Modeling The SPR-Sensor Response To Low Concentrations Of Water Nanosuspensions

Hanna Dorozinska
Department of Scientific, Analytical and Ecological Instruments and Systems
National Technical University f Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute"
Kyiv, Ukraine
e-mail: annakushnir30@ukr.net

Glib Dorozinsky
Department of Physics and technological bases of sensory materials
V.Lashkaryov Institute of Semiconductor Physics
NAS of Ukraine
Kyiv, Ukraine
e-mail: gvdorozinsky@ukr.net

Volodymyr Maslov
Department of Physics and technological bases of sensory materials
V.Lashkaryov Institute of Semiconductor Physics NAS of Ukraine
Kyiv, Ukraine
e-mail: maslov@isp.kiev.ua

***Abstract*— Adduced in this work are the results of numeric modeling and experimental confirmation of the sensor (based on surface plasmon resonance – SPR) response dependence on low concentrations of water suspensions prepared from nanoparticles of diamonds, silicon dioxide, iron and its oxide that differ by their optical properties. It has been demonstrated the efficiency of using the Maxwell-Garnett approach as well as formalism of the Jones scattering matrixes in calculations of the SPR-sensor response.**

Being based on the numeric analysis and experimental data obtained, it has been shown that the SPR-sensor possessing the detection limit 3 arc. sec. enables to control the nanoparticle concentration in suspension within the range 35 to 115 μg/mL (in dependence of the particle nature). In doing so, it has been ascertained that the lowest detection limit is inherent to diamond nanoparticles, while the highest one – to silicon dioxide particles, which is obviously related with the value of specific density proper to nanoparticle's substance ρ. The product of this value on the volume fraction of suspension nanoparticles in the case of diamond has its lowest value, and in the case of silicon dioxide this product is the highest.

Keywords—surface plasmon resonance, water suspension, sensor response

I. INTRODUCTION

Water is the most important natural resource. Pure water sources are of great importance for human health, industry and agriculture. To estimate water properties, they use four main groups of factors: physical, hydrobiological, bacteriological and chemical. Used for control are such water parameters as turbidity and suspended solids. Turbidity is the factor that characterizes the natural water property that is defined by availability of organic and inorganic particles suspended in it.

The main negative consequences of high water turbidity are related with the fact that this factor protects micro-organisms in the process of decontamination with ultraviolet light and stimulates growth of bacteria. Therefore, in all the cases when water is decontaminated, turbidity should be minimal to provide a high efficiency of this procedure. Turbidity of water is determined using the photometric technique to compare the samples of studied water with standard suspensions.

The results of measurements are usually expressed in mg/dm^3 (μg/cm^3), when using the main standard suspension of kaolin or suspension of formazin (formazin nephelometric unit – FNU). In recent times, the latter technique is worldwide adopted as the main photometric one, which is reflected in the standard ISO 7027 [1]. Standard ISO 7027-1:2016 specifies two quantitative methods using optical turbidimeters or nephelometers for determination of water turbidity. Nephelometry is applicable to water of low turbidity (for example drinking water), and turbidimetry is often applicable to highly turbid waters (for example waste waters or other cloudy waters). Turbidity measured with the nephelometric technique is usually expressed in nephelometric turbidity units (NTU). The results typically range between the values <0.05 NTU and 400 NTU, which according to the concentration range for kaolin suspension from 50 ng/mL up to 400 μg/mL and for silicium dioxide suspension from 6.5 ng/mL to 52 μg/mL. There is numerical equivalence of the units NTU and FNU. US Environment Protection Agency (US EPA) as well as World Health Organization (WHO) use NTU as the turbidity measurement unit. For determination of suspended solids in raw water, the standard ISO 11923:1997 [2] is applicable. This standard describes the method for determination of suspended solids in raw waters and waste waters by filtration through glass-fiber filters. The lowest limit of determination is approximately 2 μg/mL.

In accord with the data of US EPA, the permissible content of solid impurities in drinking water is 500 μg/mL [3]. WHO regulates the value of the drinking water turbidity to be lower than 0.2 NTU (i.e., 0.2 μg/mL) and the value of total dissolved solids less than 600 μg/mL [4]. Accordingly to the Ukrainian standard [5] concerning the turbidity and suspended solids, the content of mechanical solid particles in water should be within the range 200 to 500 μg/mL, while the concentration of colloids defining the water turbidity – from 1 to 20 μg/mL.

The available methods for controlling the suspension concentration enable to determine sizes of nanoparticles as well as their distribution by sizes [6, 7]. The most widely used in practice are the methods enabling the control of concentrations and dispersity, based on measurements of the light beam scattering and on weighing the suspended solids, namely: optical and electron microscopy, ultrasonic and electro-acoustical spectrometry, dehydratation and so on. Majority of these methods requires considerable time expenses and preparation of studied samples for analysis [8].

