

SPR chromatic sensor with colorimetric registration for detection of gas molecules

O.V. Riabchenko, O.L. Kukla, O.N. Fedchenko, Yu.M. Shirshov, Z.I. Kazantseva

V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine

41, prosp. Nauky, 03680 Kyiv, Ukraine

Corresponding author e-mail: alex.le.kukla@gmail.com

Abstract. In this work, we have proposed and tested a new version of an optoelectronic sensor for detecting gas molecules based on the effect of spectral surface plasmon resonance (SPR) in the chromatic mode with colorimetric registration of the R, G, B color components of reflected light. A thin 40-nm silver film on the base face of the prism with SPR excitation in the Kretschmann geometry is used as an optical sensitive element that allows us to realize a full-fledged SPR effect in the entire visible range of the spectrum from 450 to 700 nm. The physical nature of the sensory effect is a change in the refractive index of the sensitive coating on the silver film, which directly affects the SPR parameters. The films of polyvinyl formal ethylal were used as a coating selective to the number of organic analytes. A laboratory version of the portable device for implementation of a gas sensor based on the SPR-RGB effect was created. Performance of the proposed sensory method and the corresponding device were assessed using different types of alcohols as volatile organic analytes.

Keywords: spectral SPR, chromatic mode, white light source, optical gas sensor, silver film, colorimetric registration, R, G, B components, visible wavelengths range.

<https://doi.org/10.15407/spqeo26.03.343>

PACS 07.07.Df, 42.79.Pw, 42.79.Qx, 73.20.Mf

Manuscript received 21.07.23; revised version received 20.08.23; accepted for publication 13.09.23; published online 20.09.23.

1. Introduction

Surface plasmon-polariton resonance is a widespread physical method for recording the interactions of gas and biological molecules on the surface of a thin metal film [1]. Numerous devices for observing the specific and nonspecific binding of the analyzed molecules with receptors fixed on the metal surface have been described since the beginning of the 90's years of the recent century. Until now, this area of research remains relevant, since in relation with the progress of molecular and genetic engineering, there is a need to create multichannel analyzers capable of registering simultaneously dozens of types of substances in the analyzed mixture.

Most often in sensory researches, a variant of SPR excitation is used in the Kretschmann geometry with variation in the angle of incidence of *p*-polarized monochromatic radiation (usually at the wavelength of red light) and registration of the minimum intensity of the reflected beam. With a change in the parameters of

the external environment (refractive index, dielectric constant), the angle of the minimum of the plasmon resonance changes accordingly, shifting in one or another direction. It should be noted that sensory technologies with variation in the angle of incidence of light are widely known and have been used for over 30 years. However, lately the spectral SPR technologies using wavelength variation have attracted attention. In this case, the effect of plasmon resonance is considered not in the usual mode of recording the SPR minimum angle (at a constant radiation wavelength), but in the mode of monitoring the reflection spectrum (at a constant angle of incidence) under illumination with different wavelengths.

In fact, these approaches are based on the well-known expression describing the condition for the minimum of internal reflection in the Kretschmann geometry [2]:

$$n_p \sin \theta_{sp} = \sqrt{\frac{\varepsilon_m(\lambda)\varepsilon_d}{\varepsilon_m(\lambda) + \varepsilon_d}}, \quad (1)$$

where θ_{sp} – angle of incidence of a p -polarized beam with a wavelength λ at which the plasmon resonance is observed, n_p – refractive index of the glass prism, ε_m – real part of the dielectric function of the metal (negative), ε_d – dielectric constant of the medium. A change in the molecular composition of the external environment leads to a change in the dielectric constant of the medium ε_d . As follows from (1), this change can be registered using SPR in two ways – either by changing the angle of incidence of light θ_{sp} , at which a minimum of resonance is observed, or by changing the wavelength λ of the incident light at a constant angle of incidence.

When using the spectral SPR detection method, the question arises about the optimal type of metal used as a plasmon-generating layer. Currently, mainly thin gold films are used for SPR sensor applications; for this, surface chemistry methods have been developed for the controlled binding of ligands to the gold surface. However, the SPR effect in gold films is realized only in the red and infrared areas of the electromagnetic radiation spectrum. At the same time, for informative analysis of sensory interactions using spectral SPR devices, it is necessary to use a wider visible wavelength range, for which the suitability of other metals for implementation of a chromatic SPR sensor has to be investigated.

Thus, in [3], the question of choosing the type of metal and appropriate wavelength in spectral sensors based on SPR was first raised. Aluminum, cadmium, copper, indium, gold, and silver were considered as possible metals, and as a result of calculations it was shown that the sensitivity of SPR signal to a change in the thickness of dielectric film on the metal surface tracked by the value of the minimum angle is the highest for silver. In [4], it is also proposed to use silver films in SPR sensors instead of traditional gold, since silver demonstrates a more optimal value of the real part of the dielectric function in the visible range.

It's known a few attempts of using the effect of plasmon-polariton resonance precisely in the mode of monitoring the reflected light spectrum when varying the wavelength of the incident light. For spectral scanning, a parallel white light beam at a constant angle of incidence is usually in use, and the reflected signal is recorded by a spectrometer. So in [5–7] described are the variants of implementation of spectral (chromatic) SPR devices for measuring the adsorption of molecules in aqueous and air media, herewith a parallel beam of white light from an incandescent lamp (halogen lamp) was used as an emitter. To record the light reflected from a gold film, portable spectrometers with a fiber-optic input and a focusing lens at the end of the fiber are usually used. The SPR signal is recorded at a wavelength at which a minimum of reflection is observed; in this case, the response is the shift of the wavelength of the SPR minimum during the adsorption of biomolecules or gases.

