https://doi.org/10.15407/ujpe68.9.594

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PLASMON RESONANCE PROPERTIES OF Au, Cu, AND Ag MULTILAYERED STRUCTURES WITH P(VDF-TrFE)

The theoretical modeling of the optical response of layered metal-polymer structures, which can be employed as plasmonic sensors, is carried out. The calculation of their linearly polarized light reflection is performed with the use of the well-known matrix method, which describes the electromagnetic radiation propagation through a sequence of homogeneous flat-parallel media layers. In this way, the attenuated total reflection curves of the structures containing metal films (Au, Cu, or Ag) and a polymer dielectric are obtained and analyzed. A new sensor is proposed, which will utilize the ferroelectric P(VDF-TrFE) copolymer separating metal films. This might be a perspective idea for the creation of tunable plasmonic sensors. The dependencies of the angular position of a surface plasmon resonance versus the thicknesses of structure's layers, as well as versus the refractive index of the medium contacting to the free surface of a sensor, are considered. This makes it possible to carry out the approximate search for optimal constructive parameters of a sensor, namely, the thicknesses of metal and polymer layers, and to make conclusion about its resulting sensitivity and working range. It is found that the sensors based on a single metal film and a couple of such films separated by a polymer differ 1 ... 1.3 times in the sensitivity (single metal film demonstrates a more rapid resonant angle shift with analyte refractive index variation). It is established that the employment of Au, Cu, or Ag gives no significant changes in the sensitivity of a two-metal-layer sensor with a polymer, but the widest refractive index registration range may be expected for a Cu-based sensor.

K e y w o r d s: surface plasmon resonance, biosensor, P(VDF-TrFE), thin metal films, tunable sensor, attenuated total reflection.

1. Introduction

Today, molecular sensors working on the principles of utilization of the phenomenon of a surface plasmon resonance (SPR) on metal-dielectric interfaces have become widely used. The basis of their operation mechanism is the enormous sensitivity of surface plasmons to the local dielectric permittivity or, equivalently, to the refractive index of an analyte. All the variety of different applications of such sensors is achieved by their surface functionalization with special substances, coatings, ligands, and so on. As examples, SPR sensors are used to study protein-protein interactions [1], for drug discovery [2], and for the detection of metal ions [3]. They can provide some additional features [4] such as the temperature control [5].

Citation: Yampolskyi A.L., Zaporoshchenko D.V., Makarenko O.V. Plasmon resonance properties of Au, Cu and Ag multilayered structures with P(VDF-TrFE). *Ukr. J. Phys.* **68**, No. 9, 594 (2023). https://doi.org/10.15407/ujpe68.9.594.
Цитування: Ямпольський А.Л., Макаренко О.В., Запорощенко Д.В. Плазмонно-резонансні властивості багатошарових структур на основі Au, Cu, Ag та P(VDF-TrFE). *Укр. фіз. журн.* **68**, №9, 596 (2023).

The production technology for SPR sensors continues to be actively developed. Scientists are looking for new plasmonic materials [6], which can become a base for novel devices possessing better functional characteristics. A lot of new ideas of the functionalization of sensors are theoretically and experimentally explored. Metal-insulator multilayered structures with the coupling of plasmonic modes demonstrate the enhanced sensitivity due to a special spatial distribution of the electric field and are promising for the thin adsorbate film sensing [7].

In this article, we propose a new multilayered sensor which is formed of metal films (Au, Cu or Ag) and a ferroelectric P(VDF-TrFE) copolymer layer. Plasmonic structures with the utilization of various dielectric materials (e.g., HfO_2, as we read in [8]) are widely developed and tested. Aside from a low cost of the polymer compared to oxide dielectrics, such combination may be perspective for the creation of sensors with tunable resonant characteristics. In the literature, we can find the consideration of the magnetic field influence on the parameters of a surface plasmon resonance in permalloy/noble metal films [9]. Similar ideas, but for the electric field and P(VDF-TrFE), can be of interest. The aim of the work is a primary theoretical modeling of such sensors, calculation of their plasmonic response, and comparison with the characteristics of traditional plasmonic sensing structures.

2. Methodology

The computation of the characteristics of layered structures proposed for using as biosensors is performed by the well-known matrix method whose description can be found in [10]. This method allows one to determine the complex amplitudes of electromagnetic (particularly, optical) waves traveling through a sequence of plane-parallel interfacing media with multiple reflections inside it.