Thereof, it seems topical to study the possibility to control low concentrations of solid nanoparticles in water suspensions.

To solve this task, we chose an alternative highly-sensitive optical method based on surface plasmon resonance (SPR) phenomenon. In recent decades is intensive development of facilities based on SPR phenomenon both in fundamental researches and in practical determination of small biological or chemical components in gases and liquids, molecular recognition, detection of immune diseases etc. Plasmons are quasi-particles describing oscillations of electron gas in conducting materials. Resonance excitation of these oscillations by an electromagnetic wave in a thin layer of conducting material placed between two media with different refraction indexes obtained the name “surface plasmon resonance”. Diagnostically SPR facilities possess very high sensitivity to low concentrations of particles (0.01…2 ng/mL) [9, 10] and high accuracy of measurement results [11, 12]. Using the SPR method, one can determine the concentration of particles in suspension with account of known values of their optical constants and the amplitude of the SPR sensor response.

In the work [13], the authors performed numeric modeling the angular dependence of light reflection in the Kretschmann geometry for the interface gold/colloidal solution of spherical particles (model of erythrocytes) by using the Bruggeman approach and conception of effective medium [14], and in [15] they determined the concentration of iron nanoparticles in motor oil via the value of SPR sensor response.

In this work, the authors have studied the solution of the reverse problem, namely: determination of the SPR sensor response by using the set values of the suspension concentration with account of optical constants inherent to its components with the aim to find the minimal concentration that can be detected with the SPR method.

II. Model of Effective Medium for Suspension

Water suspension with solid nano-sized particles can be considered as the model heterosructure consisting of liquid matrix and solid-phase dispersed filler. Knowing the values of the relative dielectric permittivity for these matrix and filler, one can determine the heterostructure percentage. The most widely spread approaches to describe this system are the Maxwell-Garnett and Bruggeman ones that are valid for media with chaotical distribution of filler in matrix.

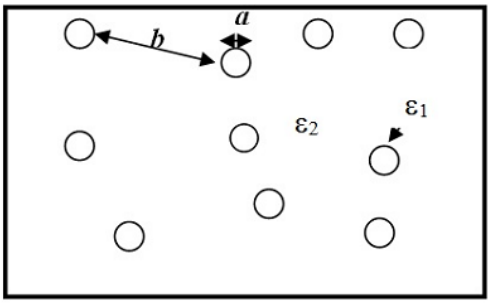

Fig. 1. Model of the two-component medium for the approaches by Maxwell-Garnett and Bruggeman [16].

Within the framework of the Maxwell-Garnett model, this medium possesses the dielectric permittivity that is related with the permittivities of components by the expression (1). The model based on the Bruggeman approach is applicable in the case when the volume fractions of components f_1 and f_2 correspond to the ratios from 1/3 up to 2/3, i.e., for high concentrations.

$$\frac{\varepsilon - \varepsilon_2}{\varepsilon + 2\varepsilon_2} = f\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}, \qquad (1)$$

where, $\boldsymbol{f}$ is the volume fraction of nanoparticles in suspension, ε – relative effective dielectric permittivity of suspension; ε_1 and ε_2 are relative effective dielectric permittivities of nanoparticle and matrix substances, respectively.

Since in accord with the set task it is necessary to control low concentrations of nanoparticles in water suspension by using the SPR method, we chose for modeling the Maxwell-Garnett approach.

III. Object and Method for Investigation

As a matrix, we considered the distilled water, and diamond nanoparticles serving as filler. Besides, in the role of filler we used nanoparticles of silicon dioxide

SiO_2, iron Fe and its oxide Fe_2O_3, since these are the most often available in drinking water. The relative dielectric permittivities of the matrix and filler for the respective light wavelength were chosen as the initial data for this modeling. The relative dielectric permittivities of the studied objects are well-known values [18-22] and are adduced in Table 1.

Table1. Relative dielectric permittivities

Object	Density, g/cm^3	Dielectric permittivity			Ref.
		ε_r	ε_i	$\lvert\varepsilon\rvert$	
Water	1.00	1.77263	0	1.77263	[18]
Diamond	3.54	5.80473	0	5.80473	[19]
SiO_2	2.65	2.37776	0	2.37776	[20]
Fe	7.80	–54.92705	27.85441	61.58611	[21]
Fe_2O_3	5.24	9.44623	0.35044	9.45273	[22]

Estimation of the SPR sensor response (i.e., the angular shift of the minimum inherent to the reflection characteristic R(θ)) was performed by plotting the theoretical dependence R(θ) for the following multi-layer system: “prism glass) – metal layer – dielectric (analyte) – external medium”, and for p-polarized monochromatic incident light in the case of analytes: distilled water and suspension water – diamond. In this system, the prism provides necessary conditions for observation SPR – total internal reflection at the boundary metal – analyte. At the surface of metal layer with the thickness 50 nm, surface plasmons are excited by monochromatic radiation with the wavelength 850 nm polarized in the plane of incidence [23, 24]. For this modeling, as a substance of metal layer we chose gold, since it provides the smallest (after silver) half width of the reflection characteristic due to its high conductivity. However, silver is quickly oxidized in water and is used in SPR sensors only for air mixtures.