It should be noted that for all the spectral SPR devices described above, the recorded optical signal is shifted to the red region of the spectrum and even beyond

the red edge of the visible range, so the spectrometer was needed to register these signals. Thus, a certain problem of the spectral SPR mode is the need to use rather expensive spectrometric equipment to record the light intensity at different wavelengths. This instrumental complexity can be avoided by going from the spectrometric measurement method to recording responses by using a color CCD camera. The works [8–16] describe a number of examples of implementing these 2-D SPR sensor arrays based on imaging, the so-called surface plasmon resonance imaging sensors (SPRI), with video registration of the color pattern of reflected light observed. However to use the colorimetric methods of the response recording, plasmon resonance has to be excited in a sufficiently wide range of visible wavelengths. So, the idea of using the SPR spectral effect in the entire visible range, available for standard color video recording systems [17–19], looks very attractive.

Unlike with most of the existing publications in the field of implementation of spectral SPR technologies, in this work we use an original approach based on the SPR effect in thin silver films in the wide range of visible wavelengths combined with a colorimetric method for recording the whole reflected light spectrum. The registered signals are the values of three main components of light R, G, B at a number of points of the color image (which is a set of colored stripes) created as a result of generation of plasmon-polaritons at the silver film surface under illumination with a white light beam [20, 21].

The sensory aspect of the proposed technique is that upon the influence of external environment (in our case, gases) the color stripes of the reflected light pattern shift due to the changes in the values of R, G, B signals at selected points. In this case, the resulting difference in the values of R, G, B components before and after exposure to the gas can be interpreted as the response signal. The physical nature of this change lies in the influence of the refractive index (dielectric constant) of the external medium or sensitive layer on the parameters of the SPR effect, which can be mathematically described by Eq. (1).

Thus, the purpose of this work was to develop a technique for implementation of spectral SPR in the chromatic excitation mode within the wide range of visible wavelengths with using the colorimetric method of registration of the R, G, B components in the reflected light by color camera, as well as to assess the sensitivity of this sensing method to detect vapors of a number of organic analytes.

2. Optical scheme and experimental setup

When a beam of light hits a silver film in the case where the angle of beam incidence exceeds the angle of total internal reflection, the light should be almost completely reflected outward (with the exception of a small fraction of the energy absorbed in metal). But when a resonance arises between the electromagnetic wave and plasmon oscillations in this metal, the energy of light wave is spent on excitation of plasmon-polaritons and in this state almost nothing is reflected.

The model calculations of the reflection spectra were carried out under conditions of SPR excitation in the Kretschmann geometry. A 45° glass prism with a refractive index of 1.51 and the silver layer with a thickness of 40...45 nm on the prism were used for it. For these calculations, the freely available program WinSpall 3.02 [22] was used to simulate the surface plasmon resonance curves based on the Fresnel formalism. The values of the optical constants for silver were taken from [23]. Examples of the obtained resonance curves in air for a 40-nm thick silver film depending on the angle of incidence of light when the prism is illuminated with a parallel light beam containing a number of wavelengths from 420 to 700 nm are shown in Fig. 1. As can be seen, the minimum of plasmon absorption for these wavelengths is observed at different angles of incidence of light in the range of 42.7 degrees for red edge up to 48.7 degrees for blue edge. At this for the three main color components R, G, B, we define the following wavelengths: red R = 650 nm, green G = 520 nm and blue B = 450 nm.

Let us consider an optical scheme for implementing spectral SPR in the Kretschmann geometry (Fig. 2). Light from a white light source passes through a set of focusing and collimating lenses (forming a parallel beam), then a *p*-polarizer, and through the side facet of a glass prism. A glass plate with a deposited thin metal film facing outward relative to the prism is applied through an immersion layer to the base face of the prism. The collimator is adjusted so that the output light beam is slightly divergent. It should be noted here that the idea of a slightly divergent beam was proposed earlier in [24], albeit in the monochromatic SPR regime. In our case, this feature is very important, because it allows us to obtain the whole spectrum and further choose the range of the spectrum where the change in R, G, B components is maximum. So,

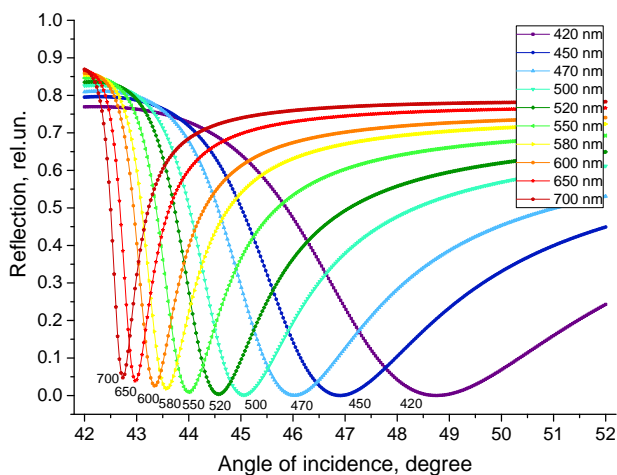


Fig. 1. Spectral dependences of the reflection coefficient upon excitation of SPR in a 40-nm thick silver film in air for the visible wavelengths from 420 to 700 nm within the range of angles of light incidence from 42 to 50 degrees. (Color online.)

