

# THEORY OF THE ELLIPSOMETRY OF A LAYER OF SEMICONDUCTOR NANOPARTICLES COVERING THE SUBSTRATE

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A theoretical model of ellipsometry of a submonolayer of semiconductor nanoparticles on a surface is built in the frame of the local field method. We calculated the effective susceptibility of the system which had been modeled as a substrate with ellipsoidal particles. These calculations allow us to determine the reflection coefficients and the ellipsometric parameters versus the wavelength and the angle of incidence. It is shown that semiconductor particles on a substrate give a measurable contribution to ellipsometric parameters. We obtain that ellipsometric parameters depend on the concentration and the shape of particles.

Hence, one meets a problem to determine the effective parameter of a coating thin film—the complex-valued refraction index—in terms of particle parameters: particle dimensions and the shape. The presented work aimed at solving this problem.

## 2. Principles of the Ellipsometric Method

The essence of the ellipsometric method consists in changing the polarization of light, when it is reflected from a specimen under investigation [6]. Taking into account the direction of electric-field vector rotation, the light polarization ellipse is a geometrical figure and can be described in any orthogonal coordinate system (Fig. 1). The most convenient is a description of this ellipse in the coordinate system connected with own modes of reflection from the investigated surface. The case of reflection from isotropic systems or systems, where the geometry predetermines the uniaxial anisotropy—the anisotropy axis is perpendicular to the surface plane,—is the most general one. In this case, the own modes are  $p$ - and  $s$ -polarized light. Ellipsometry has the sensitivity comparable with that inherent in interferometry, but, owing to phase measurements, it is a more convenient self-consistent method with internal normalization. In its framework, one measures the relative variation of the polarization ellipse which is described by two ellipsometric angles  $\psi$  and  $\Delta$ . These angles are connected with the electric field for two polarizations  $p$  and  $s$  as follows:

$$\operatorname{tg} \Psi e^{i\Delta} = \frac{E_{pr}}{E_{pi}} \bigg/ \frac{E_{sr}}{E_{si}}, \quad (1)$$

where  $E_{xy}$  is the field of the incident or reflected ( $y = i$  or  $r$ , respectively) wave with the  $x$ -polarization ( $x = p$  or  $s$ ). In the case of most widespread systems, which were indicated above, this equation transforms into the

## 1. Introduction

The study of thin films, including the films of submonolayer coatings, is an important problem of modern science. The technology aimed at manufacturing such films for their application in sensorics, plasmonics, and so on [1, 2] rapidly develops. An important part of this process is monitoring the properties of the films obtained. There are plenty of methods to study the properties of such systems. These are electron microscopy, x-ray diffraction, and other methods, but optical methods turn out to be more expedient for such researches, because they are nondestructive and noncontact ones and characterized by sufficient informativity [3–5]. The ellipsometric method [6] belongs to them. Parameters that are measured in studies of thin films within the ellipsometric method can be expressed in terms of the Fresnel reflection coefficients which are determined by the refraction indices of the film and the substrate [3, 6]. Recently, there appeared a necessity to use the ellipsometric method to study films that are layers of organic molecules (e.g., dye or biological molecules) or layers of metallic or semiconducting nanoparticles located on a solid surface [7–11]. In this case, there emerges a necessity to determine local parameters of such films, in particular, the concentration, size, and shape of particles.

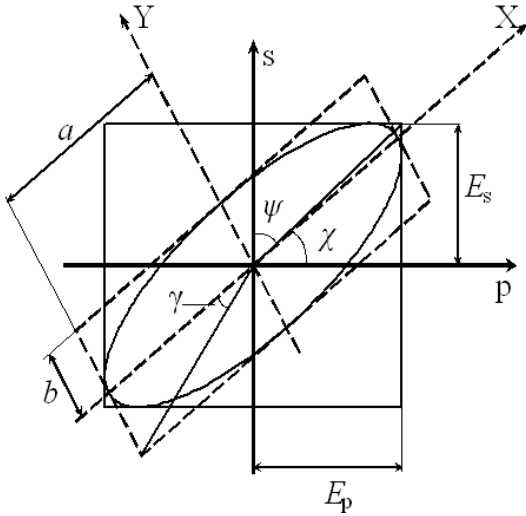


Fig. 1. Polarization ellipse and various coordinate systems

so-called fundamental equation of ellipsometry,

$$\operatorname{tg} \Psi e^{i\Delta} = \frac{r_p}{r_s}, \tag{2}$$

where  $r_p$  and  $r_s$  are the Fresnel reflection coefficients for the parallel and perpendicular polarizations, respectively [6].

