The Simulation of Gold Nanoparticle in a TiO$_2$ Matrix Absorption and Reflection Spectra

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Abstract. In this work results of a nanocomposite structures optical parameters modelling are presented. The variable parameters were: shape of nanoinclusions, matrix width and incident radiation angle. The quasiperiodic nanocomposite structures consisting of a titanium dioxide matrix and gold nanoparticles were simulated. A spectral analysis of these structures showed the nonlinear nature of the absorption and reflection spectra and influence of the nanoparticles shape on it.

1. Introduction
A steady interest in the optical properties of complex structures has been observed for more than 35 years [1]. The nanocomposite structures in which excitation of surface plasmon polaritons (SPPs) is possible are widely studied [2]. Moreover, a significant local increase in the fields can be observed depending on the shape and size of the nanoinclusions [3]. Due to the quasiperiodic arrangement of nanoparticles, surface plasmon polaritons are excited in the nanocomposite layer. This effect affects the propagation of light through the structure. Both a significant increase in the transmitted light flux and its decrease are possible depending on the relative position of the nanoparticles. This allows to design both passive [4-6] and active optical elements [7-9]. In addition, study of fundamental optical properties is first stage to create a highly efficient optoelectronic systems, including MEMS [10, 11]. The introduction of SPP-based optical elements will significantly reduce the size of integrated circuits and increase their efficiency [12].

One of the first steps in the manufacture of optoelectronic components of integrated circuits is its optical and electrical characteristics modeling. This is important in terms of creating nanocomposite quasiperiodic structures, since it is possible to evaluate the effect of the parameters of the matrix and nanoinclusions. Results of the reflection spectra of TiO$_2$/AuNP/TiO$_2$ nanocomposite film modeling are presented in this paper.

2. Object
This study is aimed at determining the influence of the shape and size of nano inclusions on the spectral characteristics of a nanocomposite containing AuNP. The analysis was carried out by numerically simulating the reflection spectra of nanocomposite film Si/TiO$_2$/AuNP/TiO$_2$ in the visible and near infrared spectral regions and comparing the obtained data with the spectra of prototyped structures Si/TiO$_2$/AuNP/TiO$_2$. Real nanostructures were produced by two-stage TiO$_2$ magnetron sputtering onto a silicon substrate (100), with intermediate formation of the nanoparticle layer. The thicknesses of the oxide layers comprised 90 and 150 nm for the first and the second plating layer, respectively. The formation of AuNP was carried out from a gold layer preliminarily deposited by
thermal sputtering, followed by annealing in an argon atmosphere at a temperature of 500 °C. The thickness of the deposited gold t was 2.25 nm. A schematic cross section of a nanocomposite is shown in Figure 1a. The heat processing of the formed gold film [13, 14] leads to the formation of a quasi-periodic array of individual nanoparticles [15]. The shape of individual formations can be represented as a spherical cap of radius $R_R$ and height $h$, which are determined by the surface tension of AuNP [14]. The volume of an individual nanoparticle $V_{sph}$ and the radius of the initial sphere $R(Q)$ are defined as (1) and (2), respectively:

$$V_{sph} = \frac{\pi h^2}{3} (3R_R - h),$$

$$R_R(Q) = \begin{cases} \frac{c}{2\sin^{\frac{3}{2}}}, & Q < \pi \\ \frac{c}{Q \geq \pi} \end{cases},$$

where $c$ diameter of the projection of the sphere onto the c plane, $Q$ – the angle of spherical cap.

In determining the geometric parameters of the nanocomposite, an assumption was made about the periodic arrangement of the AuNP array (figure 1b). This assumption allows to make modelling within a single unit cell of a periodic structure using the Floquet periodicity condition mode on the side faces of the cell. As the type of periodic structure, the hexagonal type of AuNP arrangement was chosen as having the highest packing density. The period of the calculated hexagonal cell $a$ was determined on the basis of the assumption that the fill factor of the surface with a nanocomposite (the ratio of the volume of the metal to the volume of the matrix) is the same for the entire surface of the silicon substrate. In other words, the side $a_{hex}$ equal to (3):

$$a_{hex} = \frac{2V_{sph}}{3\sqrt{3}c}.$$  

The fill factor for the investigated structure is equal to 0.0094.

Figure 1. Schematic of simulated periodic plasmonic structure Si/TiO$_2$/AuNP/TiO$_2$.

