Application of Dielectric Layers in Surface Plasmon Resonance Sensors

Sergiy Kurlov, Tetyana Lebyedyeva, Leonid Poperenko, Pavlo Shpylovyy

Abstract:

Sensors based on surface plasmon resonance (SPR) are widespread in modern devices of biochemical application. As a rule, a technique of diagnostic is a measurement of angle dependence of the refraction index from incident angle of p-polarised monochromic light R(φ) from the substrate at plasmon excitation supporting metal film contacted by enviro nment or layer under investigation. Potentialities of SPR sensors may be extended with the inclusion of additional dielectric films into the structure of SPR substrates.

Keywords: *surface plasmon resonance, sensor, modelling, anodization, sputtering.*

1. Introduction

Perspective phenomenon for sensory application is long range surface plasmon resonance (LRSPR). It may be observed under excitation of SPR by the combination Otto and Kretchman methods. In such a case the plasmon waves are exited on the both sides of plasmon supporting metal film. LRSPR is experimentally appeared as two minima in the SPR curve (Fig.1) and realized by the deposition of additional dielectric film located between the glass plate and the metal film.

(a)

(b)

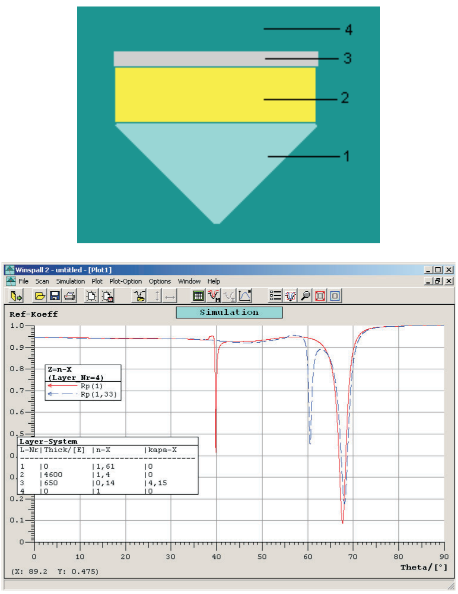

Fig. 1. a) schematic LRSPR structure: 1 - prism, 2 - additional dielectric layer, 3 - metal film, 4 - enviro nment; b) calculation of R (φ) curves of dielectric/Ag structure; substrate is a glass (n=1.61); enviro nments are air (n=1, red line) and water (n=1.33, blue line).

The given method may be useful for SPR sensors. The angle of non-shifted right minimum in Fig. 1, corresponding to the interface metal-additional dielectric film may serve as a strong signal response. Then during analytical work such disadvantages of the sensor device as inaccuracies and backlashes of mechanics will not influence at the results of measurements. The possible mistakes of experimental determination of angles may be minimized.

Using additional dielectric films deposited on plasmon supporting metal films.

All plasmon supporting metals (Au, Ag, Al, Cu) are rather soft. The SPR chips covered by metal film of 20-50 nm thickness under multiple usages are easy damaged. On our opinion thin but hard and chemically stable dielectric films formed by vacuum deposition or anodic oxidation are reliable protections of SPR chips in many cases. But the presence of protective film has an influence on the sensor properties. In this relation the structures Au/Al_2O_3 and Au/Nb_2O_5 were under investigations. The wavelength of p-polarized light was equal 650 nm. The results of calculations carried out by computer modelling are presented in Fig. 2 and Fig. 3.