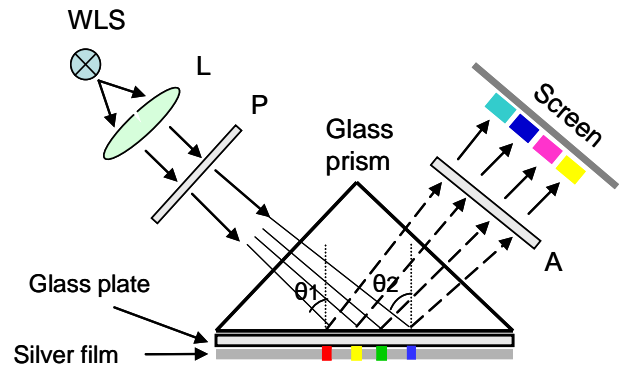


Fig. 2. Optical scheme for implementation of spectral SPR in the Kretschmann geometry: WLS – white light source, L – lens, P – polarizer, A – analyzer. (Color online.)

Fig. 2 shows the outermost rays from this beam, the angles of incidence of which θ_1 and θ_2 are slightly different (within 5-6 degrees, as can be seen from Fig. 1). Naturally, between them all the intermediate rays lie within the given beam divergence. According to the equation (1), at a certain fixed angle of incidence θ_{sp} for a certain wavelength λ , the plasmon-polariton resonance appears at a given place of the metal film, and the light of a given wavelength is almost completely absorbed in the metal film (note that for silver the SPR spectrum covers the entire visible range from red to blue – the local resonance regions in the metal film are indicated by the corresponding colored squares in Fig. 2). At the same time, the other non-resonant wavelengths at a given angle of incidence are freely reflected, and as a result of this, the color of reflected beam will be complimentary related to the color corresponding to the wavelength of the plasmon resonance, since it just will not contain the absorbed resonant wave. This means that in the presence of a slightly diverging incident light beam, we will see two sequential sets of defined color stripes, the first on the outer surface of the silver film (plasmon-generated scattering light), and the second on the screen of reflected light (complimentary related illumination). In this case, the stripes will be arranged in the following order of correspondence – the resonant red wavelength in the metal corresponds to the appearance of the cyan stripe on the screen of the reflected light, the resonant yellow wavelength – the blue stripe, green – the violet stripe, and blue – the yellow stripe (see colored designations in Fig. 2).

Fig. 3 shows a schematic diagram of an experimental setup for implementing the method of chromatic registration of molecular adsorption by monitoring the R, G, and B components of reflected light in the case of excitation of plasmon-polariton resonance in a silver film. The optical scheme uses a variant with a fixed angle of incidence of light and a broad-spectrum light source. Radiation from an ultra-bright white LED (Cree XTE Star 1-5W White, continuous spectrum, color temperature 5000 K) passes inside a black cylindrical tube and,

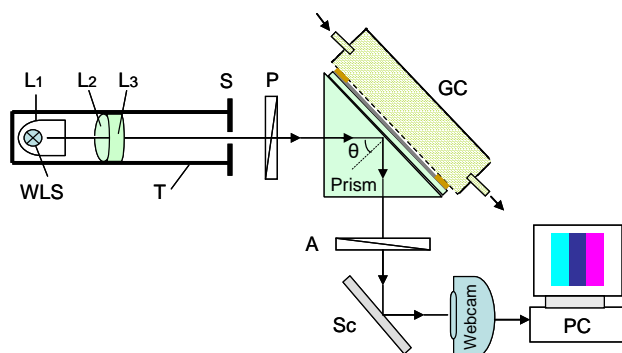


Fig. 3. Experimental setup for recording SPR signals in the chromatic mode: WLS – white light source, T – tube, L1 – condenser (concave mirror with a divergence angle of 10 degrees), L2 – focusing lens, L3 – collimator lens, S – slot, P – polarizer, A – analyzer, Sc – reflective screen, GC – gas chamber, PC – personal computer. (Color online.)

using a set of focusing collimator lenses, is formed into an output beam with a diameter of about 5 mm, which through a diaphragm with a narrow vertical slit and the *p*-polarizer hits the base facet of the glass prism. The angles of incidence of light rays (considering their small divergence) is selected in the range of 40...50° (relevant for gases), so that the plasmon-polariton resonance can be excited in the silver film at different wavelengths. The reflected light passes through the *p*-analyzer, matte white reflective screen, and is directed to the lens of a color webcam (Logitech C-170), which captures the image of the reflected picture as a set of colored stripes in X, Y coordinates. The resulting color picture is processed by specialized software on a personal computer.

A typical real view of the resulting webcam spectrogram of reflected light is shown in Fig. 4. It displays a number of color stripes in the coordinates of 640×360 pixel grid in the field of view of the webcam. Note that each point of the spectrogram corresponds to its own set of three parameters R, G, and B.

