# PHYSICAL SENSORS

# СЕНСОРИ ФІЗИЧНИХ ВЕЛИЧИН

UDC 535-7, 535.016, 53.043

## APPLICATION OF TEMPERATURE SENSORS FOR IMPROVING THE DEVICE BASED ON THE PHENOMENON OF SURFACE PLASMON RESONANCE

*Yu. V. Ushenin[1], G. V. Dorozinsky[1], V. P. Maslov[1], T. A. Turu[2], N. V. Kachur[1]*

[1]V. Lashkaryov Institute of Semiconductor Physics,
41, Prospekt Nauky, 03680 Kyiv, Ukraine,
phone: +38(044)525-58-30, fax: +38(044)525-13-66, e-mail: vpmaslov@ukr.net

[2]National Technical University "Kyiv Politechnical Institute",
37, Prospekt Peremogy, 03056 Kyiv, Ukraine,
e-mail: kpi_naeps@ukr.net

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*Yu. V. Ushenin, G. V. Dorozinsky, V. P. Maslov, T. A. Turu, N. V. Kachur*

**Abstract.** The device based on surface plasmon resonance (SPR) is used to determine the refraction index of liquids. At the same time, it is known that the value of this index depends on the temperature of this liquid. Therefore, this work was aimed at investigation of possibilities to enhance accuracy of such two-channel SPR devices by using the temperature sensors directly in each measuring cell. It has been experimentally proved that application of miniature temperature sensors (like to thermistors) in cells of both channels simultaneously enables to doubly reduce the error of refraction index measurements. In the case of multi-channel devices, it seams reasonable to use an array of semiconductor thin-film temperature sensors in the unit cell.

**Keywords:** surface plasmon resonance, temperature sensor, precision measurement of the refraction index

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# ВИКОРИСТАННЯ СЕНСОРІВ ТЕМПЕРАТУРИ ДЛЯ ВДОСКОНАЛЕННЯ ПРИЛАДУ НА ОСНОВІ ЯВИЩА ПОВЕРХНЕВОГО ПЛАЗМОННОГО РЕЗОНАНСУ

*Ю. В. Ушенін, Г. В. Дорожинський, В. П. Маслов, Т. А. Туру, Н. В. Качур*

**Анотація.** Прилад на основі поверхневого плазмонного резонансу (ППР) використовують для визначення показника заломлення рідин. В той же час відомо, що цей показник залежить від температури цієї рідини. Метою роботи було дослідження можливості підвищення точності двоканального приладу на основі ППР за рахунок використання сенсорів температури для контролю температури безпосередньо в кожній вимірювальній кюветі. Експериментально доведено, що використання мініатюрних сенсорів температури (на прикладі терморезисторів) для вимірювання температури безпосередньо на кожному каналі кювети для вимірювання показника заломлення дозволяє зменшити похибку вимірювання майже вдвічі. Для багатоканальних приладів ППР перспективним є використання лінійки напівпровідникових плівкових сенсорів температури в кюветі приладу.

**Ключові слова**: поверхневий плазмонний резонанс, сенсори температури, точність вимірювання, показник заломлення

# ИСПОЛЬЗОВАНИЕ СЕНСОРОВ ТЕМПЕРАТУРЫ ДЛЯ СОВЕРШЕНСТВОВАНИЯ АППАРАТА НА ОСНОВЕ ЯВЛЕНИЯ ПОВЕРХНОСТНОГО ПЛАЗМОННОГО РЕЗОНАНСА

*Ю. В. Ушенин, Г. В. Дорожинский, В. П. Маслов, Т. А. Туру, Н. В. Качур*

**Аннотация.** Прибор на основе поверхностного плазмонного резонанса (ППР) используют для определения показателя преломления жидкостей. В то же время известно, что этот показатель зависит от температуры этой жидкости. Целью работы было исследование возможности повышения точности двухканального прибора на основе ППР за счет использования сенсоров температуры для контроля температуры непосредственно в каждой измерительной кювете. Экспериментально доказано, что использование миниатюрных сенсоров температуры (на примере терморезисторов) для измерения температуры непосредственно на каждом канале кюветы для измерения показателя преломления позволяет уменьшить погрешность измерения почти вдвое. Для многоканальных приборов ППР перспективным является использование линейки полупроводниковых пленочных сенсоров температуры в кювете прибора.