The diagram of such sequence is shown in Fig. 1. Each layer is assumed to be homogeneous and isotropic. So, its optical properties are completely described by the complex refractive index $N_j = n_j - ik_j$, where n_j are real refractive indices of the layers, and k_j are extinction coefficients. The incident wave is considered as flat-front, monochromatic, and linearly polarized. The general solution of Maxwell's equations for j-th layer consists of two sinusoidal waves

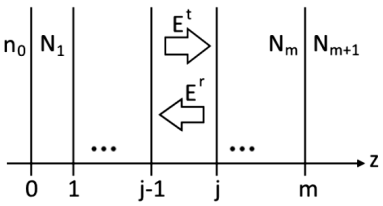


Fig. 1. Illustration to the indexing of layers

traveling contrary to each other:

$$E(z,t) = a_j \exp\left[i\left(\omega t - \frac{2\pi}{\lambda} N_j z + \alpha_j\right)\right] + \\ + b_j \exp\left[i\left(\omega t - \frac{2\pi}{\lambda} N_j z + \beta_j\right)\right]. \quad (1)$$

The constants a_j, b_j, α_j, and β_j are found from the continuity of the boundary conditions:

$$E(z_j - 0, t) = E(z_j + 0, t). \quad (2)$$

As we will deal with relative and averaged field amplitudes, the time-dependent multiplicands can be excluded, and the last boundary's amplitude can be put to be of a unit value. Then the following recurrent relations can be derived for the sequence of layers:

$$E^t(z_{j-1} - 0) = \frac{1}{2}\left(1 + \frac{N_j}{N_{j-1}}\right) E^t(z_j - 0)\exp[i\Phi_j] + \\ + \frac{1}{2}\left(1 - \frac{N_j}{N_{j-1}}\right) E^r(z_j - 0)\exp[-i\Phi_j], \quad (3)$$

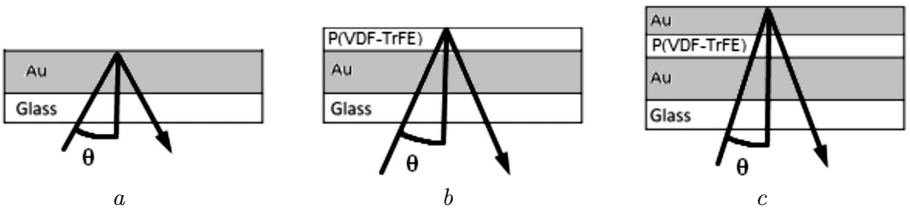
$$E^r(z_{j-1} - 0) = \frac{1}{2}\left(1 - \frac{N_j}{N_{j-1}}\right) E^t(z_j - 0)\exp[i\Phi_j] + \\ + \frac{1}{2}\left(1 + \frac{N_j}{N_{j-1}}\right) E^r(z_j - 0)\exp[-i\Phi_j], \quad (4)$$

where Φ_j are phase thicknesses, and t and r are the indices corresponding to the transmitted and reflected waves, respectively. For the convenience, these relations can be arranged into matrices.

The magnetic field amplitudes can be found in a similar way. Finally, the Poynting vector averaged values give relations for the transmittance and reflectance coefficients (m is the last boundary's index):

$$R = \frac{P^r(z_0 - 0)}{P^t(z_0 - 0)} = \left|\frac{E^r(z_0 - 0)}{E^t(z_0 - 0)}\right|^2, \quad (5)$$

$$T = \frac{P^t(z_m + 0)}{P^t(z_0 - 0)} = \frac{\mathrm{Re}(N_{m+1})}{n_0}\left|\frac{E^r(z_m + 0)}{E^t(z_0 - 0)}\right|^2. \quad (6)$$



a *b* *c*

Fig. 2. The structures considered at different stages of the modeling of plasmonic sensors (by the example of Au): simple one-metal layer (*a*), metal with a polymer coating (*b*), two metal layers separated by a polymer one (*c*)