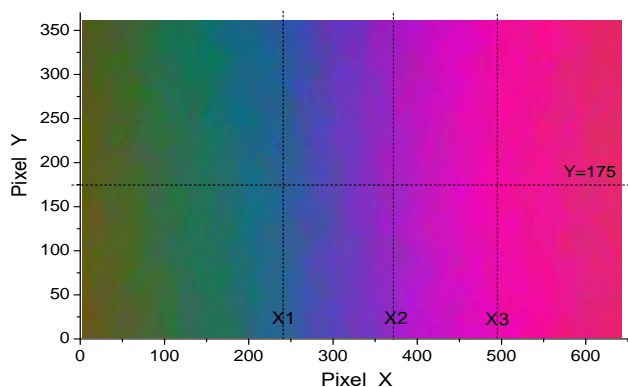


Fig. 4. Output spectrum of color bands of reflected light recorded by webcam Logitech C-170 at a resolution of 640×360 pixels; from left to right: green, blue, magenta and pink bands. (Color online.)

In the initial state (before introduction of the analyte), the initial values of the R, G, B components were recorded at selected points of all the colored stripes, *i.e.* at a given Y coordinate, a color slice along the horizontal axis in the X direction was registered. To calculate the sensor responses, it was necessary to find the optimal coordinates on the spectrogram. Consequently, the points in the transition areas at the boundaries of color bands, where the sensitivity of the responses reaches the highest value, were selected for subsequent analysis (in Fig. 4, these points are located at the intersections of the vertical dashed lines indicated by the coordinates X1, X2, X3, with a horizontal line with the coordinate Y in the middle). Further, when the analyte vapor was injected into the sample chamber, the values of the color components changed synchronously, leading to a shift of the spectrogram along the X coordinate that was registered by re-recording the R, G, and B values of the same color slice.

3. Materials and methods

The films of polyvinyl formal ethylal (PVFE) were used as sensitive coatings for sensory elements in our experiments. The chemical grade purity PVFE was dissolved in chloroform to obtain of 5% solution. Polymer films at the surface of glass/Ag substrates have been formed by means of dipping technique by using the equipment for Langmuir–Blodgett film deposition R&K (Wiesbaden, Germany). For this purpose, substrates were dipped into solution of PVFE followed by vertically lifting along the direction of the nano-grooves at the constant speed 2 mm/min. After deposition sensory elements were dried with fresh dry air for 12...15 hours to draw out remaining solvent from the coatings. Film thickness (about 50...70 nm) and morphology were estimated using the AFM measurements. As known, the responses of sensors coated with PVFE film show high sensitivity to alcohols but low sensitivity to chlorine organic vapors [25].

Isobutyl, isopropyl and ethyl alcohols with concentrations near the saturated vapors were involved in our experiments as tested volatile organic analytes. To detect gases, a 4-ml sealed gas cell with an attached air/analyte inlet system was tightly pressed to the silver surface. The gas supply system consisted of a container with a liquid organic substance (analyte), a bubbler, a mini-pump and connecting pipes. The measurement was carried out in a flow-through mode in three stages (each with the duration of about 70 s). At the first stage, clean air was supplied to the sample cell, at the second stage, saturated analyte vapors in air were injected, and at the third stage, the cell was purged with clean air. At all stages, the pictures of the resulting spectrogram were taken with the webcam at 7-second intervals. All the measurements were performed at the same gas flow rate of about 30 ml/min and a constant room temperature of 20 ± 0.5 °C.

4. RGB data processing technique

The processing of the obtained color images was carried out using the specially developed software that calculates the corresponding values of the color components R, G and B for the selected point on the image, on the scale of 0 to 255 (for this, the coordinate of the point in pixels and the parameter of averaging over the number of neighboring pixels around the selected point are set). The obtained absolute values of R, G, B components are further converted into dimensionless relative values for more convenient calculations. For example, in [26] it is proposed to take the ratio of each individual component to the sum of all three color components. In this work, the value of each component is reduced to the length of the so-called color vector \vec{L} in the three-dimensional RGB space [27], i.e., the ratios R/L , G/L , B/L are taken, which are actually equal to the cosines of the angles of inclination α , β , γ of the considered vector \vec{L} relative to the coordinate axes R, G and B, respectively (Fig. 5):

$$\cos\alpha = \frac{R}{L}, \quad \cos\beta = \frac{G}{L}, \quad \cos\gamma = \frac{B}{L}, \quad (2)$$

where L is the color vector length, $L = \sqrt{R^2 + G^2 + B^2}$.

It should be also noted that another goal of this conversion of color components into relative values is to reduce the influence of fluctuations in the intensity of the light source on the computed magnitudes of the obtained responses [28].

In the above representation, the sensor response can be related to the change in the angular position of the color vector from its initial position \vec{L}_0 to subsequent position \vec{L}_1 in the RGB space (see Fig. 5).

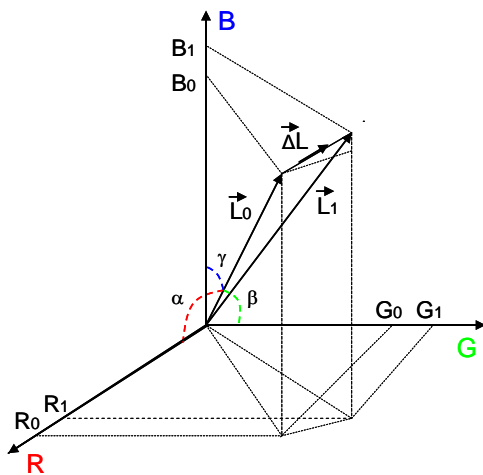


Fig. 5. Schematic representation of the color vector L in the three-dimensional RGB space, and the definition of the sensor response as the difference vector $\Delta\vec{L}$ between its initial (\vec{L}_0) and subsequent (\vec{L}_1) positions.