**Ключевые слова**: поверхностный плазмонный резонанс, сенсоры температуры, точность измерения, показатель преломления

## Introduction

The leading tendencies in development of analytic devices require implementation of new physical methods for measurements that are based on up-to-date achievements in science and technique. The main requirements to these methods are as follows: enhancement of their accuracy and sensitivity, shortening the time for measurements, reduction of the volume of studied substances. It is known that optical methods possess a high operation speed and enable to reach high accuracy and sensitivity in measurements. One of the promising optical methods for analysis of various compounds and micro-objects as well as processes at the molecular level is the refractometric method based on surface plasmon resonance (SPR) phenomenon. The respective devices (SPR-devices) are mainly designed using chemical and biological sensors that consist of a sensitive element and some physical transducer. As compared with traditional measuring methods, the SPR-method provides possibility to study processes of molecular interaction in micrometer-thickness layers in the real-time scale; low value of the sample volume required for measurements (10 μl); the method does not require any markers or fluorescent labels for studying the substance (analyte).

The SPR-devices are widely used in scientific researches, in medicine and ecological monitoring [1-3], therefore, enhancement of accuracy inherent to these devices seems to be a topical task.

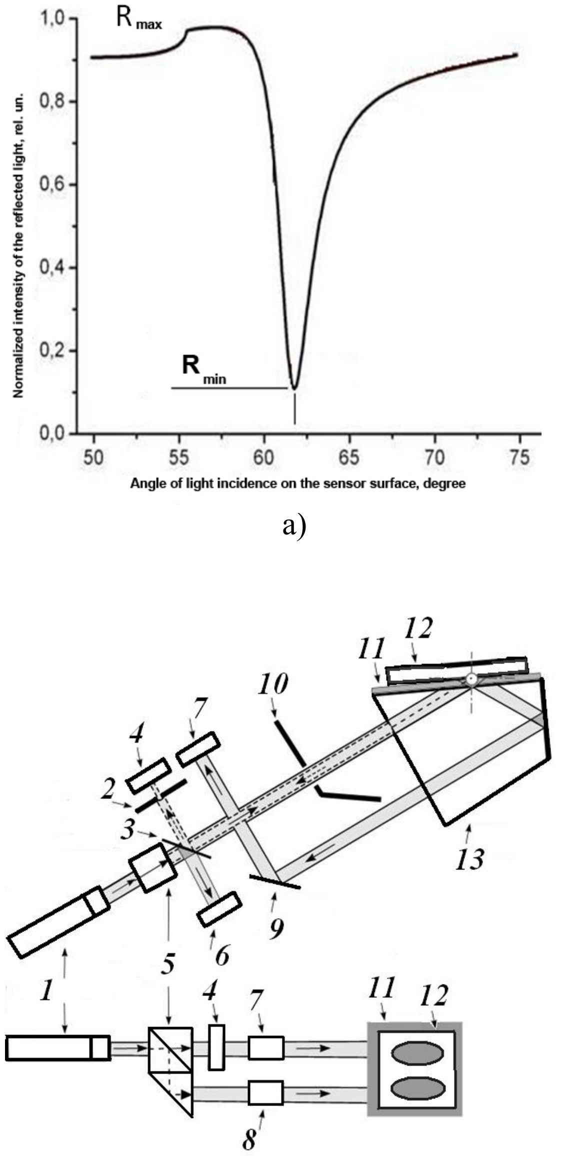
As shown in the previous works [4-6], account of the temperature factor is essential for enhancement accuracy of measurements when using the SPR-device.

This work is aimed at improvement of SPR-device accuracy due to use of temperature sensors.

## Devices and methods of investigation

Investigation of the temperature influence on accuracy of measurement results was performed using the SPR-device «Plasmon-71». The devices of "Plasmon" series are computer-controlled optoelectronic small-scale two-channel refractometers based on SPR for determination of the SPR curve shift inherent to the studied analyte. Operation surface of the "Plasmon" sensitive element is formed from a gold film with the thickness 48 to 52 nm. As a source for excitation, there used is *p*-polarized light from the semiconductor injection laser diode.