### 3. Self-Consistent Field Equation

The interpretation of the results obtained in ellipsometric researches for systems with nanoparticle layers is rather a complicated problem. It is associated with difficulties that arise at the construction of theoretical models, because the use of the dielectric function formalism becomes problematic for thin films, whose thicknesses are comparable with that of the transition near-surface layer, where local fields change strongly in space [12–16]. Therefore, in order to construct a theoretical model, it is desirable to apply such methods which do not use the dielectric function directly. One of them is the development of the electrodynamics of ultrathin films which is based on the idea of effective susceptibility [14]. In particular, in this work, we used the method of Green’s functions in the framework of the self-consistent field theory. The main idea of the local (near-) field theory consists in that a relation between the local and external fields should be determined at an arbitrary point of the system. This relation has a universal character, and it can be found in terms of the linear response function of the system with respect to an external field action (the effective susceptibility) [17].

The essence of the method consists in searching for the solution of the Lippmann–Schwinger equation [18, 19] for the self-consistent field,

$$E_i(\mathbf{R}, \omega) = E_i^{(0)}(\mathbf{R}, \omega) - a \sum_{\alpha=1}^N \int_{V_\alpha} d\mathbf{R}' G_{ij}(\mathbf{R}, \mathbf{R}', \omega) \chi_{jl}(\omega) E_l(\mathbf{R}', \omega) \tag{3}$$

where  $G_{ij}(\mathbf{R}, \mathbf{R}', \omega)$  is Green’s function (the photon propagator) of the medium, where the particles are located;  $\chi_{jl}(\omega)$  is the susceptibility of a material the particles are made of (in the general case,  $\chi_{jl}$  is a tensor); the coefficient  $a = \omega^2/c^2$  is introduced for the SI system of units; and the integration is carried out over the volume of all particles in the system under consideration.

The physical meaning of the Lippmann–Schwinger equation consists in that it determines the local field at any point of the system. This field is a sum of the external field  $E_i^{(0)}(\mathbf{R}, \omega)$  and the field  $-(\omega^2/c^2) \int_{V_\alpha} d\mathbf{R}' G_{ij}(\mathbf{R}, \mathbf{R}', \omega) \chi_{jl}(\omega) E_l(\mathbf{R}', \omega)$  induced by self-consistent currents in the object which are governed by local fields.

For simple media—e.g., for free space, two homogeneous and isotropic media separated by a plane interface, or planar layered structures—Green’s function can be found easily [14, 15, 19]. The Green’s function method is universal, and it can be applied to various problems dealing with optical researches of thin films [14, 15], in particular, with ellipsometric studies.

### 4. Effective Susceptibility of a Submonolayer of Nanoparticles Covering a Surface

Let us consider a system consisting of a substrate and particles located on its surface. The particles are ellipsoids of revolution. The field at any point of the system satisfies Eq. (3). We assume that the system is macroscopically uniform in the substrate plane, i.e. the linear dimensions of particles are much less than the field wavelength and less than the distances between neighboring particles in the layer. As follows from the results of work [19], if the average distance between neighboring particles exceeds their linear dimensions, the interparticle interaction can be considered as the interaction between quasi-pointlike electric dipoles. In this case, the polarization of individual particle on the surface has to be found with regard for the dimension and the shape of particles. Such calculations, with the account of all multipoles [19], demonstrate that, even if the surface is

covered with spherical nanoparticles up to a level of almost half a monolayer, the dipole approximation remains valid. Therefore, the right-hand side of Eq. (3) can be substantially simplified by applying the approximation of quasi-pointlike dipoles:

$$\begin{aligned} \sum_{\alpha} \int_{V_{\alpha}} d\mathbf{R}' G_{ij}(\mathbf{R}, \mathbf{R}', \omega) \chi_{jl}(\omega) E_l(\mathbf{R}') &\approx \\ \approx \sum_{\alpha} G_{ij}(\mathbf{r} - \mathbf{r}_{\alpha}, z, z_{\alpha}, \omega) \tilde{\chi}_{jl}(\omega) E_l(\mathbf{r}_{\alpha}, z_{\alpha}). \end{aligned} \quad (4)$$

