the entire ligand volume is divided into individual layers, between which diffusion fluxes and the change in analyte concentration in the layers are calculated through a finite arbitrary unit of time. Figure 2b shows the distribution of $\varepsilon_{Lg}$ in a ligand layer with thickness 100 nm at various time instants $\tau$ (in arbitrary units).

![Figure 2](image-url)

**Figure 2.** The structural scheme of the investigated model (a), the distribution of dielectric constant in the ligand layer at different time instants $\tau$ (time is indicated in legend in arbitrary units) (b).

Thus, using the obtained distribution of permittivity in the ligand layer, we can estimate the temporal dynamics of changes in the resonance conditions for excitation of plasmon waves and evaluate the change in the signal of the plasmonic sensor.

4. Results and its discussion

Figure 3a shows the characteristic resonance curves at different times $\tau$ (indicated in the legend) for a plasmonic sensor with a ligand layer 100 nm thickness under the condition of the dielectric constant allocation in the ligand layer as shown on figure 2b.

It can be seen that over time, the Kretschmann resonance peak has a significant shift, while the Otto peak shifts relatively weakly. Figure 3b shows the change in the position of the resonance peak by Kretschmann over time. It is seen that over time (during the ligand “saturation” with analyte over the entire volume), the shift of the resonance peak slows down, approaching a constant value of 38.87 deg (within the framework of the investigated model). Qualitatively similar results were obtained for sensors with a ligand layer of 20, 40, 60, and 80 nm. The only difference is the resonance angles and the magnitude of the resonances shifting.

The most informative in the case of practical application is the response speed of the plasmonic sensor, i.e. rate of change of the sensor signal over time. In the classical version with prism excitation, such signal is determined by the intensity of the reflected beam at a fixed incident angle. If we fix the beam incident angle in the resonance condition (without analyte), the sensor signal will have the smallest possible value. When an analyte will emergence, the dielectric constant of the ligand began to change and the resonance will shift. This will increase the sensor signal.
Figure 3. Temporal dynamics of changes in the SPPR excitation conditions in a double-resonance sensor: (a) general form of the resonance curves at different time instants \( \tau \) (indicated in the legend); (b) the temporal dependence of the Kretschmann peak position.

Figure 4a shows the time change in the signal of the plasmonic sensor with different thicknesses of the ligand layer (indicated in the legend), and figure 4b shows the rate of the sensor signal change at different times (the time derivative of the signal \( dI/d\tau \)).

Figure 4. Temporal dependence of the signal parameters of a plasmonic sensor when the incidence angle equal to the resonance angle (without analyte): change in the intensity of the reflected beam per time (a), rate of change in intensity \( dI/d\tau \) (b)

It can be seen that in the initial time period (immediately after the emergence of the analyte), the signal of sensor with a ligand layer of 100 nm increases slowly. In this case, the rate of the signal increase also increases in the initial time period, which is associated with a certain "flatness" of the plasmon resonance peak bottom. This fact leads to a certain time delay in the detection of the analyte. However, in process of time when the deeper ligand layers have reacted with the analyte, the sensor signal increases rapidly.

Reducing the thickness of the ligand layer up to a thickness of 40 nm become to increases the reaction rate of the sensor in the initial time period. The analysis shows that at the initial stage (immediately after
the emergence of the analyte), the sensor signal with a ligand layer of 40 nm is more than 5 times greater than the sensor signal with a ligand layer of 100 nm. But in the ligand saturation mode by analyte, the signal ratio is 1/3 in favor of a sensor with a ligand layer of 100 nm.

A further decrease in the thickness of the ligand layer to 20 nm does not lead to an increase in the reaction rate of the sensor to the emergence of analyte, but the maximum sensor signal (in saturation) is an order of magnitude lower than the ligand layer with 100 nm thickness.

So, for obtaining the most sensitive plasmonic sensor in the saturation mode, it is advisable to use a ligand layer with 100 nm thickness or more, and for creating a sensor with the minimum time of reaction to the analyte emergence, it's effective to use a ligand layer with 40 nm thickness.

The sensitivity and reaction rate of the plasmonic sensor to the emergence of the analyte can be increased by changing the incident angle of the exciting beam by a small value (0.3 – 0.6 deg) relative to the resonance angle (without analyte), so that the primary signal of the sensor differs from the resonant signal by 5 – 10 %. It will lead beyond from range of flat bottom of the plasmon resonance peak, and the slightest change in the dielectric constant of the ligand will lead to a change in the sensor signal. It is advisable to change the incident angle of the exciting beam in the direction opposite to the displacement of plasmonic resonance during the reaction of the ligand on the emergence of the analyte.

Figure 5a shows the temporal dynamics of the plasmonic sensor signal with a ligand layer of various thicknesses (indicated in the legend) for a beam incident angle different from the resonant angle.

As can be seen on figure 5, there is no delay in the response of the sensor at the initial time interval even when using a thick ligand layer of 100 nm. Reducing the thickness of the ligand layer to 40 nm gives a gain of the sensor reaction rate only 2 times for this operation mode of the sensor at the initial time interval. It should be noted that at this operating mode, for all thicknesses of the ligand layer, a significant amplification of the effective signal (relative to resonant mode) is observed. The maximum response speed (dI/dτ) of the sensor has increased more than 3 times.

Thus, the described configuration of the plasmonic sensor operation (when the incident angle of the exciting beam differs somewhat from the resonant angle) is more preferable for increasing the sensitivity and reaction rate to the emergence of the analyte than the configuration when the incident angle of the exciting beam is equal to the resonant angle. In this case, to create the most sensitive sensor, a ligand
layers with a thickness of 100 nm or more should be used, and to obtain a sensor with a minimum reaction time, a ligand layer with a thickness of about 40 nm should be used.

5. Conclusions
So, a double-resonance model of a plasmonic sensor containing sensitive ligand layers with various thicknesses has been considered in the work. A model of a layer (ligand) saturation with a detectable agent (analyte) based on the classical diffusion theory has been constructed. The temporal dynamics of the ligand saturation profile by analyte and the permittivity distribution in the ligand layer have been calculated.

The temporal dynamics of changes in the resonance curves for the plasmonic sensor with various thicknesses of the ligand layer has been calculated. It has been shown that the Kretschmann resonance peak has a significant shift when the ligand is saturated by analyte. The Otto peak in this case is shifted slightly.

An analysis of the plasmonic sensor response rate to the emergence of the analyte showed that, in the initial period a time delay of sensor signal is observed when an incident angle of the exciting beam equal to the resonant angle. This is due to the “flatness” of the bottom of the plasmon resonance peak. This delay is most pronounced for a thick ligand layer, which is due to the finite rate of the analyte diffusion into the ligand volume.

An increase in the sensitivity and reaction rate of the plasmonic sensor is observed when the incident angle of the exciting beam deviates by 0.3 - 0.6 deg relative to the resonant angle (without analyte). In this case, to create the most sensitive sensor, ligand layers with a thickness of 100 nm or more should be used, and to obtain a sensor with a minimum reaction time, a ligand layer with a thickness of about 40 nm should be used.

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