Necessary conditions for plasmon excitation are reached by changing the angle of incidence of *p*-polarized light on the surface of the sensitive element. The angular dependence of the intensity of light reflected from the surface of the sensitive element is the main output chacteristic in these measurements and is called as the SPR curve (Fig. 1a). The optical scheme of the device (Fig. 1b) corresponds to the Kretschmann geometry and consists of the laser diode 1, sensitive element 11, half-pentaprism 13, and two photodetectors 7 and 8.



a)

b)

**Fig. 1. SPR curve (a) and optical scheme of the device «Plasmon-71» (b).**

The laser diode 1 generates light with the wavelength 850 nm. This light passes through the half-pentaprism 13, is reflected from the surface of the sensitive element 11, from the mirror on the back face of the prism, from the additional mirror 9, and falls onto photodetector 7. The gold film is deposited onto a glass plate joined with the retroprism by using immerse liquid. Data for plotting the SPR curve are obtained by rotating the retroprism and simultaneous measuring the intensity of light reflected from the sensitive element. The channels are formed by the measuring cell 12 made of polymethylmetacrylate, which is mounted on the sensitive element via the silicone spacer. To excite surface plasmons in both channels, light from the laser diode is separated by two beams with the prism 5. Control and stabilization of the light intensity is provided with the photodetector 6 and the device electronics, respectively. Calibration of the absolute angle is performed with the photodetector 4 and diaphragm 2 (slot width is close to 100 µm) by measuring the intensity of light reflected from the prism front face. Measurements of the laser light intensity and calibration of the angle are provided with the separating plate 3 and diaphragm 10. Except prism, all the elements of this optical scheme, sensitive element and measuring cell form a separate assembly – the optical unit. Angular scanning and determining the minimum position of the SPR curve are provided within the range of angles 38 to 73 degrees for rotation of the half-pentaprism on the platform-holder with the step-motor and reducer.

To ascertain the influence of temperature directly in each channel, the authors mounted contact temperature sensors consisting of platinum temperature-sensitive elements in each measuring cell (Fig. 1b, pos. 12). Used here are temperature-sensitive elements M222Pt100 (Heraeus Sensor Technology, Germany) with dimensions 2×2×1.2 mm, linear temperature characteristic within the range from –203 up to +773 K and initial resistance 1 kOhm at the temperature 293 K (DIN EN6075 accordingly to IEC 751). These elements were fixed inside the case of measuring cells by using a compound in such a way that provided thermal contact with the studied liquid.

In these experiments, we used distilled de-mineralized water in accord with technical conditions ТУ У 24.1-31826636-004:2009 (ТДВ «Тхорівське», Ukraine). The refraction index and temperature coefficient of distilled water were studied in detail in [7]. This water was pumped through the two-channel cell. Temperature of water was measured separately in each measuring channel. First, our measurements were performed at room temperature (297 K). Then, the temperature was increased up to 309.6 K, using a resistive heater made of nichrome and installed into the cell.

To reduce the temperature influence on results of measuring the refraction index of the studied substance (analyte) with “Plasmon-71”, we used mathematical processing the obtained results with the aim to compensate the temperature drift of the operation point (minimum of the SPR curve $R(\theta)$). Compensation of the temperature influence was reached by multiplication of the measured value of the angle corresponding to the SPR-minimum by the correcting coefficient $K_t$ determined using the formula (1):

$$K_{ti} = [1+\gamma \cdot TK_n \cdot (T_i - T_0)], \tag{1}$$

where $K_{ti}$ is the correcting coefficient for the *i*-th measurement of the SPR minimum;

$\gamma$ – feedback coefficient, its optimal value $\gamma = 0.55$ provides minimum overcorrection;

TKn – temperature coefficient of the distilled water refraction index;

TKn = $-1.15 \cdot 10^{-4}$ K$^{-1}$ (respective shift of the operation point is 34.5 ang. sec/K$^{-1}$);

$T_i$ – temperature of distilled water for the *i*-th measurement of the SPR minimum, K;

$T_0$ – temperature of distilled water before heating it, $T_0 = 297$ K.

Thus, the results of measurements provided two sets of data: without thermal compensation and with it, which enabled to determine the averaged value of the SPR minimum position.