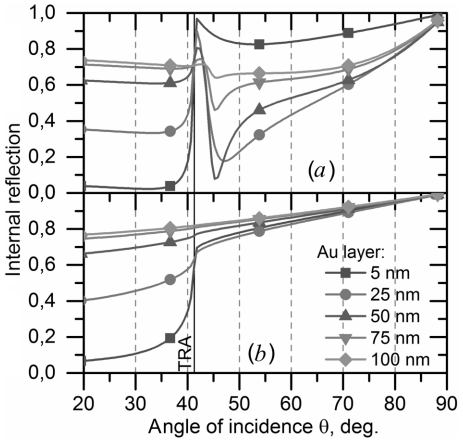


Fig. 3. ATR curves calculated for different thicknesses of Au: *p*-polarization (*a*), *s*-polarization (*b*). The curves are marked with symbols to distinguish them. TRA – total reflection angle

The approach mentioned above can be successfully applied to the case of non-right-angle input ray incidence by introducing the concepts of effective refractive indices and phase thicknesses.

The key advantage of this method (besides the ease of the addition of new layers to the model and the interference account) is that the formalism describes correctly non-trivial reflection cases, namely, the total internal reflection and the attenuated total reflection (ATR) with its specific minimum related to the surface plasmon resonance phenomenon. That is why it can be involved in calculations of the response of plasmonic structures and the analysis of their efficiency.

The modeling of a common practical situation was performed in the case where the layered structure on a glass substrate slide is placed onto the reflective face of a total internal reflection prism, while the outer side of the structure is exposed to the influence of an analyte. The wavelength of a probe beam was accepted to be equal to $\lambda = 625$ nm. For calculations, the optical constants n and k of gold, copper, and silver were taken from [11]. The angular or wavelength scanning is easy simulated by the variation of corresponding parameters, and the analyte effect on the sensor is modeled by a change of the outside medium refractive index. The changes in the governed structure and its properties due to the ferroelectric P(VDF-TrFE) layer can be taken into account in the same way (keeping in mind, however, that the electrical field application to the ferroelectric polymer changes, in general, its dielectric permittivity tensor). As a result, the ATR-curves are theoretically obtained for the further analysis.

3. Discussion

When studying the properties of improved sensors, one should choose some known reference object to compare the obtained results. For the start, we took the traditional plasmonic structure in the form of a gold film few tens nanometers in thickness, which was deposited on a glass substrate (Fig. 2, *a*).

The curves of the attenuated total reflection calculated for several gold layer thicknesses are shown in Fig. 3. The outer medium refractive index is $n = 1$. One can see a minimum corresponding to the plasmonic resonance in the case of *p*-polarized radiation (*a*); for the *s*-polarization (*b*), there is no such effect.

The main response of a plasmonic sensor to analyte composition changes is the shift of the resonant angle. So, for the effective and precise sensor functioning, a well-defined resonant dip on its ATR-curve is required. In spite of the tendency of such a dip to decrease in depth, as the refractive index of the analyte increases, it is logical to choose a metal layer thickness appropriate to provide the resonance amplitude as large as possible at the starting point ($n = 1$). This is the first step. Second, if the resonant dip is located not far from the angle of total internal reflection at

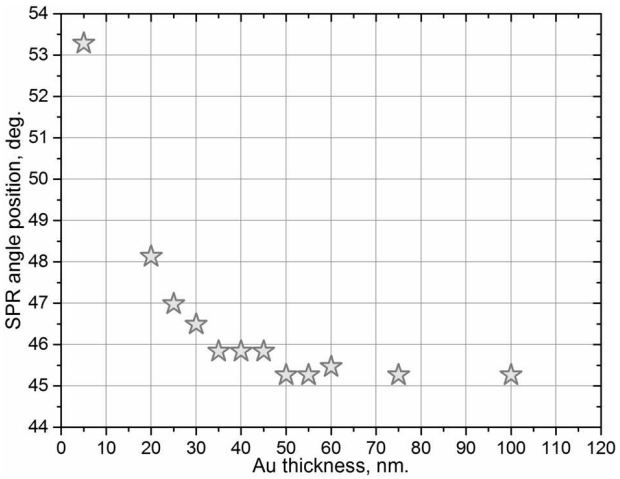


Fig. 4. Plasmonic resonance position versus the Au layer thickness

$n = 1$, this leaves a wider range for its swing under working conditions. The dependence of the resonance position on the gold layer thickness is presented in Fig. 4. Third, the thicker the metal layer, the higher the cost and duration of the fabrication. These criteria prompt one to choose the Au layer thickness of about 50 nm as the optimal value for the wide-range plasmonic sensor development.

Similar estimates for Cu and Ag give 30 nm and 40 nm, respectively.

