ADVANCED DESIGN AND TECHNOLOGY FOR PRODUCTION OF SENSOR ELEMENTS IN DEVICES BASED ON SURFACE PLASMON RESONANCE

Doc.Sc. Maslov V.P., Phd-student Dorozinsky G.V.
V. Ye. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine

vladmaslov@mail.ru, gvdorozinsky@isp.kiev.ua

Abstract: *Results of researches are showed, that fabrication technology of sensor elements are used in devices based on surface plasmon resonance significantly affects on the increasing uptime of measuring and substantially increases the sensitivity to low concentrations of analytes. The results of investigations have shown that deposition of plasmonexciting metal layer on glass substrate at the chosen angle enables to enhance sensitivity of the surface plasmon resonance sensor by 1.5 times for liquid media and 2 times for gas-like media as compared with standard gold chips as well as improve uniformity of deposition and durability of ligand binding to the sensitive layer. Diagnostic facilities based on surface plasmon resonance possess a high sensitivity to low concentrations of studied substances, which enables one to use them as precise analytical devices in lab investigations in industry, agriculture, medicine, and ecology.*

Keywords: SURFACE PLASMON RESONANCE, NANOTECHNOLOGY, SENSOR ELEMENT, PRECISE ANALYTICAL DEVICES

1. Introduction

The *objective*s of the research are advanced sensor elements, their production technology and their sensor properties for use in devices based on surface plasmon resonance for accurate measurements. Optical measurements are based on the phenomenon of surface plasmon resonance (SPR) is widely used for chemical and biological analyzes based on detection of adsorption of gaseous or liquid media. Surface plasmon resonance is an optical excitation of surface plasmons or a charge density wave on the interface between the conductor (e.g., gold or silver) and a dielectric (insulator may be a gas, liquid or solid). The resonance wave vector related to the optical excitation of surface plasmon waves is dependent on the refractive index of the metal and the dielectric contacting them. SPR occurs in a thin metal film with a negative dielectric constant (high conductivity), which is arranged on a transparent dielectric substrate. The phenomenon of SPR is that at the corners corresponding to total internal reflection within the thin metal film by laser radiation conduction electrons in the metal film are excited, that is observed as a sharp decrease in the intensity of reflected light at a specific (resonance) angle of incidence. For analytical instrumentation is important that the magnitude of the resonance angle depends on the concentration of the substance on the surface of the sensor element. Most sensitive as the metal layer is used as the gold metal layer with a high conductivity and a high chemical inertness. Based on the SPR phenomenon refractometric method has been successfully used for the analysis of the optical properties of a wide range of substances, from gases (e.g., anesthetic gases) [1] to liquids (e.g., analysis of the binary system of methanol in water), [2] and the solids (e.g. inorganic solid particles [3] and the organic film Langmuir-Blodgett [4]). Diagnosing the devices working on the phenomenon of SPR is highly sensitive to low concentrations of analytes, allowing them to be used not only as a gas analyzer [5], but also as high-precision analytical instruments for laboratory analysis in the food, chemical and pharmaceutical industry, in agriculture, medicine, environment [6-11]. At the same time, up to date the influence of state and topology of sensor element surface on accuracy and stability in operation of SPR sensor appliance is investigated insufficiently. As known, increasing the area of the excitation surface plasmon layer SPR sensor affects to growing response and the adhesion surface to immobilize ligands (receptors) or adsorbers.