The difference of the corresponding cosines (2) in the analyzed points of the spectrum before and after the exposure to an analyte was taken as a response signal of individual color components to the influence of a gaseous substance. An example of the kinetics of R, G and B color components change under the influence of vapors of one of the analyzed gases – isopropanol, at a selected point near the boundary between the blue and green stripes is shown in Fig. 6 (the trend of changing the color components in other points of the available color bands and for other tested analytes was similar, differing only in the magnitude and in some cases the sign of the response, so we do not show them).

Next, the generalized integral response S for all three components was calculated from the responses of individual color components. This response was determined by the deviation of the angular position of the color vector from its previous state, and was calculated from the sum of squared differences of the corresponding cosine values before and after the exposure to the analyte, according to the following formula [29]:

$$S = \sqrt{\left(\frac{R_1 - R_0}{L_1 - L_0}\right)^2 + \left(\frac{G_1 - G_0}{L_1 - L_0}\right)^2 + \left(\frac{B_1 - B_0}{L_1 - L_0}\right)^2}. \quad (3)$$

For the real responses observed in the experiments, the change in the length of color vector \vec{L} in the RGB space as a rule is insignificant, in that case the expression (3) turns into a simpler form, corresponding to the diagram in Fig. 5:

$$S = \Delta L/L = \frac{1}{L} \sqrt{(R_1 - R_0)^2 + (G_1 - G_0)^2 + (B_1 - B_0)^2}, \quad (4)$$

where ΔL is the length of the difference color vector, indices 0 and 1 refer to the initial and subsequent states of the sensor (before and after exposure to the analyte vapor).

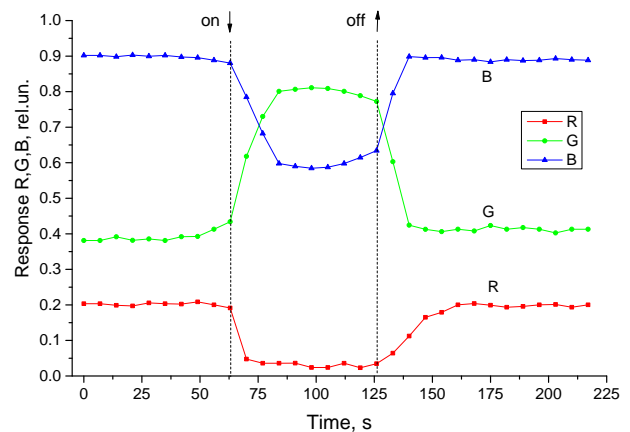


Fig. 6. Sensograms for individual R, G, B color components upon the influence of saturated isopropanol vapor, obtained at the X1 coordinate near the blue-green boundary of the color bands of reflected light (see Fig. 4); along the ordinate axis, the cosines of the angles of the color vector according to the expression (2) are plotted. (Color online.)

5. Results and discussion

Fig. 7 shows the integral responses of SPR sensor to the vapors of three tested analytes, calculated using the formula (3). As can be seen, the values of the relative responses ranged from 0.15 up to 0.55 (which, in terms of the maximum possible relative response, ranges from 8 to 32%). Application of sensitive layers, such as PVFE on the surface of silver, considerably improves the selective sensitivity of the sensor to alcohol analytes. As it was mentioned above, the reason for this is associated with a significant change in the refractive index (dielectric constant) of the sensitive film, when analyte vapor enters it, and even with some change in the film thickness, which inevitably leads, according to (1), to a change in the SPR condition and, hence, to reposition of the angle of resonant minimum at different wavelengths.

At the same time, it is noteworthy that the responses to the tested analytes could be also obtained on a pure unmodified silver surface. As shown in our preliminary experiments on pure silver, responses to gaseous analytes also occurred, but their magnitude was very low – only a few percents, which is an order of magnitude lower than the responses obtained with sensitive films. The physical nature of these responses consists in some change in the refractive index of the environment when exposing to gas, which leads to a certain shift in the reflected light spectrum. Responses to different analytes showed the same trends in the change of R, G, B components, with only slightly different quantitative values of responses. However, this was to be expected for the sensor with the bare silver surface, because it lacks any pronounced selectivity, and all the differences in the responses to various analytes may be due to the different values of their molecular refraction.