## Results of experiments and discussion

The results of experiments (Fig. 2) show that compensation of heating the distilled water when measuring the kinetics of the SPR minimum (operation point) shift with time (curve 2) essentially decreases its deviation as compared with that in the case when thermal compensation is absent (curve 1).

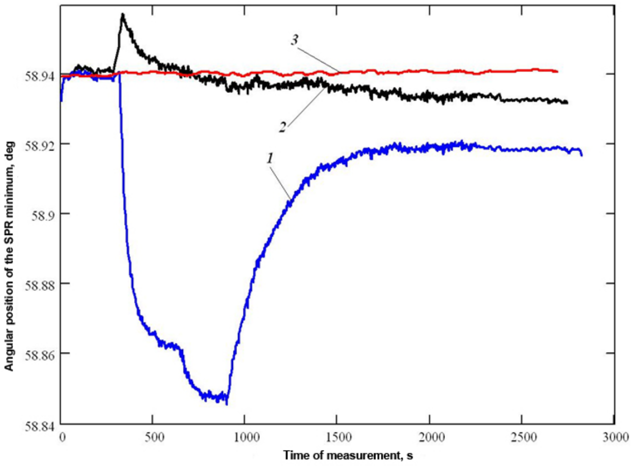


**Fig. 2. Kinetics of the SPR minimum shift for the distilled water when its temperature changes from 297 K up to 309.6 K: (1) without thermal compensation; (2) with compensation and (3) the same with averaging by 10 measurements.**

The jump of operational point at the initial part of the plot (2) is related with inertial character of processes of heat transfer from liquid to the thermal-sensitive element: the response of surface plasmons on the temperature change is faster than that of the thermal-sensitive element, which causes overcompensation. Elimination of this undesired phenimenon was reached using another (reference) channel in the measuring cell. We determined the difference signal between these two channels with additional averaging its value (by 10 consecutive values of measurements). This way not only eliminated overcompensation but, in addition, enabled to reduce the amplitude of the noise track by 12 times from $\delta_{NL} = 31.4 \cdot 10^{-5}$ down to $\delta_{NL} = 2.7 \cdot 10^{-5}$. In this case, the error of measurements without compensation reached the value $24 \cdot 10^{-4}$, while in the case of compensation it was equal to $8.7 \cdot 10^{-4}$ or even $2.1 \cdot 10^{-4}$ after compensation with averaging by 10 consecutive values of measurements.

The obtained experimental values for the temperature error are considerable as compared with the detection limit of “Plasmon-71” ($dN_{min} = 1.8 \cdot 10^{-5}$), which can be explained by a large change in temperature. In real conditions of experiments, such a change is impossible. Therefore, in addition we determined the temperature drift of the operation point in the Multiple regime for the period of measurements in conditions of thermal compensation without artificial heating the analyte. For water, the thermal drift of the operation point reached 40.64 ang. sec/K. The temporal drift of the refraction index was $-7.6 \cdot 10^{-5}$ min$^{-1}$. It enabled to determine the speed of changing the analyte temperature, namely: 0.182 K/min. For the time of one measurement, the temperature of distilled water changed by the value $\Delta T = 0.608$ K. The respective changes in the analyte temperature caused the absolute error in measurements of the SPR minimum shift for the distilled water $\delta_{NT} = 0.76 \cdot 10^{-5}$, which was considerably lower than the detection limit of SPR-device.

It means that thermal compensation reduces the error of measuring the refraction index at least by 3 times in the case of considerable changes in temperature of studied substance (12.6 K) and enables to enhance accuracy of measurements with “Plasmon-71”.

When using the device with larger number of channels (from 8 to 32), it seems reasonable to apply an array of semiconductor thin-film temperature sensors instead of thermistors that have larger dimensions and dependence of thermal conductivity on design solution.

## Conclusions

1. Developed in this work is the method that takes into account the temperature influence on the results of studying the substance refraction index on the example of distilled water.
2. It has been experimentally proved that application of a miniature temperature sensors like to thermistors for measuring the temperature in each channel of the measuring cell when determining the refraction index enables to doubly reduce the error of measurements.
3. In the case of multi-channel SPR-devices, it seems promising to use linear semiconductor thin-film temperature sensors in the measuring cell.