2. Preconditions and means for resolving the problem

Sensitivity of detection change of refractive index is determined by the lowest minimum SPR angular shift, which can be registered. This shift corresponds to the minimum value of the minimum detectable change in refractive index. Some manufacturers of devices, that use the phenomenon of SPR, are using values shift SPR curve minimum relative angular values RU (RU = 8.3×10^{-5} angular degrees, which is equivalent to one picogram substance on the surface of the sensor SPR) to estimate the sensitivity, while others are measuring the absolute sensitivity values of the refractive index RIU (refractive index unit) [12]. And the change of the angle is proportional to the concentration of the substance analyzed volume. Therefore, in liquids such sensor responds only to changes of refractive index and absorption of the medium. In a gas medium components of admixture adsorption on the surface of the sensor is observed, which leads to higher concentration in the zone of sensitivity in compared to the volume. So, sensor responds as to changes of refractive index and absorption, as to thickness of the adsorbed layer on a surface of the sensor element. The quantity of adsorption depends on the material and surface properties (roughness, porosity, etc.). The increasing of sensing element`s surface porosity allows to increase the response of the sensor as in the gas medium analysis [13, 14], as in the aqueous solutions analysis [15].

Sensitivity of the method also determined by SPR`s width and shape of the absorption curve, which determines the accuracy of detecting the position of its minimum. Therefore, a possible way to significant increase (by orders of magnitude) the sensitivity of SPR sensors is to apply the methods of narrowing the resonance spectrum. This can be achieved by placing on a sensitive area holographic and diffraction structures that produced on the sensor surface [16]. Narrowing of the resonance spectrum is also possible through the using of bimetallic silver-gold layers on the sensor surface [17] and increasing the laser wavelength excitation SPR [18].

Evolution of increasing sensitivity of SPR instruments looks like follows. In 1998, the company a BIACORE reported of achieving sensitivity of 2×10^{-5} RIU, three years later, the sensitivity increased to 1×10^{-5} RIU. At the same time, other authors [19] reported of sensitivity 1.2×10^{-6} RIU. In 2014, the BIACORE reported of achieving sensitivity of 10 RU, and the company Reichert reported of achieving sensitivity of 1×10^{-7} RIU [20].

Further increase in sensitivity is limited by frequency stability and spectral width of semiconductor lasers [21], noise and thermal drift of photo detectors equipment. Reducing the influence of temperature on the sensitivity of devices based on SPR thermostatization achieved not only the sensor but also the whole device together with receptacles for the test substances [22]. In addition, as a result of experimental studies suggested that optimization of thermal temperature regimes of the device [23].

Increasing the sensitivity of SPR measurement devices is possible by modifying the surface of the sensor and optimization of manufacturing technology. Depending on the particular problem to be solved, the simplest way is to use highly selective sorbents, or mixtures deposited on the sensing surface.

It follows from the mentioned above that it is necessary to determine and investigate experimentally the influence of plasmon exciting layer topology that provides increasing response of sensor transducer in optical measurements based on SPR when performing measurements in various media.

3. Solution of the investigated problem

To solve the problem was used optical measurement equipment developed in Ukraine [24]. The equipment measures the change in the refractive index of the test substances on which to judge the processes of deterioration, adsorption processes, etc. In V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, performed for many years are experimental investigations of applied aspects for designing biosensors based on SPR. One of the designed models is the spectrometer "Plasmon-71" (Fig. 1) suitable for operation in labs of biochemical and biophysical profiles. This device allows you to measure the refractive index over a wide range from 1 to 1.5 RIU, refractive index shift measuring range 5 RU (relative units) to 130 000RU with an accuracy $\pm 3\times 10^{-6}$ RIU (refractive index unit).

Fig. 1. *Appearance of the SPR spectrometer Plasmon-71*

Devices based on the SPR allow quickly determining the optical properties and monitoring processes in real time.

Within the frameworks of these investigations, developed and manufactured was the thermostat that enables to keep the set temperature with rather high stability. The thermostating, offered after performed investigations, were not only of the studied object but also of all the measuring equipment including boxes with the studied substances. This approach enabled to minimize the temperature error in measurement results and, in addition, temperature loading the measuring equipment, which prolongs its functioning term [25].