The reflection characteristics R(θ) were calculated as functions of the angle of incidence by using the Fresnel formulae and mathematical formalism of Jones scattering matrixes [16] as well as the method [25].

To study reflection and transmission of polarized light by a multilayer film situated between the semi-infinite medium and substrate for inclined incidence, we applied the scattering matrix *S* (2) for a multilayer planar structure [16] consisting of m parallel layers located between two semi-infinite media: ambient medium (0) and substrate (m+1). We considered these media as linear, homogeneous and isotropic, and the complex index of refraction in the j-th layer is N_j and its thickness is d_j. The indexes of refraction for medium and substrate were designated as N_0 and N_{m+1}.

$$S = I_{10} L_1 I_{12} L_2 \ldots. I_{(j-1)j} L_j \ldots. L_m I_{m(m+1)} \qquad (2)$$

The scattering matrix was determined as a product I_{ab} of matrixes at the boundary between adjacent layers *a* and *b* as well as matrixes of the respective layers *L* [16] (3).

$$I_{ab} = \begin{bmatrix} 1 & r_{ab} \\ r_{ab} & 1 \end{bmatrix} \qquad L = \begin{bmatrix} e^{i\beta_j} & 0 \\ 0 & e^{-i\beta_j} \end{bmatrix} \qquad (3)$$

where, r_{ab} is the reflection index of the respective boundary; β_j – phase thickness of the respective layer (4) [16];

$$\beta = 2 N_j \pi \frac{d}{\lambda} \cos\theta_j \qquad (4)$$

where N_j is the complex index of refraction in the layer considered $N_j = n_j - ik_j$; θ_j – angle of incidence inside the *j*-th layer; λ – wavelength of the incident electromagnetic radiation; d_j – layer thickness.

The Fresnel indexes of reflection and transmission at the boundary, which appear in (3), were calculated with account of the values for complex indexes of refraction inherent to the considered media forming the boundary and values of the angle of incidence at this boundary. The latter was determined sequentially using the Snell law (5) [16].

$$N_0 \sin\phi_0 = N_1 \sin\phi_1 = \ldots = N_j \sin\phi_j = \ldots N_{m+1} \sin\phi_{m+1} \qquad (5)$$

The integrated Fresnel reflection index for the layered structure in the case of p polarization is determined by the elements of the first column in the scattering matrix (6) [16]:

$$\mathrm{R_p} = \frac{\mathrm{S_{21p}}}{\mathrm{S_{11p}}} \qquad (6)$$

The sensor response was determined as a difference between angular positions corresponding to the reflection characteristic minima R_p(θ) for distilled water and respective model suspension. To determine the minimal concentration of nanoparticles that can be detected using the SPR method in water suspension (limit of detection – LOD), we set the baseline noise typical for the most spread and sensitive commercially available SPR facilities. Adduced in Table 2 are the main technical performances of these facilities: baseline noise and range of measuring the refraction index ΔN for the studied substance and the SPR sensor response Δθ corresponding to it.

Table 2. Main performances of SPR facilities.

Product	Typical baseline noise		Measuring range	
	ΔN, μRIU	Δθ, ang.sec	ΔN, RIU	Δθ, deg
Plasmon-71	9	3.00	1.00…1.48	38…74

In addition, we performed experimental investigation of the water suspension with diamond nanoparticles by using the SPR refractometer

"Plasmon-71" developed in Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine [28]. The operation surface of sensitive element in the SPR refractometer was formed using the gold layer with the thickness 50 ± 2 nm on the substrate made of the glass Ф1. To excite surface plasmons in this layer, we used p-polarized light from the semiconductor injection laser diode with the wavelength 850 nm.

The response of SPR sensor was measured for 7 samples of suspensions water – diamond nanoparticles with their various concentrations, namely: 0.25, 0.5, 1.0, 2.0 and 3.0 mg/mL (ppm). The mean size of particles was less than one micrometer. Step-by-step substitution of distilled water with suspensions in the device measuring cell was provided by a peristaltic pump, the analytes being pumped with the velocity 50±1 μL/min. The volume of cell with its input pipes was 50 μL, which provided express analyzing the samples (less than 2 min). The refractometer, peristaltic pump and reservoirs with the studied samples were placed inside a thermostat operating at the temperature 20±0.1°C.