Figure 2a shows the spectral dependences of the real $n$ and imaginary $k$ parts of the refractive index [16-18]. The blue graph was constructed by the authors of [16] based on the Drude-Lorenz model for gold layers, the red is the experimental values given by Lemarchand in the work for thin gold coatings of 3.96 nm [17]. It can be seen from the above data that the highest optical activity of such samples is observed in the region of 300–500 nm, depending on the shape and size of the particles under consideration. In the case of titanium dioxide (Figure 2a, black), the highest optical activity is observed at about 250–300 nm [18], which corresponds to the optical band gap of the oxide. The results of numerical simulations of the refractive index of Si/TiO$_2$/AuNP/TiO$_2$ (Figure 2, a) shows that the best coincidence was for the data obtained using the Drude – Lorentz model for gold layers [16]. For the corresponding absorption and reflection spectra (Figure 2 b, blue and red), the most active regions are 400–500 nm and 720 nm. The same graph shows the experimental reflection spectrum of the Si/TiO$_2$/AuNP/TiO$_2$ structure prototyped in this work. Differences in the intensities of peaks with a
maximum near 425 nm (silicon peak) may be due to oxidation of the surface layer of the substrate during magnetron sputtering of the TiO$_2$ matrix. The differences in the width of the reflection peak at a wavelength of 725 nm between the theoretical and experimental results can be due to the size distribution of nanoparticles and the absence of a strictly periodic arrangement of AuNP in the experimental sample.

Figure 2(a, b). (a) Real and imaginary part of refractive index of Si/TiO$_2$/AuNP/TiO$_2$; (b) Reflection and Absorption spectra of Si/TiO$_2$/AuNP/TiO$_2$ ($Q = 270^\circ$, $c = 15$ nm) [16-18].

3. FEA of optical properties

3.1. Incidence angle

The dependence of spectral reflectivity on the angle of radiation incidence is characteristic for nanocomposite films. So, in the case of working with experimental samples, a change in the color of the nanostructure was observed at different viewing angles. To describe this phenomenon, at the initial stage, the influence of the angle of incidence radiation on the spectral characteristics of the reflection of structures was determined. The simulation results for the Si/TiO$_2$/AuNP/TiO$_2$ structure are shown in Fig. 3.

Figure 3(a, b). Reflection spectra of Si/TiO$_2$/AuNP/TiO$_2$ ($c = 15$ nm; $Q = 270^\circ$) on incidence angle (a) Color map surface of reflection spectra; (b) reflection and absorption spectra.

It may be noted that the model observed changes in the spectral characteristics at different incidence angle. Moreover, at angles above 60$^\circ$ changes in the spectral characteristics acquire a pronounced character. The observed interference pattern is typical for situation where, when the incidence angle changes, its optical path changes. This changes the interval between the interference
maxima, and consequently their position. The position of the plasmon resonance peak at 725 nm AuNP does not change, which confirms the plasmonic nature of this peak.

3.2. Effect of AuNP form
The results of spectral characteristics of the nanocomposite modelling on angle of the spherical cap $Q$ are shown in Figure 4. It can be seen from the obtained data that, as the shape of the golden particle approaches the sphere, a strong shift of the reflection maxima from 725 nm to 650 nm is observed. This shift is accompanied by the superposition of two reflection peaks. This can be caused by the weakening of the interaction of particles with each other with increasing distance between them. To confirm this assumption reflection and absorption spectra of Si/TiO$_2$/AuNP/TiO$_2$ with different diameters particle projection on a plane (Figure 4) was simulated.

![Figure 4(a, b). Reflection and absorption spectra of Si/TiO$_2$/AuNP/TiO$_2$ on Q (a) Color map surface of reflection spectra (b) reflection and absorption spectra.](image)

Changing the diameter of the particle projection onto the plane, first of all, affects the volume of the metal layer and the metal-semiconductor contact area. It should be noted that increasing the particle diameter by an amount not exceeding the skin layer (25 nm at wavelengths of 700–800 nm [20]) does not significantly affect the absorption of electromagnetic radiation. However, in this work, the size of the considered nanoinclusions ranged from 10 to 30 nm, which allows us to neglect this effect. Thus, it can be assumed that the change in contact surface area metal-semiconductor is decisive.

![Figure 5(a, b). Reflection and absorption spectra of Si/TiO$_2$/AuNP/TiO$_2$ on c (a) Color map surface of reflection spectra (b) reflection and absorption spectra.](image)
It can be seen from the obtained dependences that a change in the particle size primarily leads to a shift in the long-wavelength reflection and absorption peaks towards higher frequencies. Changing the particle size in these ranges has a significantly smaller effect compared to the influence of the particle shape, that is, the parameter of the angle of the segment, and the influence of the incidence angle radiation.

4. Results
In this work, the optical characteristics of nanocomposite structures consisting of a matrix of titanium dioxide containing gold hemispheres were simulated. The aim of the work was to determine the influence of the geometric parameters of the structure on its optical characteristics. Spectral optical characteristics were obtained for nanocomposite structures with a diameter of gold nanoparticles from 5 nm to 100 nm. The obtained simulation results are consistent with published experimental data for particles with a diameter of 10–20 nm were presented. The results show that increasing the diameter of the hemispheres leads to a nonlinear character of the shift of the absorption and reflection peaks. It was shown that the optical properties of Si/TiO$_2$/AuNP/TiO$_2$ nanostructures are mainly determined by the AuNP shape, rather than its size.

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