The investigations were carried out to optimize the geometry of the deposition layers on the surface of bimetallic sensing elements. As a material used gold layers. Alternating layers sprayed onto a glass substrate F1 in a vacuum depositing device VUP-5M (Fig. 2) with vacuum of 5×10^{-5} mmHg. Depositing a first layer of a thickness of 35 nm, produced at the location of the substrate parallel to the surface of the evaporator (typically sputtering), a second layer was sprayed on the first layer at the location of the substrate at an angle to the evaporator. The thickness of the second layer, considering deposition at an angle, was of approximately 30 nm. The thickness of the deposited layer was monitored by a quartz thickness indicator by change of its oscillation frequency.

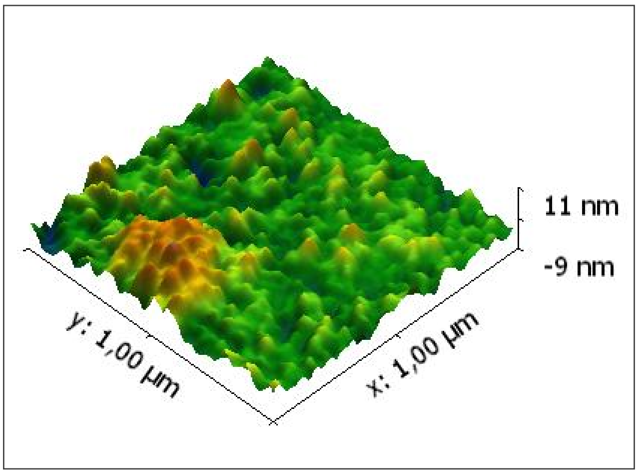
Fig.2. *Appearance of the vacuum depositing device VUP-5M*

The two test sample of sensing elements was used in a experiment: a typical plated gold layer thickness of 50 nm on the substrate (structure number 1) and the modified geometry deposition (structure number 2). Experiments were carried out in the Multiple mode. In this mode, the minimum of SPR curve was determined and recorded at each scan. To determine the sensitivity of the sensory of structures known aqueous solutions used in the tow-channel flow cell that provide contact of fluid with the structure number 1 or number 2. Flow cell was equipped by injection and removal of tested liquid or gas tubes. The study was conducted on a samples of two liquids with different refractive indices: distilled water (n = 1,33154) and 0.6% potassium chloride solution (KCl) in water (n = 1,33241). A substitution of fluid sample was performed by a peristaltic micro-pump, which also produced in V. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine (Fig. 3). The room air and ethanol vapor in flow cell was used as gas-sensing. The changes of the refractive index in time were recorded on the moment when distilled water was in the cell, and after the substitution with solution. Likewise, sample gas substitution was carried out. Kinetics shift SPR minimum recorded by developed program.

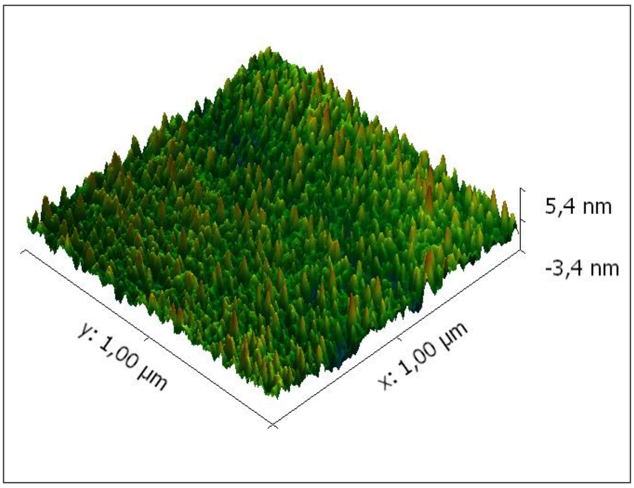
Fig.3. *Appearance of the peristaltic micro-pump*

4. Results and discussion

Surface topology of the samples number 1 and number 2 was studied by atomic force microscope (AFM) using [26]. It has been found that the structure of the gold layer number 2 obtained by spraying angle has a developed surface and hence it in compare to a large surface area compared to the structure number 1 (Fig.4). SPR curves for this samples performance on Fig.5.