Here,  $\tilde{\chi}_{jl}(\omega) = V_M \chi_{jl}(\omega)$ ,  $\chi_{jl}(\omega)$  is the tensor of linear response for a particle, and  $(\mathbf{r}_{\alpha}, z_{\alpha})$  are the coordinates of the center of the  $\alpha$ -th particle, where the vector  $\mathbf{r}_{\alpha}$  lies in the surface plane. Assuming the distribution of particles over the surface to be uniform, let us make averaging over the particle distribution in the layer. We obtain

$$\begin{aligned} \sum_{\alpha=1}^N G_{ij}(\mathbf{r} - \mathbf{r}_{\alpha}, z, z_{\alpha}, \omega) \tilde{\chi}_{jl}(\omega) E_l(\mathbf{r}_{\alpha}, z_{\alpha}, \omega) &= \frac{N-1}{S} \times \\ \times \int \frac{d\mathbf{k}}{(2\pi)^2} e^{-i\mathbf{k}\mathbf{r}} G_{ij}(\mathbf{k}, z, z_{\alpha}, \omega) \tilde{\chi}_{jl}(\omega) E_l(\mathbf{k}, z_{\alpha}, \omega). \end{aligned} \quad (5)$$

Then, making the Fourier transformation in the surface plane, we obtain the equation for a self-consistent field

$$\begin{aligned} E_i(\mathbf{k}, z_{\alpha}, \omega) &= E_i^{(0)}(\mathbf{k}, z_{\alpha}, \omega) + \\ &+ na G_{ij}(\mathbf{k}, z, z_{\alpha}, \omega) \tilde{\chi}_{jl}(\omega) E_l(\mathbf{k}, z_{\alpha}, \omega), \end{aligned} \quad (6)$$

where  $n = \lim_{N, S \rightarrow \infty} (N/S)$  is the surface concentration of particles in the layer. Since the tensor  $\tilde{\chi}_{jl}(\omega)$  describes a response to the local field, i.e. it couples the particle polarization and the local field,

$$P_j(\mathbf{k}, z_{\alpha}, \omega) = \tilde{\chi}_{jl}(\omega) E_l(\mathbf{k}, z_{\alpha}, \omega), \quad (7)$$

Eq. (6) yields another equation that connects the polarization with the external field,

$$\begin{aligned} (\tilde{\chi}_{ij}(\omega))^{-1} P_j(\mathbf{k}, z_{\alpha}, \omega) &= E_i^{(0)}(\mathbf{k}, z_{\alpha}, \omega) + \\ &+ na G_{ij}(\mathbf{k}, z, z_{\alpha}, \omega) P_j(\mathbf{k}, z_{\alpha}, \omega). \end{aligned} \quad (8)$$

The solution of this equation looks like

$$P_j(\mathbf{k}, z_{\alpha}, \omega) = \left[ (\tilde{\chi}_{ji}(\omega))^{-1} - na G_{ij}(\mathbf{k}, z, z_{\alpha}, \omega) \right]^{-1} \times$$

$$\times E_i^{(0)}(\mathbf{k}, z_{\alpha}, \omega). \quad (9)$$

It means that the parameter of effective susceptibility of a submonolayer particle coating located on the solid surface, which connects the layer polarization with the external field, is expressed by the formula

$$X_{ij}(\mathbf{k}, z_{\alpha}, \omega) = \left[ (\tilde{\chi}_{ij}(\omega))^{-1} - na G_{ji}(\mathbf{k}, z_{\alpha}, z_{\alpha}, \omega) \right]^{-1}. \quad (10)$$

The tensor of effective susceptibility can be easily written down in the own coordinate system for  $s$ - and  $p$ -polarized waves (in this system, the light incidence plane coincides with the plane  $XOZ$  of the Cartesian coordinate system):

$$X_{ij}(k, \omega) = \begin{pmatrix} X_{xx}(k, \omega) & 0 & X_{xz}(k, \omega) \\ 0 & X_{yy}(k, \omega) & 0 \\ X_{zx}(k, \omega) & 0 & X_{zz}(k, \omega) \end{pmatrix}, \quad (11)$$

where

$$\begin{aligned} X_{xx} &= \frac{1}{D} \left[ \frac{1}{\alpha_{\perp}} + 2\pi ni \frac{k^2}{\varepsilon_0 k_{z1} \varepsilon_1} (1 + R_p^0) \right], \\ X_{zz} &= \frac{1}{D} \left[ \frac{1}{\alpha_{\parallel}} + 2\pi ni \frac{k_{z1}}{\varepsilon_0 \varepsilon_1} (1 - R_p^0) \right], \\ X_{yy} &= \left[ \frac{1}{\alpha_{\parallel}} + 2\pi ni \frac{k_0^2}{\varepsilon_0 k_{z1}} (1 - R_s^0) \right]^{-1}, \end{aligned} \quad (12)$$