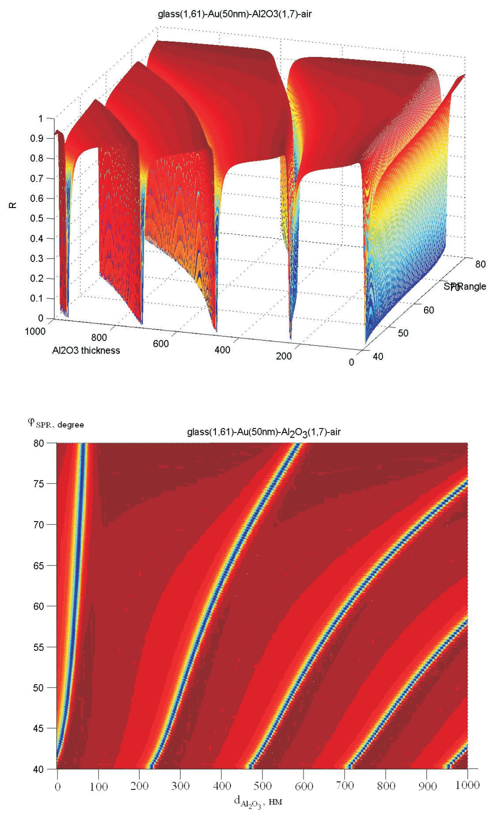

Fig. 2. Results of modelling SPR in structure Au/Al_2O_3.

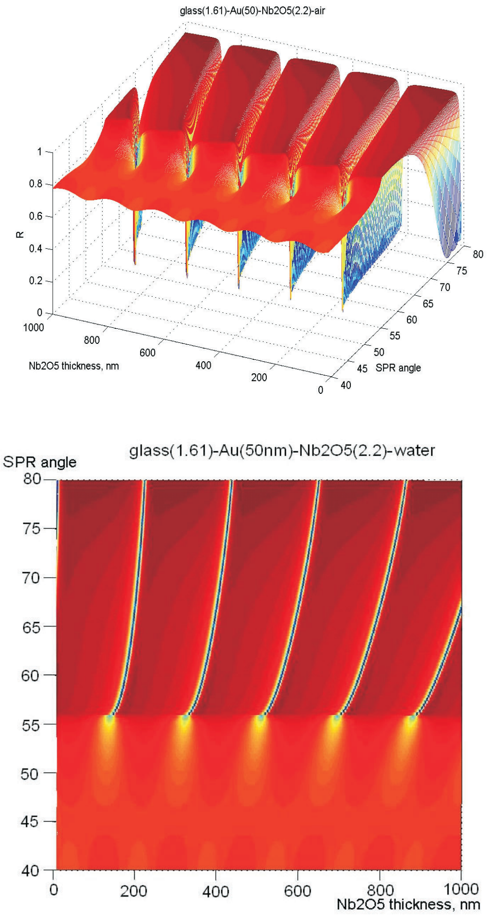

Fig. 3. Results of modeling SPR in structure Au/Nb_2O_5.

As these figures show, changing substituting dielectric layer covering the substrate leads to an appearance of a number of minimums. The angles of a minimum observation are dependent on dielectric layer thickness and enviro nment.

Such a way, there is opportunity to create appropriate sensors with plasmon supporting metal film and suitable transitional film of dielectric with interference effect.

(a)

(b)

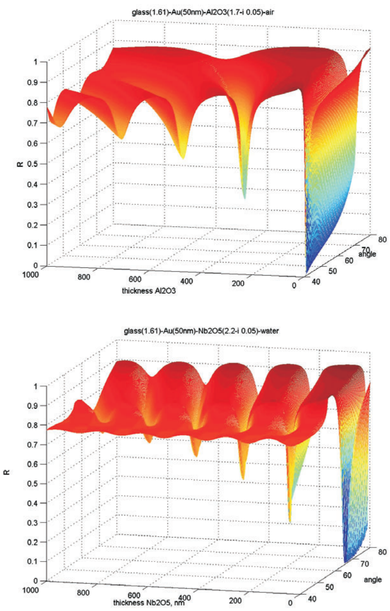

Fig. 4. Results of SPR modelling for absorption dielectric layer of Au/Al2O3(a) and Au/Nb2O5(b).

Under light absorption the intensities of minima are decreased due to increasing thickness of dielectric layer (Fig. 4). It should be noted that the sensors chips with observation of the second minimum are practically realized in our laboratory.

2. Experiment

In these papers the new technology of making a SPR chips Au/Al_2O_3 by film deposition of Al with thickness more than optimal for SPR chips and by the oxidation of excess Al- layer by electrochemical anodic oxidation is presented. The formed layer of anodic oxide Al_2O_3 with bigger chemical inertness and hardness than in Al provides the steadiness of chips during investigations in aqueous solutions. From other hand the controllable anodic oxidation allows the production of oxide film with bigger thickness accuracy thereby to accurately control the Al thickness which remained as plasmon supporting layer.