A)



B)

Fig.4. *AFM images of researching sample: structure number 1(A) and structure number 2 (B)*

After two fluid replacement procedures on 24 minutes of measurement by using structure number 1 refractive index of liquids significantly changed the in compare to its initial value (Fig. 5, curve №2). To the structure number 2 the refractive index of distilled water and salt solution remained almost unchanged during the measurement (Fig. 5, curve №1). Furthermore, the response to the replacement fluid in the flow cell structure number 2 was 1.5-fold greater than the response to the structure of number 1, and the refractive index of the salt solution potassium chloride (KCl) is closer to the theoretical value (n = 1,33248), than in the case of using the structure number 1 (n = 1,33219). Kinetics of substitution in the measuring cuvette SPR spectrometer PLASMON room air ethanol vapor concentrations varying shown in Fig. 7. Shows the kinetics of the samples for the two sensitive elements of the SPR sensor: standard topology (line 1) and modified (line 2). From Fig. 7 shows that the technology of production of modified topology can increase response sensor 2 times.

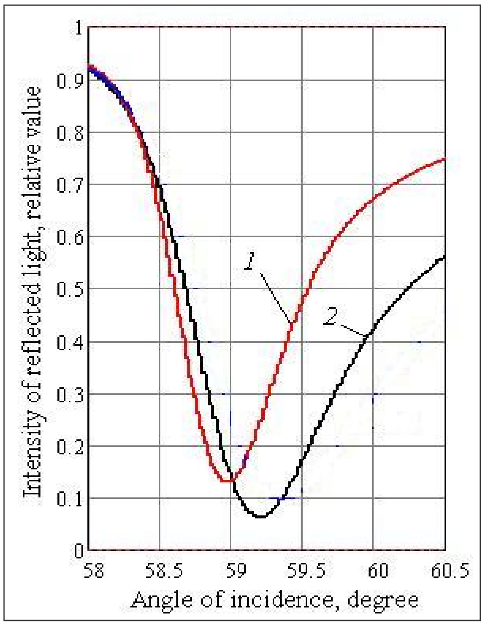


Fig. 5. *SPR curves of measured samples: structure number 1(red line) and structure number 2 (black line)*