It should be noted that it is possible to considerably increase the sensitivity and selectivity of the considered gas sensor by using, first of all, not only one analyzed

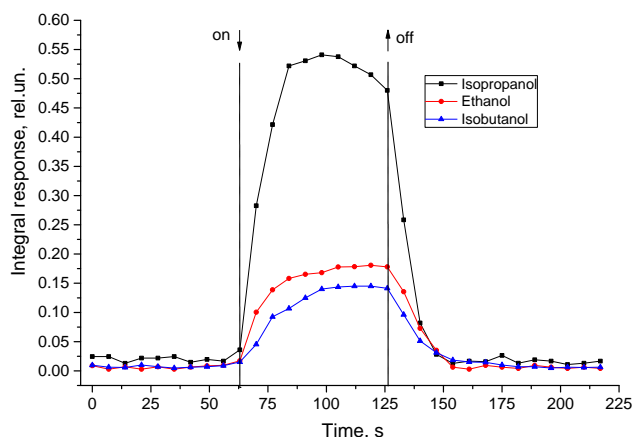


Fig. 7. Integral responses to saturated vapors of isobutyl, isopropyl and ethyl alcohols obtained at the X1 coordinate near the blue-green boundary of the color bands of reflected light calculated using the formula (3). (Color online.)

boundary in the reflected spectrum, but all the available color boundaries X1, X2, X3 (see them in Fig. 4). The second, it is possible to calculate the differential responses of individual color components R and G, B and G, taking advantage of the fact that they tend to change in the opposite directions (see Fig. 6), equally for all the tested analytes. Using these additional means of processing the obtained data allows us to increase the integral response values by at least 2-3 times. However, in this work, we did not use these methods for data processing, since the main purpose of the work was to demonstrate the principal operability of the proposed SPR-RGB registration method and, accordingly, the optoelectronic sensor device based on it.

It is also important to note that for the use in SPR sensor applications, the surface of silver should be protected from direct exposure to the environment, thereby avoiding its oxidation, as well as penetration of water and analyte molecules into the film, with subsequent adsorption and condensation inside the nanosized pores. With a thickness of about 40 nm, the metal film is sufficiently porous, and molecules can penetrate inside it by diffusion, settle in the pores and thereby change the physicochemical parameters of the film. The correct solution to avoid it is to cover the silver with an organic film that could act as a sensitive receptor layer, and at the same time protect the silver surface from degradation. In this case, the analyte molecules will act only on the sensitive layer, changing the value of its optical/dielectric constants, allowing for detection of gases, while the dielectric parameters of the metal itself will not be affected.

6. Conclusions

With the help of modeling and experimental evaluation of the characteristics of light reflection under the conditions of plasmon-polariton resonance upon excitation by a white light source, it has been shown that thin silver films (of the 40...45-nm thickness) allow for realization of a full-fledged SPR effect in the entire visible spectral range from 450 up to 700 nm. To measure the optical response, a colorimetric method of recording the R, G, B components of reflected light by using a color webcam was used.

A distinctive feature of the presented SPR sensor is the use of thin silver films as a plasmon-generating layer and implementation of the chromatic regime for SPR excitation simultaneously in the entire visible range. Also, an important feature of the sensor's optical design is formation of an output slightly divergent light beam (within 5...6 degrees) to illuminate the prism. This leads to implementation SPR simultaneously in the entire visible range, with a spatial distribution (according to the angle of light incidence) of local plasmon generation sites with different wavelengths. This, in its turn, allows obtaining the whole output spectrum of plasmon-reflected light and subsequently selecting from it spectral ranges with the maximum R, G, B responses.

It has been shown that the spectral reflection dependence in implementation of SPR in the Kretschmann geometry with colorimetric RGB registration can be successfully used to assess and monitor the concentration of volatile molecules in a gas sample. The films of polyvinyl formal ethylal have been used as the coatings sensitive to organic analyte vapors. The change of refractive index of the sensitive film under gas analyte influence directly correlates with the magnitude of the SPR-RGB sensor response. The recorded integral relative response values, for the case of saturated vapors of three organic analytes (different types of alcohols), ranged from 8 to 32% without any special processing the measured data.

The paper experimentally demonstrates that the SPR effect in the chromatic mode has been achieved without mechanical rotating the prism relative to the light source and realized without applying the expensive spectrometric equipment. In combination with colorimetric registration of responses by using the color webcam, it opens the possibility to create portable SPR-RGB detectors for gas molecules.