For these three metals at the mentioned thicknesses, we have modeled the plasmonic response. Figure 5 shows how the resonant "antipeak" travels, as the refractive index of the medium varies. It is seen that the inclinations of the graphs are slightly different. Their value allow us to conclude that the sensor sensitivities (near $n = 1.3$) are approximately 120 deg/RIU for Au film, 92 deg/RIU for Ag, and 80 deg/RIU for Cu one, where RIU is Refractive Index Unit. These curves also relate sensor's operating range to the measurement apparatus geometry. For example, if the maximum accessible angle of the light internal reflection is $\vartheta_{\max} = 80°$, the refractive index in the interval $1.0 \ldots 1.4$ can be registered (more precise values vary from graph to graph).

The next intermediate step in the sensor development is the deposition of a P(VDF-TrFE) copolymer layer onto the free metal surface (Fig. 2, *b*). It can play a chemically protective role (similar to the available approaches utilizing the oxide dielectric covering [12] to preserve the plasmonic metal film from

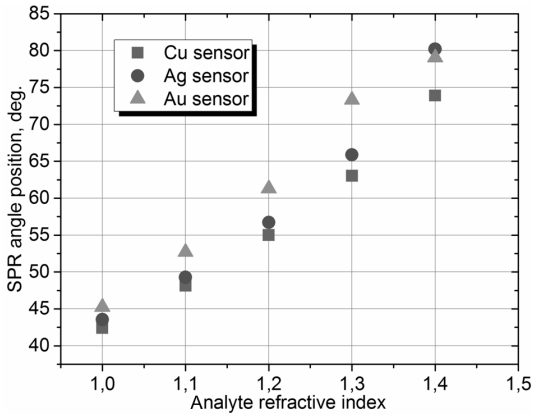


Fig. 5. SPR angle dependences on the outer medium refractive index in the cases of Au, Cu, and Ag single layer on glass

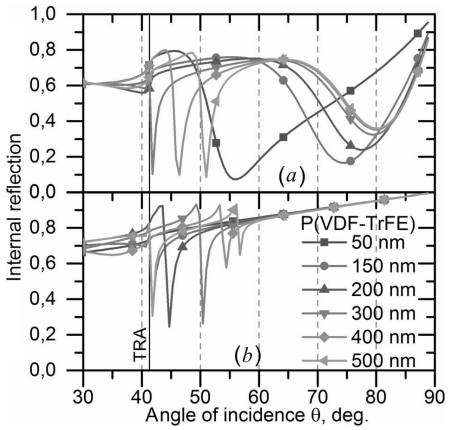


Fig. 6. ATR curves calculated for different thicknesses of the P(VDF-TrFE) layer on the top of a 50-nm-thick Au layer: *p*-polarization (*a*), *s*-polarization (*b*). The curves are marked with symbols to distinguish them. TRA – total reflection angle

a degradation [13]), as well as be used for a modification of sensor's characterictics. Figure 6 might be interesting to watch the consequent complication of ATR-curves (the refractive index of the outer medium is 1). One can find some additional minima on them, having the interference origin. The resonant angles now occupy an area predominantly from $\vartheta = 75°$ and higher.

At the next step, the theoretical model involves the second metal layer as well, placed on the top of the polymer (Fig. 2, *c*). The case of the same material and thickness of two metal layers was selected for consideration. The results of the simulation of ATR-curves for different polymer thicknesses are presented in Fig. 7.

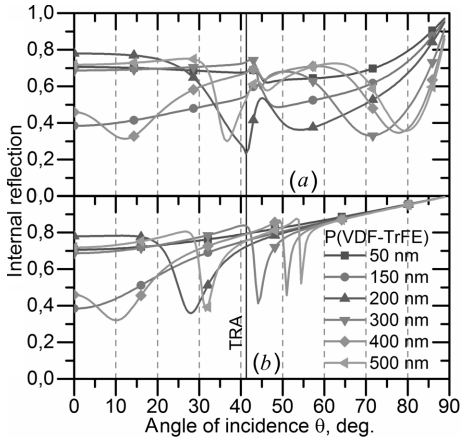


Fig. 7. ATR curves calculated for different thicknesses of the P(VDF-TrFE) layer between two 50-nm Au films. (a) – p-polarization, (b) – s-polarization. The curves are marked with symbols to distinguish them. TRA – total reflection angle