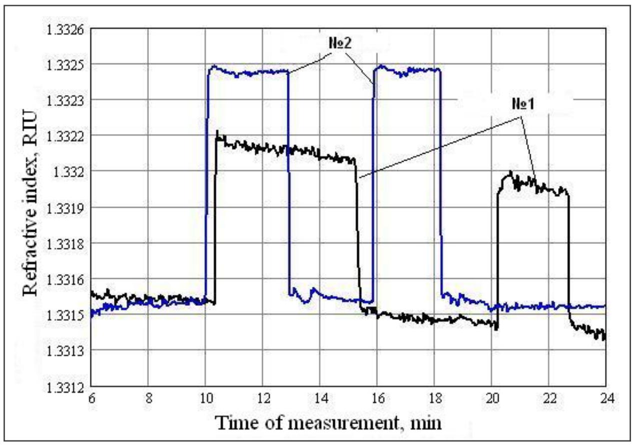


Fig. 6. *Measured curve kinetic process in liquid media*

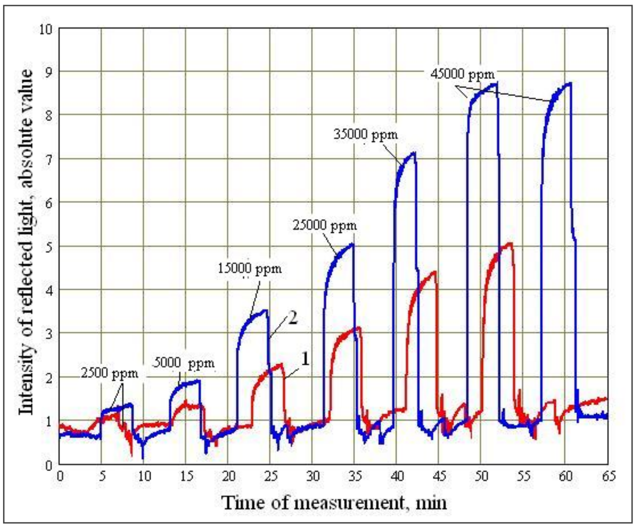


Fig. 7. *Measured curve kinetic process in gas-like media*

5. Conclusion

The geometry of gold sputtering films with optimum thickness, which provides a 1.5-fold greater response to changes of the refractive index of the liquid medium above the SPR sensor, and a 2-fold greater response with a change in the refractive index of a gaseous medium, in comparison with the standard gold chips was proposed. This will improve precision of measurement and increase the use of surface plasmon resonance in the industry and ecology for diagnosis and monitoring structures and elements of goods, manufacturing processes and for monitoring production safety.

References

[1] Liedberg B., Nylander C., Lundstrom I. Surface Plasmon Resonance For Gas Detection and Biosensing // Sensors and Actuators. — 1983. — N 4. — P. 299–304.

[2] Matsubara K., Kawata S., Minami S. Optical Chemical Sensor Based on Surface Plasmon Measurement // Applied Optics. — 1988. — **27**. — P. 1160–1163.

[3] H. Xu and M. Kall Modeling the optical response of nanoparticle-based surface plasmon resonance sensors // Sensors and Actuators. — B Vol. 87, N 2. — P. 244-249.

[4] Rella R., Siciliano P., Quaranta F., Primo.T., Valli.L., Schenetti L., Mucci A., Iarossi D. Gas Sensing Measurements and Analysis of the Optical Properties of Poly [3-(butylthio)thiophene] Langmuir-Blodgett films Sensors and Actuators B68 (2000) 203-209

[5] A.V. Samoylov, V.M.Mirsky, Q. Hao, C. Swart, Y.M. Shirshov, O.S.Wolfbeis. Nanometer-thick SPR sensor for gaseous HCl // Sensors and Actuators B Chem. – 2005. – Vol.106. – P.369-372.

[6] Gridina N., Dorozinsky G., Khristosenko R., Maslov V., Samoylov A., Ushenin Yu., Shirshov Yu. Surface plasmon resonance biosensor // Sensors & Transducers Journal. – 2013. – Vol.149, № 2. – P.60-68.

[7] A. V. Samoylov, Yu. V. Ushenin, R. V. Khristosenko. Application of surface plazmon resonance spectrometer for determination of optical parameters of the thin polyaniline films.. “International Conference «Functional Materials» ICFM ’ 2007”.

[8] N.Ya.Gridina, A.V.Samoilov, Yu.V.Ushenin, Yu.M.Shirshov, Diagnostic possibility demonstration’ of cerebrum oncologic diseases by biosensor based on surface plazmon resonance, International Conference “Functional MAterial” ICFM-2009, 5-10 October, 2009, Partenit, Ukraine.

[9] Shirshov Yu.M., Samoylov A.V., Zinyo S.A., Surovceva E.R., Mirskiy V. Bimetallic Layers Increase Sensitivity of Affinity Sensors Based on Surface Plasmon Resonance // Sensors – 2002.– Vol.2, – 62-70.

[10] K.V. Kostyukevych, R.V. Khristosenko, Yu.M. Shirshov, S.A. Kostyukevych, A.V. Samoylov, V.I. Kalchenko Multi-element gas sensor based on surface plasmon resonance: recognition of alcohols by using calixarene films // Semiconductor Physics, Quantum Electronics and Optoelectronics.- 2011. – V.14, N3. P. 313-320.