References

1. *Handbook of Surface Plasmon Resonance*, 2nd Edition, Eds. R.B.M. Schasfoort, The Royal Society of Chemistry, 2017.
<https://doi.org/10.1039/9781788010283-FP010>.
2. Kretschmann E. Die Bestimmung optischer Konstanten von Metallen durch Anregung von Oberflächenplasmaschwingungen (The determination of the optical constants of metals by excitation of surface plasmons). *Z. Phys. A: Hadron. Nucl.* 1971. **241**. P. 313–324. <http://dx.doi.org/10.1007/BF01395428>.
3. de Bruijn H.E., Kooyman R.P.H., Greve J. Choice of metal and wavelength for surface-plasmon resonance sensors: Some considerations. *Appl. Opt.* 1992. **31**, No 4. P. 440–442.
https://doi.org/10.1364/AO.31.0440_1.
4. Manickam G., Gandhiraman R., Vijayaraghavan R.K. *et al.* Protection and functionalization of silver as an optical sensing platform for highly sensitive SPR based analysis. *Analyst.* 2012. **137**. P. 5265–5271. <https://doi.org/10.1039/c2an35826c>.
5. Daly S.M., Grassi M., Shenoy D.K. *et al.* Supramolecular surface plasmon resonance (SPR) sensors for organophosphorus vapor detection. *J. Mater. Chem.* 2007. **17**. P. 1809–1818.
<https://doi.org/10.1039/B615516B>.
6. Wong C.L., Chen G.C.K., Ng B.K. *et al.* Multiplex spectral surface plasmon resonance imaging (SPRI) sensor based on the polarization control scheme. *Opt. Exp.* 2011. **19**, No 20. P. 18965–18978.
<https://doi.org/10.1364/OE.19.018965>.
7. Hlubina P., Urbancova P., Pudis D. *et al.* Ultrahigh-sensitive plasmonic sensing of gas using a two-dimensional dielectric grating. *Opt. Lett.* 2019. **44**, No 22. P. 5602–5605.
<https://doi.org/10.1364/OL.44.005602>.
8. Wong C.L., Olivo M. Surface plasmon resonance imaging sensors: A review. *Plasmonics.* 2014. **9**. P. 809–824. <https://doi.org/10.1007/s11468-013-9662-3>.
9. Wong C.L., Chen G.C.K., Li X. *et al.* Colorimetric surface plasmon resonance imaging (SPRI) biosensor array based on polarization orientation rotation. *Biosens. Bioelectron.* 2013. **47**. P. 545–552. <https://doi.org/10.1016/j.bios.2013.02.040>.
10. Bellasai N., D'Agata R., Marti A. *et al.* Detection of tumor DNA in human plasma with a functional PLL-based surface layer and plasmonic biosensing. *ACS Sensors.* 2021. **6**, No 6. P. 2307–2319. <https://doi.org/10.1021/acssensors.1c00360>.
11. Fasoli J.B., Corn R.M. Surface enzyme chemistries for ultrasensitive microarray biosensing with SPR imaging. *Langmuir.* 2015. **31**. P. 9527–9536. <https://doi.org/10.1021/la504797z>.
12. Swiontek S.E., Pulsifer D.P., Lakhtakia A. Surface multiplasmonics for optical sensing. *Proc. SPIE.* 2013. **8833**. P. 883309.
<https://doi.org/10.1117/12.2022273>.
13. Wang D., Loo J.F.C., Chen J. *et al.* Recent advances in surface plasmon resonance imaging sensors. *Sensors (Basel).* 2019. **19**, No 6. P. 1266. <https://doi.org/10.3390/s19061266>.
14. Nguyen H.H., Park J., Kang S., Kim M. Surface plasmon resonance: A versatile technique for biosensor applications. *Sensors (Basel).* 2015. **15**, No 5. P. 10481–10510.
<https://doi.org/10.3390/s150510481>.
15. Puiu M., Bala C. SPR and SPRI imaging: Recent trends in developing nanodevices for detection and real-time monitoring of biomolecular events. *Sensors (Basel).* 2016. **16**, No 6. P. 870. <https://doi.org/10.3390/s16060870>.
16. Zhou C., Jin W., Zhang Y. *et al.* An angle-scanning surface plasmon resonance imaging device for detection of mismatched bases in caspase-3 DNA. *Anal. Methods.* 2013. **5**. P. 2369–2373. <https://doi.org/10.1039/c3ay26602h>.
17. García A., Erenas M.M., Marinetto E.D. *et al.* Mobile phone platform as portable chemical analyzer. *Sens. Actuators B.* 2011. **156**. P. 350–359. <https://doi.org/10.1016/j.snb.2011.04.045>.
18. Mudanyali O., Dimitrov S., Sikora U. *et al.* Integrated rapid-diagnostic-test reader platform on a cellphone. *Lab Chip.* 2012. **12**. P. 2678–2686. <https://doi.org/10.1039/c2lc40235a>.
19. Liu Y., Liu Q., Chen S. *et al.* Surface plasmon resonance biosensor based on smart phone platforms. *Sci. Rep.* 2015. **5**. P. 12864. <https://doi.org/10.1038/srep12864>.
20. Kukla O.L., Fedchenko A.N., Vahula O.A. *et al.* Features of the operation of biosensors based on the PPR effect in chromatic mode. *12th Int. conf. "Electronic processes in organic and inorganic materials" (ICEPOM-12)*, June 1–5, 2020, Kamianets-Podilskyi, Ukraine. P. 327.

21. Kukla O.L., Fedchenko A.N., Vahula O.A. *et al.* Detection of gas molecules using colorimetric registration under conditions of excitation of SPR in silver films in chromatic mode. *9th Int. Sci. Techn. Conf. "Sensor Electronics and Microsystem Technologies"*, September 20–24, 2021, Odesa, Ukraine. P. 103.
22. *Resonant Technologies GmbH*. <http://www.res-tec.de> (accessed 30.05.2023)
23. Yang H.U., D'Archangel J., Sundheimer M.L. *et al.* Optical dielectric function of silver. *Phys. Rev. B*. 2015. **91**. P. 235137. <https://doi.org/10.1103/PhysRevB.91.235137>.
24. Tokel O., Yildiz U.H., Inci F. *et al.* Portable microfluidic integrated plasmonic platform for pathogen detection. *Sci. Rep.* 2015. **5**. P. 9152. <https://doi.org/10.1038/srep09152>.
25. Koshets I.A., Kazantseva Z.I., Shirshov Yu.M. Polymer films as a sensitive coating for quartz crystal microbalance sensors array. *SPQEO*. 2003. **6**, No 4. P. 505–507. <https://doi.org/10.15407/spqeo06.04.505>.
26. Barnard K., Martin L., Coath A., Funt B. A comparison of computational color constancy algorithms – Part II: Experiments with image data. *IEEE Trans. Image Process.* 2002. **11**, No 9. P. 985–996. <https://doi.org/10.1109/TIP.2002.802529>.
27. Fedchenko A.N., Vahula O.A., Kukla O.L. *et al.* Use of composite calixarene films for optoelectronic colorimetric gas detection. *Optoelectronics and Semiconductor Technology* (Kyiv, Naukova Dumka). 2013. **48**. P. 60–68.
28. Manorik P.A., Shulschenko O.V., Kukla O.L. *et al.* Optoelectronic sensor leak detector for detecting ammonia leaks. *Technical Diagnostics and Non-destructive Control*. 2018. **2**. P. 53–58. <https://doi.org/10.15407/tdnk2018.02.07>.
29. Kukla O.L., Fedchenko O.M., Vahula O.A. *et al.* Optoelectronic colorimetric gas detector based on array of composite calixarene films. *Sensor Electronics and Microsystem Technologies*. 2013. **10**, No 4. P. 28–39. <https://doi.org/10.18524/1815-7459.2013.4.110645>.