By the specially made MATLAB program the calculations of the optical reflection coefficient from SPR substrates with refraction index 1.61 and with different thickness of deposited Al layer were made. The results of SPR modelling in Al films depends on thickness of Al layer are shown in Fig. 5(a), 5(b).

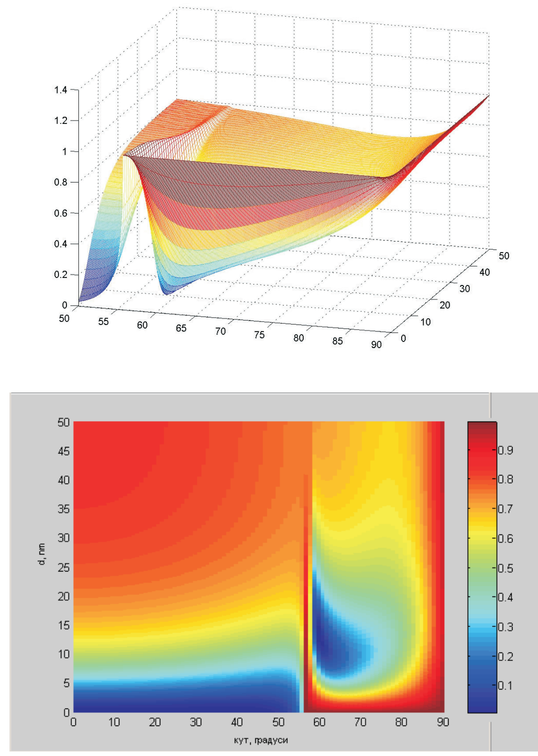

Fig. 5. 3-D (a) and 2-D (b) dependences of R(φ) from thickness of Al layer.

As we can see from Fig. 2 the optimal thickness of Al layer for excitation of SPR is the range from 12 to 18 nm.

It was simulated the experiment of Al film different thickness (18, 22, 26, 30 and 40 nm) oxidation of for detection of the optimal Al film thickness. SPR-curves were evaluated with discreteness of Al oxidation 2 nm to termination of plasmon resonance. The results from one of these experiments with initial Al thickness 30 nm are shown in Fig. 6.

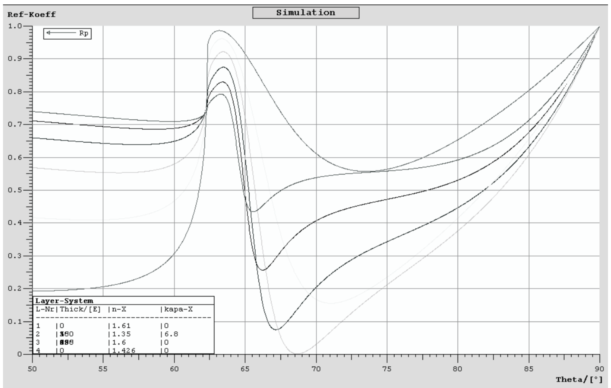

Fig. 6. R(φ) dependence of layer structure Al/Al_2O_3 obtained by the anodic oxidation of Al films. Thickness of layers (from left to right) - Al(30 nm), Al(25 nm)/Al_2O_3 (6.5 nm), Al(20 nm)/Al_2O_3(13 nm), Al(15 nm)/Al_2O_3 (19.5 nm), Al(10 nm)/Al_2O_3(26 nm), Al(5 nm)/Al_2O_3 (32.5 nm).

The question of SPR-sensitivity during the changes of environmental refractive index is very important for practice.

For each curve (Fig. 6) and for different Al film thickness the shift resonance angle in dependence on environmental refractive index were calculated. From calculated shifts the sensitivity, where n - environmental refractive index, was evaluated (Fig. 7).

At optimal parameters of SPR - substrate the dependence of the resonance angle shift on the changes of environmental refractive index is linear:

$$\varphi=\varphi_0+\frac{\partial\varphi}{\partial n}\cdot n,$$

where

$$\frac{\partial\varphi}{\partial n}=tg(\theta)$$

Is sensitivity of SPR sensors, where θ - the angle of inclination in dependence $\varphi(n)$.