[11] A. Rachkov, Yu. Holodova, Yu. Ushenin, D. Miroshnichenko, G. Telegeev, A. Soldatkin, „Development of Bioselective Element of SPR Spectrometer for Monitoring of Oligonucleotide Interactions and Comparison with Thermodynamic Calculations”, *Sensor Letters*, 2009, Vol. 7.

[12] Кобзева И.Н. Оптические сенсоры для биосенсорных диагностических систем на основе поверхностно-плазмонного резонанса // Вісник КДПУ імені Михайла Остроградського. Випуск 4/2009 (57). Частина 2..

[13] Ушенин Ю.В., Христосенко Р.В., Самойлов А.В., Дорожинский Г.В., Каганович Э.Б., Манойлов Э.Г., Снопок Б.А. Оптоэлектронные сенсорные структуры на основе пленок пористого оксида алюминия, полученных импульсным лазерным осаждением // Оптоэлектроника и полупроводниковая техника. – 2012 – № 47. – С.40-45.

[14] Ushenin Yu.V., Khristosenko R.V., Samoylov A.V., Kaganovich E.B., Manoilov E.G., Snopok B.A., Dorozinsky G. W., Maslov V.P. Porous alumina films obtained by pulsed laser deposition for sensors applications // International Conference “Functional Material” (ICFM-2013). – Partenit: Ukraine. – 2013. – P.451.

[15] Вакарюк Т.Є., Громовой Ю.С., Данько В.А., Дорожинський Г.В., Зиньо С. А., Індутний І.З., Самойлов А.В., Ушенін Ю.В., Христосенко Р.В., Шепелявий П. Є. Використання поруватих плівок SiOx в сенсорах на основі поверхневого плазмонного резонансу // Оптоэлектроника и полупроводниковая техника. – 2013 – № 48. – С.89-95.

[16] Palagushkin A.N., Prokopenko S.A., and Sergeev A.P. Plasmonic Holographic Nanostructures // Optical Memory and Neural Networks (Information Optics). 2009. Vol. 18. No. 3, pp. 156–163. Allerton Press, Inc.

[17] Shirshov Yu.M., Samoylov A.V., Zinyo S.A., Surovceva E.R., Mirskiy V. Bimetallic Layers Increase Sensitivity of Affinity Sensors Based on Surface Plasmon Resonance // Sensors – 2002.– Vol.2, – 62-70.

[18] Ю.В. Ушенін, А.В. Самойлов, Р.В. Христосенко. Увеличение чувствительности сенсоров изменения показателя преломления среды на основе поверхностного плазмонного резонанса // Технология и конструирование в электронной аппаратуре -2011.- №1-2(90) - С. 12-14.

[19] Dostalek J., Ctyroky J., Homola J., Nekvindova P., Spikova J., Skvor J., Schrofel J. Surface plasmon resonance biosensor based on integrated optical waveguide // Sensors and Actuators, B. –2001. – Vol.76. – P.8-12.

[20] www.reichertspr.com

[21] Байбородин Ю.В. Основы лазерной техники. – 2-е изд. перераб. И доп. – К.: Выща шк. Головное изд-во, 1988. – 383 с.

[22] Dorozinsky G., Maslov V., Samoylov A., Ushenin Yu. Reducing measurement uncertainty of instruments based on the phenomenon of surface plasmon resonance // American Journal of Optics and Photonics. – 2013. - Vol.1, № 3. – P.17-22.

[23] Dorozinsky G., Dunaevsky V., Maslov V. Thermal-vision method of investigations and control of device based on surface plasmon resonance // Universal Journal of Control and Automation. – 2013. - Vol.2. – P.34-39.

[24] www.plasmon.org.ua

[25] Gleb Dorozinsky. Surface plasmon resonance as a tool for research in nanotechnology and industry // 10th International Congress “Machines.Technologies.Materials’13” (MTM-2013). – Varna: Bulgaria. – 2013. – P.59-62.

[26] www.microscopy.org.ua