$$X_{xz} = -X_{zx} = \frac{1}{D} 2\pi ni \frac{k}{\varepsilon_0 \varepsilon_1} R_p^0,$$

$$\begin{aligned} D &= \left[ \frac{1}{\alpha_{\perp}} + 2\pi ni \frac{k^2}{\varepsilon_0 k_{z1} \varepsilon_1} (1 + R_p^0) \right] \times \\ &\times \left[ \frac{1}{\alpha_{\parallel}} + 2\pi ni \frac{k_{z1}}{\varepsilon_0 \varepsilon_1} (1 - R_p^0) \right] + 4\pi^2 n^2 \frac{k^2}{\varepsilon_0^2 \varepsilon_1^2} R_p^{02}, \end{aligned}$$

$\alpha_{\parallel, \perp}$  are the components of the susceptibility tensor for a particle on the surface (see Appendix),  $n$  is the surface concentration of particles,  $\varepsilon_0$  is the vacuum dielectric permittivity,  $\varepsilon_1$  is the dielectric permittivity of the external medium (the half-space, where the particles are located),  $R_i^0$  are the Fresnel reflection coefficients of a clean surface for the corresponding polarization which are multiplied by the phase factor  $\exp(-2k_0 h_z \cos \vartheta)$ .

In the electrostatic approximation, this phase factor is considered equal to 1. The quantity  $k_0 = \omega/c$  is the wave vector of light in vacuum, and the wave vectors  $k_x = \sqrt{\varepsilon_1}k_0 \sin \vartheta$  and  $k_z = \sqrt{\varepsilon_1}k_0 \cos \vartheta$  along the axes  $X$  and  $Z$ , respectively, in the external medium are expressed in terms of the angle of incidence  $\vartheta$ , which is reckoned from a normal to the surface, if the latter is illuminated from the same side of the substrate, where the particle layer is. In the general case, the quantity  $k_z$  is defined by the equation  $k_x^2 + k_z^2 = \varepsilon_1 k_0^2$ .

Now, polarization (7) which enters the right-hand side of Eq. (6) can be expressed in terms of the effective susceptibility tensor (11) and the external field. Therefore, we obtain the following solution of the Lippmann-Schwinger equation for a thin submonolayer film of nanoparticles on a surface:

$$E_i(\mathbf{k}, z_\alpha, \omega) = [\delta_{ij} + naG_{il}(\mathbf{k}, z_\alpha, z_\alpha, \omega)X_{lj}(\mathbf{k}, z_\alpha, \omega)] \times \\ \times E_j^{(0)}(\mathbf{k}, z_\alpha, \omega). \quad (13)$$

That is, the local field which changes rapidly in space can be determined, by knowing the long-wave external field, with the help of the effective susceptibility.

The last step of the presented calculations is the inverse Fourier transformation of expression (9) to obtain the polarization in the  $r$ -space. In the general case, it is rather a complicated problem, but since the excitation in our case is made by a monochromatic plane wave, the situation becomes considerably simpler similarly to that with Eq. (5). In the  $(\mathbf{k}, z)$ -space, the dependence of the external field on the wave vector looks like  $E(k) = E\delta(k_{\parallel} - k_x)$ . Using this equality, as well as the surface concentration of particles  $n$ , we obtain the following formula for the average polarization of the layer in the case where no  $z$ -dependence is taken into account:

$$P(x) = nX(k_{\parallel} = k_x)Ee^{-ik_x x}. \quad (14)$$

It completely agrees with the Floquet theorem [20].

Hence, by calculating the relation between the polarization of the system or the scattered field, on the one hand, and the external field, on the other hand, we can find the reflection coefficients of the system and use them to determine ellipsometric parameters.