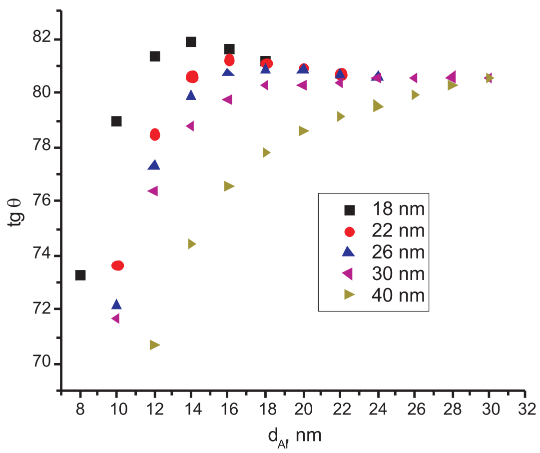

Fig. 7. Sensitivity of SPR-sensors for all series of Al/Al_2O_3 structure with different initial thickness of Al.

From the analysis of the data the optimal structure of Al/Al_2O_3 (with minimum R at φ_{SPR} and with high sensitivity) is the structure with initial thickness of Al layer 30 nm and post-oxidation thickness 18 nm. The thickness of oxidised layer is 15,6 nm.

It should be noted that under initial oxidation of Al 22 nm thickness to 18 nm the better SPR sensitivity can be achieved. But the oxide layer is very thin then - about 3 nm, a little thicker than natural oxide layer on the Al surface (2 nm) so it is not enough for protection of the substrate during using.

The Al films were sputtered on glass substrate with refractive index 1.61 by the method of magnetron spattering at constant current and deposition rate about 1 nm/s.

After sputtering on the Al film the two photoresist masks with different areas for anodisation were formed. At the first step the small area (1 mm^2) used for control of total Al film thickness by the anodisation. Then on the largest area by the anodic oxidation with depth control the area of 50 mm^2 for SPR-curves investigation was formed.

In our laboratory was made the special unit which providing the electrochemical oxidation directly on SPR-sensor. The scheme of unit is shown in Fig. 8.

After first anodic oxidation the Al films thickness on the substrate can be calculated by the formula:

$$d_{Al}=C_{Al}\cdot V$$

where C_{Al} = 0,88 nm/V anodisation constant for Al, V voltage of anodising.

This way calculated the full Al thickness on three samples was 22, 25 and 30 nm. Then the SPR chips were formed by anodic oxidation on the largest area in regime of constant current density with discreteness in 1 V.

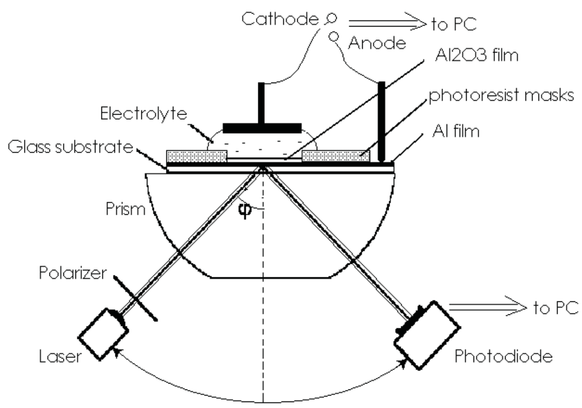

Fig. 8. Scheme of unit for providing of electrochemical oxidation directly on SPR-sensor.

The SPR-curve was recorded after each stage of oxidation. The curves of controllable anodic oxidation and SPR-curves for the substrate with initial thickness 30 nm are shown in Fig. 9 a, b.

The values of optical film indexes (the changes of effective refractive index with the film thickness changes were not registered) were calculated by cut-and-try approach by comparison of theoretical and experimental curves. The results are shown in Fig.10.

During comparison of the curves it was determined the parameters of the films: the aluminium has the refractive index 1.35-i6.83, the oxide - n=1.6.