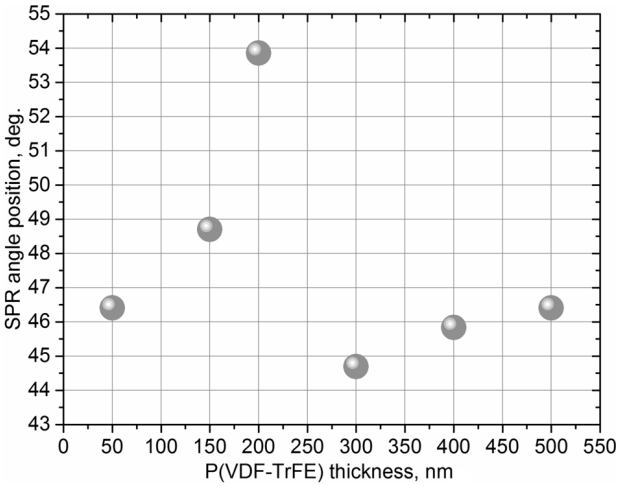


Fig. 8. SPR angles for different polymer thicknesses in the structures with two 50-nm Au layers

Similar to the previous case, the plasmonic resonant peak for these structures is located at the domain with a relatively high angle ($\vartheta_{\mathrm{SPR}} > 70°$ for the polymer thickness above 300 nm), and they are possess a more round and smooth shape. In spite of this, the more careful and accurate numerical processing of the curves is needed to achieve the required sensor precision, in comparison to the case of a single metal layer. The overall sensitivity improvement may be reached due to a more extended evanescent wave localization zone. This takes place in the case of multilayered structures with surface plasmons from the

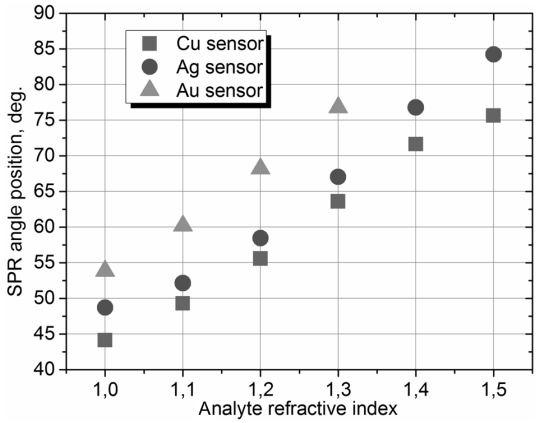


Fig. 9. SPR angle dependences on the outer medium refractive index in the cases of Au, Cu, and Ag double-layer sensors with P(VDF-TrFE)

interaction of different interfaces [7]. But this question needs to additionally compute a spatial distribution of the electromagnetic field. Moreover, the interference in the polymer layer contributes to the formation of extrema of the curves. This may be used for the control over the tunable parameters of sensors (especially, over the recording of additional auxiliary ATR-curves in s-polarized light).

There are several criteria for the choice of a P(VDF-TrFE) thickness. First, it is necessary to provide a wide range for the resonant dip traveling toward large angles of the light incidence on ATR-curves. This limits the maximum allowable thickness at 200 nm (as a last resort, no more than 300 nm). Second (optional) – to have any interference extrema within the recorded curve area. This may be actual for tunable sensors, satisfied, when the polymer thickness is 300 nm and more. Third, the application of a voltage to the metal layers (using them as electrodes) must have possibly a strong effect on SPR conditions. Assuming that the main mechanism is a piezoelectric extension of the polymer layer, one can choose a value within 200 ... 300 nm from the graph presented in Fig. 8. This graph shows the SPR peak position versus the polymer thickness in the structures under study. Thus, summing up, the 200-nm thickness of P(VDF-TrFE) can be chosen as the optimal value.

We recall that the above-mentioned thicknesses correspond to the sensor containing two 50-nm Au layers. For other metals – 30-nm Cu and 40-nm Ag –

a similar reasoning leads to the choice of 250-nm and 250-nm P(VDF-TrFE) layers.

The dependence of the SPR angle on the analyte refractive index was computed for the structures based on all these three metals. Corresponding graphs are presented in Fig. 9.