## 5. Reflection Coefficients

In order to calculate the coefficient of reflection of light from a substrate covered with a layer of nanoparticles, we use the approach of molecular optics. The field emitted

by one dipole is determined at the distance  $R$  as follows [21]:

$$E_{em1} = -\frac{k_0^2}{\varepsilon_0 R} p_{\perp} e^{i(\omega t - kR)}, \quad (15)$$

where  $p_{\perp}$  is the dipole component perpendicular to the direction, in which the radiated field is considered. As was shown in work [21], the field generated by a layer of cophased dipoles propagates perpendicularly to the layer and equals half the field produced by the first Fresnel zone, the form of which being a circle in this case:

$$E_{em} = 2\pi i \frac{k_0}{\varepsilon_0 \sqrt{\varepsilon_1}} n p_{\perp} e^{i(\omega t - kR)}. \quad (16)$$

At the oblique incidence of an exciting wave, the phases of dipoles in the layer are not equal, changing as  $k_x x$ , as was obtained in formula (14). Therefore, the wave reflected (scattered) by this dipole layer propagates according to the reflection laws, and the Fresnel zones transforms into ellipses, which are extended along the  $X$ -axis, and the area of which exceeds the area of circles by a factor of  $\frac{1}{\cos \theta}$ . Therefore, field (16) increases at that by the same factor  $\frac{1}{\cos \theta}$  together with the number of dipoles in the first Fresnel zone.

If the dipole layer is located on a surface, the surface changes both the exciting and emitted fields. Dipoles located at the distance  $h_z$  over the surface are excited by a field, which is a sum of the incident and reflected ones:

$$E_x = E_p(1 - R_p^0) \cos \vartheta,$$

$$E_y = E_s(1 + R_s^0),$$

$$E_z = E_p(1 + R_p^0) \sin \vartheta, \quad (17)$$

where the quantity  $R_i^0$  is the same as in expression (12). Since the particle dimensions are much smaller than the wavelength, such a dipole approximation is correct. In the same way, by summing up the fields emitted directly and reflected from the surface and by taking the directions of their propagation into account, we obtain the field that is additionally scattered by the particles in the surface layer. The corresponding dipole projections for expression (16) are

$$p_{p\perp} = p_z(1 + R_p^0) \sin \theta - p_x(1 - R_p^0) \cos \theta,$$

$$p_{s\perp} = p_y(1 + R_s^0). \quad (18)$$

Combining expressions (16)–(18) and taking the additional factor  $\frac{1}{\cos\theta}$  in Eq. (16) and expression (11) for the nanoparticle layer response into account, we obtain

$$R_s = R_s^0 + 2\pi i \frac{k_0^2}{\varepsilon_0 k_{1z}} n X_{yy} (1 + R_s^0)^2,$$

$$R_p = R_p^0 - 2\pi i \frac{n}{\varepsilon_0 \varepsilon_1 k_{1z}} \left[ X_{xx} k_{1z}^2 (1 - R_p^0)^2 + \right.$$

$$\left. + 2X_{xz} k_{1z} k_x (1 - R_p^0)^2 - X_{zz} k_x^2 (1 + R_p^0)^2 \right]. \quad (19)$$

These expressions completely coincide with ones from work [22], which were derived in a different way. Unfortunately, the expression for the reflection coefficient of  $p$ -polarized light obtained in work [23] includes some errors which are insignificant, if  $\varepsilon_1 = 1$ . In expression (19), we also took into account that  $\cos\theta = \frac{k_{1z}}{\sqrt{\varepsilon_1 k_0}}$ ,  $\sin\theta = \frac{k_x}{\sqrt{\varepsilon_1 k_0}}$ , and that there is a phase delay between the fields reflected by the substrate and the particle layer.

With the help of expressions (12), the result obtained for the reflection coefficient of  $p$ -polarized light, which enters formula (19), can be simplified to the following one:

$$R_p = R_p^0 - 2\pi i \frac{1}{\varepsilon_0 \varepsilon_1 k_{1z}} \frac{n}{D'} \times$$

$$\times \left[ \alpha_{\parallel} k_{1z}^2 (1 - R_p^0)^2 - \alpha_{\perp} k_x^2 (1 + R_p^0)^2 \right], \quad (20)$$

where the denominator

$$D' = \left[ 1 + 2\pi n i \frac{k^2 \alpha_{\perp}}{\varepsilon_0 k_{z1} \varepsilon_1} (1 + R_p^0) \right] \times$$

$$\times \left[ 1 + 2\pi n i \frac{k_{z1} \alpha_{\parallel}}{\varepsilon_0 \varepsilon_1} (1 - R_p^0) \right] + 4\pi^2 n^2 \frac{k^2 \alpha_{\perp} \alpha_{\parallel}}{\varepsilon_0^2 \varepsilon_1^2} R_p^{02}$$

is somewhat different from the denominator  $D$  in Eq. (12). That is, the layer of dipoles on a surface modifies the reflection as a layer with the effective susceptibilities  $\frac{n\alpha_{\parallel}}{D'}$  along the  $X$ -axis and  $\frac{n\alpha_{\perp}}{D'}$  along the  $Z$ -one. Though the dipole moments induced along the  $Z$ - and  $X$ -axes are described by the more complicated expressions (12), the contributions of those two components partially compensate each other, when the reflected field is formed. The effective susceptibility along the  $Y$ -axis remains to be equal to  $nX_{yy}$  as in Eqs. (12) and (19).