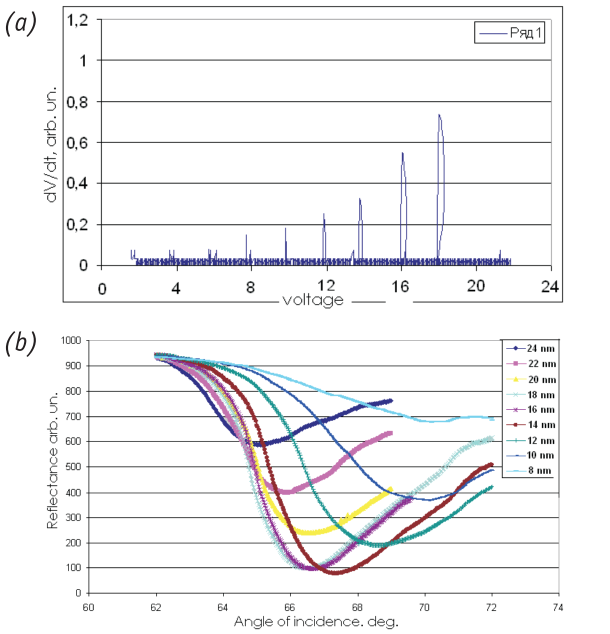

Fig. 9. Curve of controllable anodic oxidation of Al with initial thickness 30 nm (a), SPR-curves after each stage of oxidation (b).

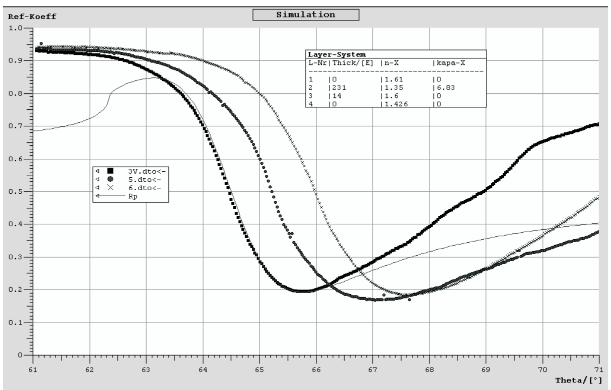

Fig. 10. Comparison of the theoretical and experimental curves in program Winspall.

As we can see from Figures 3, 8 (b) and 9 the experimental results correspond to theoretical. The disagreement can be explained by factors which were not taken into account in theoretical model (surface roughness, the deflection from stehiometry on the surface boundary, the presence of accidental pinholes in the films, the ingress of electrolyte in oxide film etc.)

Also the experimental researches of the formed substrates sensitivity were made in liquids with different refraction indexes. For the films with initial thickness 40 nm oxidized to 20 nm the sensitivity is $tg(\theta)$=82.37, but the theoretical value is 78.59 in this case. It means that experimental curves have better values than in theory. The changes of effective refraction indexes with changes of film thickness were not taken into account in the calculations, so it can explain this paradox in results. Also it can be explained by the decrease of real part of Al refraction index with the film thickness reduction and it is conformed to statements of optics of thin metal layers.

3. Conclusion

The theoretical modelling of SPR in structure Al/Al_2O_3 was made. The optimal layer thickness of Al/Al_2O_3 for SPR-sensors with maximal sensitivity was determined.

The new technology of making the SPR substrates glass-Al/Al_2O_3 using the magnetron spattering method and controllable anodic oxidation is developed.

The unit and procedure for simultaneous Al/Al_2O_3 forming and express-control of SPR-curve were developed. The experiments on the formed SPR-substrates show that received results are conformed with theoretical generally.

AUTHORS

Leonid Poperenko - Physics Department in Taras Shevchenko Kyiv National University, Kyiv, Ukraine
Tetyana Lebyedyeva, Pavlo Shpylovyy - Glushkov Institute of Cybernetics, Kyiv, Ukraine.
Sergiy Kurlov* - Physics Department in Taras Shevchenko Kyiv National University, Glushkov Institute of Cybernetics, Kyiv, Ukraine. E-mail: kurlov_s@rambler.ru.
* Corresponding author

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