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[1]V. Lashkaryov Institute of Semiconductor Physics,
41, Prospekt Nauky, 03680 Kyiv, Ukraine,
phone: +38(044)525-58-30, fax: +38(044)525-13-66, e-mail: vpmaslov@ukr.net

[2]National Technical University "Kyiv Politechnical Institute",
37, Prospekt Peremogy, 03056 Kyiv, Ukraine,
e-mail: kpi_naeps@ukr.net

## Summary

The device based on surface plasmon resonance (SPR) is used to determine the refraction index of liquids. At the same time, it is known that the value of this index depends on the temperature of this liquid. Therefore, this work was aimed at investigation of possibilities to enhance accuracy of such two-channel SPR devices by using the temperature sensors directly in each measuring cell. To ascertain the influence of temperature directly in each channel, the authors mounted contact temperature sensors consisting of platinum temperature-sensitive elements in each measuring cell. Used here are temperature-sensitive elements M222Pt100 (Heraeus Sensor Technology, Germany) with dimensions 2×2×1.2 mm, linear temperature characteristic within the range from –203 up to +773 K and initial resistance 1 kOhm at the temperature 293 K (DIN EN6075 accordingly to IEC 751). These elements were fixed inside the case of measuring cells by using a compound in such a way that provided thermal contact with the studied liquid First, our measurements were performed at room temperature (297 K). Then, the temperature was increased up to 309.6 K, using a resistive heater made of nichrome and installed into the cell. Developed in this work is the method that takes into account the temperature influence on the results of studying the substance refraction index on the example of distilled water. It has been experimentally proved that application of a miniature temperature sensors like to thermistors for measuring the temperature in each channel of the measuring cell when determining the refraction index enables to doubly reduce the error of measurements. In the case of multi-channel SPR-devices, it seems promising to use linear semiconductor thin-film temperature sensors in the measuring cell.

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*Ю. В. Ушенін[1], Г. В. Дорожинський[1], В. П. Маслов[1], Т. А. Туру[2], Н. В. Качур[1]*

[1]Інститут фізики напівпровідників ім. В.Є. Лашкарьова НАН України, 03680,
пр.-т. Науки, 41, Київ, Україна, тел.: +38(044)525-58-30, факс: +38(044)525-13-66,
e-mail: vpmaslov@ukr.net
[2]Національний технічний університет України «Київський політехнічний інститут», 03056,
пр.-т. Перемоги, 37, Київ, Україна, тел.: +38(044) 204-85-03,
e-mail: kpi_naeps@ukr.net

## Реферат

Прилад на основі поверхневого плазмонного резонансу використовують для визначення показника заломлення рідин. В той же час відомо, що цей показник залежить від температури цієї рідини. Метою роботи було дослідження можливості підвищення точності двоканального приладу на основі ППР за рахунок використання сенсорів температури в вимірювальній кюветі. Для визначення впливу температури безпосередньо на кожному каналі нами були встановлені контактні сенсори температури на основі платинових термодатчиків на кожну вимірювальну кювету. Платинові термодатчики типу M222Pt100 (Heraeus Sensor Technology, Німеччина) габаритами 2×2×1.2 мм з лінійною температурною характеристикою від -203 К до 773 К та початковим опором 1 кОм при температурі 293 К (DIN EN6075 згідно IEC 751). Термодатчики фіксували у корпусі вимірювальної кювети компаундом таким чином, щоб забезпечити тепловий контакт з рідиною, що досліджували. Спочатку виконували вимірювання при кімнатній температурі (297 К), а потім резистивним нагрівачем, виконаним з ніхрому, вбудованим у кювету, виконували примусове нагрівання від 297 К до 309,6 К. Розроблено методику яка враховує вплив температури на результати дослідження показника заломлення на прикладі дистильованої води. Експериментально доведено, що використання мініатюрних сенсорів температури (на прикладі терморезисторів) для вимірювання температури безпосередньо на кожному каналі кювети для вимірювання показника заломлення дозволяє зменшити похибку вимірювання майже вдвічі. Для багатоканальних приладів ППР запропоновано використання лінійки напівпровідникових плівкових сенсорів температури в кюветі приладу.

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