One can see from this figure that the accessible ranges to measure refractive indices are different for these three cases. The plasmonic peak of the Au-based structure disappears already at $n = 1.4$. The sensor with the widest range (as expected from the corresponding graph extrapolation) is constructed on the base of copper. Then the silver-based one follows. Exploiting them allows registering the local refractive index changes up to $n = 1.5$, even more. We note that the inclination of the graphs is approximately the same, namely, 80 ... 86 deg/RIU in the vicinity of $n = 1.3$. This indicates similar sensitivities of such sensors. However, they are lower in comparison to single-layer structures.

4. Conclusions

Thus, the matrix method describing the propagation of electromagnetic radiation in a sequence of flat-parallel layers can be applied to the development of plasmonic resonant sensors. From this viewpoint, metals such as gold, copper, and silver, which are used in plasmonics, differ from one another only in optical constants n and k (i.e., complex refractive index). Calculations show that, in the films of each of these metals, the plasmon resonance phenomena manifest themselves approximately to the same extent. So, all they can be utilized as materials for biochemical sensors.

The maximum value of the resonant absorption of optical radiation by a single metal layer (when the refractive index of the medium forming the interface with its surface is equal to 1) is reached, when the thickness of Au is about 50 nm, Cu – 30 nm, and Ag – 40 nm. These values can be chosen as optimal.

The passage from the single-metal-layer structure to a double-metal-layer one, which includes the P(VDF-TrFE) separating layer, gives, up to 1.4 times, a decrease of the SPR angle sensitivity to changes in the refractive index of an analyte (overall sensor's sensitivity, though, may be higher due to a wider zone of the interaction between the electrical field of a plasmon and the medium, but achieving this requires a careful optimization of the structure). But such structure might potentially be used for tunable plasmonic sensors with driven resonant characteristics. Preferable values of the P(VDF-TrFE) layer thickness are 200 nm for an Au-based sensor and 250 for Cu- and Ag-based ones.

5. Authors' contribution

The study conception statement and supervising were performed by Makarenko O.V. Numerical modeling and calculations were carried out by Zaporoshchenko D.V. Graphs preparation and article text writing were performed by Yampolskyi A.L. All authors participated in the discussion of results, read and approved the final manuscript.

The work was supported by the Ministry of Education and Science of Ukraine in the framework of projects No. 22BF051-01, which are performed on the basis of Taras Shevchenko National University of Kyiv.

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Received 10.05.23

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ПЛАЗМОННО-РЕЗОНАНСНІ
ВЛАСТИВОСТІ БАГАТОШАРОВИХ СТРУКТУР
НА ОСНОВІ Au, Cu, Ag ТА P(VDF-TrFE)

У роботі проведено теоретичне моделювання оптичного відгуку шаруватих металополімерних структур, які можуть бути використані як плазмонні сенсори. Розрахунок відбивання ними лінійного поляризованого світла проводився з використанням відомого матричного методу, що описує поширення електромагнітного випромінювання через послідовність однорідних плоскопаралельних шарів середовищ. Таким чином отримано та проаналізовано криві порушеного повного внутрішнього відбивання структур, що містять металеві плівки (Au, Cu або Ag) та полімерний діелектрик. Запропоновано новий сенсор, який матиме в своєму складі сегнетоелектричний кополімер P(VDF-TrFE), що розділяє металеві плівки. Це може бути перспективною ідеєю для створення регульованих плазмонних сенсорів. Розглянуто залежності кутового положення поверхневого плазмонного резонансу від товщини шарів структури, а також від показника заломлення середовища, яке контактує з вільною поверхнею сенсора. Це дозволило здійснити наближений пошук оптимальних конструктивних параметрів сенсора, а саме, товщини металевих і полімерних шарів, та зробити висновки про їх результуючу чутливість і робочий діапазон. Виявлено, що сенсори на основі однієї металевої плівки та пари плівок, розділених полімером, відрізняються за чутливістю в 1 ... 1,3 рази (одинарна металева плівка демонструє більш швидкий резонансний зсув кута при зміні показника заломлення досліджуваної речовини). Встановлено, що використання Au, Cu або Ag не дає суттєвих відмінностей у чутливості сенсора з двома металевими шарами та полімером, але найширшого діапазону реєстрації показника заломлення серед них можна очікувати від сенсора на основі Cu.

Ключові слова: поверхневий плазмонний резонанс, біосенсор, P(VDF-TrFE), тонкі металеві плівки, настроюваний сенсор, порушене повне внутрішнє відбивання.