IV. RESULTS AND DISCUSSION

The results of our numeric analysis have been plotted as the dependence of the SPR sensor response on the concentration of water suspensions for four kinds of fillers: diamond nanoparticles, silicon dioxide SiO_2, iron Fe and its oxide Fe_2O_3 (Fig. 1).

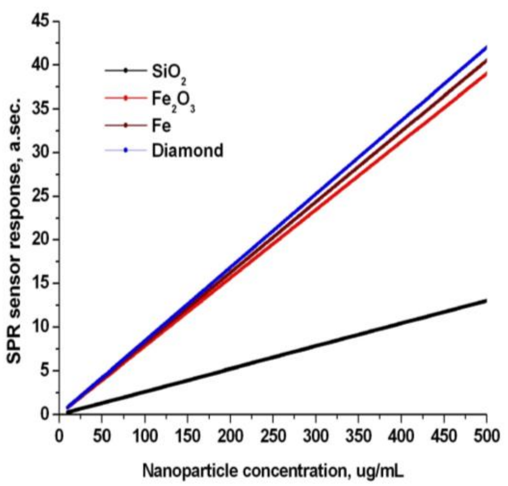

Fig. 2. Analytical dependences for the SPR sensor response on the concentration of water suspensions for four kinds of fillers.

To ascertain the detection limit inherent to the SPR refractometer "Plasmon-71", the limit concentration for each kind of solid particles was determined through the coefficient of proportionality K_C (Table 3) that was calculated as a ratio of the concentration value to the amplitude of the respective SPR sensor response.

Table 3. Limit concentration and coefficient of proportionality

Suspended solids	K_C, μg/ang.sec·mL^2	Limit concentration, μg/mL
Diamond	11.905	35.71
SiO_2	38.462	115.43
Fe	12.346	37.05
Fe_2O_3	12.821	38.52

Summarized in Table 4 for comparison are the results of experiments and our numeric analysis.

Table 4. Results of measurements and calculations

№	Prepared concentration, mg/mL	Sensor response, ang. sec.	Calculated concentration, mg/mL
1	0.25±0.01	11±3	0.13±0.01
2	0.50±0.01	21±3	0.25±0.01
3	1.00±0.01	40±3	0.48±0.01
4	2.00±0.01	73±3	0.87±0.01
5	3.00±0.01	112±3	1.33±0.01

Our numeric analysis showed that the plot for the dependence of the SPR sensor response for low concentrations of nano-disperse water suspensions has a linear character, which enables to determine the minimal concentration of suspension for a definite kind of filler and known value of the baseline noise typical for this measuring facility. Using the numeric analysis and our experimental data, it was shown that SPR refractometer "Plasmon-71" allows controlling the concentration of nanoparticles in suspension from 35 up to 115 μg/mL (in dependence on the nanoparticle nature), which corresponds to requirements adopted in Ukraine. Within this range, the least detection limit was obtained for diamond nanoparticles, and the largest – for silicon dioxide, which is obviously caused by the value of specific density inherent to the nanoparticle substance ρ, the product of which by the volume fraction of nanoparticles in suspension for diamond has its lowest value, while for silicon dioxide – the highest one.

The difference between our experimental and theoretical results can be related with the process of conglomeration in these suspensions at some larger distances from the sensitive element than the distance of surface plasmon field decay (λ/2.7 = 314 nm). It can result in reducing the nanoparticle concentration in the zone of sensitivity, the main consequence of which should be some decrease in the value of angular shift of the reflection characteristic, which corresponds to a lower value of the suspension concentration.

V. CONCLUSIONS

1. Shown in this paper is the efficiency of applying the Maxwell-Garnett approach and formalism of Jones matrixes for determination of the SPR sensor response to low concentrations of nano-disperse water suspensions consisting of nanoparticles of diamond, silicon dioxide, iron and its oxide.

2. The results of our numeric analysis aimed at dependences of the SPR sensor response to the concentration of water suspensions have shown that:

- dependences of the SPR sensor response to these concentrations have a linear character, and the minimal concentration can be determined with account of the proportionality factor that was defined as the ratio of concentration to the value of respective SPR sensor response;

- using the SPR method enables to control the nanoparticle concentrations from 35 up to 115 μg/mL. In this case, the lowest detection limit was determined for diamond, while the highest – for silicon dioxide. It is probably related with the value of specific density proper to the nanoparticle substance ρ, product of which by the volume fraction of nanoparticles in suspension has the lowest value for diamond and the highest – for silicon dioxide.

3. The results of experiments have shown that experimental data somewhat differ from the calculated ones, which is related with conglomeration of nanoparticles over the zone of plasmon decaying field that causes lowering the sensor response value.

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