Authors and CV



O.V. Riabchenko graduated from Taras Shevchenko Kiev National University in 2020 with bachelor degree in applied physics. Since 2020 he works at the Institute of Semiconductor Physics, NAS of Ukraine as engineer and since 2022 as post-graduate student. His professional activities include measuring equipment setup and development of optoelectronic liquid/gas sensors based on the spectral plasmon-polariton resonance and spectroscopy of radiation from plasmon-photon scattering in thin metal films with colorimetric registration of response signals. E-mail: oleksandrriabchenko98@gmail.com



O.L. Kukla graduated from the Radiophysical faculty of the Kiev State University in 1980. Since 1981 he is working at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. He received his PhD (2000) and Doctor of Sciences (2016) degrees in Physics of Devices, Elements and Systems at the V. Lashkaryov Institute of Semiconductor Physics. Currently, he is the Head of the Department of Chemobiosensorics. His area of scientific activity includes the development and design of chemical and biological sensors and sensor arrays for biotechnology, medicine and ecology, study of molecular adsorption effects in polymer, biopolymer and composite thin layers. <https://orcid.org/0000-0003-0261-982X>



O.N. Fedchenko graduated from Lviv Polytechnical Institute in 1964 with M.S. degree in semiconductor devices. Since 2010 he is with the Institute of Semiconductor Physics, NAS of Ukraine as researcher. His scientific interests include the study of thin-film chemical gas sensors using optical and spectrometric methods, color RGB-spectroscopy and the development of optoelectronic colorimetric analyzers for detecting vapors of organic substances and leaks of volatile gases. E-mail: fedchenkoaleksandr50@gmail.com



Yu.M. Shirshov graduated from Chernovtsy State University in 1963. He received his PhD in 1970 and Doctor of Sciences Degree in Physics and Mathematics in 1991 at the Institute of Semiconductor Physics, NAS of Ukraine. Now he is Professor – scientific consultant at the the V. Lashkaryov Institute of Semiconductor Physics. The area of his scientific interests includes molecular phenomena on semiconductor and insulator surfaces, optoelectronic and microelectronic chemical sensors and biosensors. E-mail: y_shirshov@hotmail.com



Z.I. Kazantseva graduated from the Radiophysical faculty of Kiev State University in 1973. Since 1986, she is working at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. She received her PhD degree in Physics and Mathematics in 1995. Currently, she is Senior Researcher of the Department of Electrical and Galvanomagnetic Properties of Semiconductors. Her scientific interests include thin organized films, LB-technology and sensory materials. E-mail: kazants@isp.kiev.ua

Authors' contributions

Riabchenko O.V.: formal analysis, investigation, methodology, data curation.

Kukla O.L.: project administration, writing – original draft, visualization.

Fedchenko O.N.: investigation, methodology, data curation.

Shirshov Yu.M.: conceptualization, resources.

Kazantseva Z.I.: methodology, resources.

ППР хроматичний сенсор з колориметричною реєстрацією для детектування газових молекул

О.В. Рябченко, О.Л. Кукла, О.М. Федченко, Ю.М. Ширшов, З.І. Казанцева

Анотація. У даній роботі запропоновано та випробувано новий варіант оптоелектронного сенсора для детектування молекул газу на основі ефекту спектрального поверхневого плазмонного резонансу (ППР) у хроматичному режимі з колориметричною реєстрацією R, G, B колірних компонент відбитого світла. Як оптичний чутливий елемент використовується тонка 40 нм срібна плівка на базовій грані призми з ППР збудженням у геометрії Кречмана. Фізична природа сенсорного ефекту полягає в зміні показника заломлення чутливого покриття на плівці срібла, що безпосередньо впливає на параметри ППР. У ролі покриття, селективного до ряду органічних аналітів, використовували плівки полівініл формаль етилалю. Створено лабораторний варіант портативного пристрою для реалізації газового сенсора на основі ефекту ППР-RGB. Ефективність запропонованого сенсорного методу та відповідного пристрою оцінювали з використанням різних типів спиртів як летких органічних аналітів.

Ключові слова: спектральний ППР, хроматичний режим, джерело білого світла, оптичний газовий сенсор, срібна плівка, колориметрична реєстрація, R, G, B компоненти, видимий діапазон довжин хвиль.