It should be noted that, since every component of the susceptibilities includes the dielectric permittivity of vacuum  $\varepsilon_0$ , all final expressions for fields and reflection coefficients do not depend on this quantity.

## 6. Numerical Calculations

Let the particles covering the surface be made of a substance that is characterized by the following dielectric function in its operating frequency range:

$$\varepsilon_p(\omega) = 1 + \frac{f}{-\omega^2 + \omega_0^2 - i\omega\gamma}, \quad (21)$$

where  $\omega_0 = 3 \times 10^{15} \text{ s}^{-1}$  is the resonance frequency,  $\gamma = 0.01\omega_0$  is the damping coefficient, and  $f$  is the oscillator strength which was selected to be equal to  $\omega_0^2$ . This means that the resonance frequency is close to the frequency of a helium-neon laser, and the dielectric function simulates the behavior of a semiconductor with the frequencies of transverse and longitudinal optical phonons  $\omega_{TO} = \omega_0$  and  $\omega_{LO} = \sqrt{2}\omega_0$ , respectively. The substrate is characterized by the real-valued dielectric constant  $\varepsilon_r = 4$  in this frequency range, i.e. it behaves like an insulator. We suppose that particles are ellipsoids of revolution with the fixed volume  $V_p = (4\pi/3)h_x h_y h_z = (4\pi/3) \times 10^{-24} \text{ m}^3$ . Hence, spherical particles were assumed to have a diameter of 20 nm, and the prolate and oblate particles to be characterized by the eccentricities  $h_x/h_z = 5$  and  $1/5$ , respectively. The particle concentration was so selected that the average distance between particles exceeded their linear dimensions, namely,  $n = 4 \times 10^{15} \text{ m}^{-2}$ , which corresponds to about 0.14 of a monolayer in the case of spherical particles, if the dense hexagonal coating is taken for one monolayer. The change of the eccentricity parameter within the limits from  $1/5$  to  $5$  gives rise to the variation of the coating level within the limits from 0.05 to 0.4 monolayer, provided that the model of equal particle volumes is used. However, if the coefficient of surface filling is maintained constant, i.e. the linear dimensions along the surface are fixed, the eccentricity change is accompanied by the variation of the particle volume. The following scheme was used in calculations. First, we determined the components of the linear response of a separate particle with a given shape on the substrate. Then, the components of the effective susceptibility were calculated for a submonolayer coating film by formulas (11). Afterwards, formulas (19) were used to calculate the reflection coefficients of the system as functions of the angle of incidence and the frequency.

## 7. Results and Their Discussion

The numerical results obtained for the model described above are exposed in Figs. 2 to 8. In Fig. 2, the general

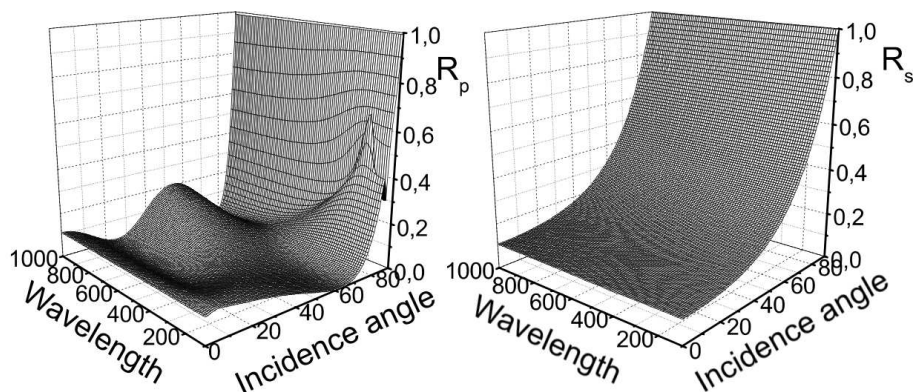


Fig. 2. Dependences of the coefficient of reflection from the system on the wavelength and the angle of incidence for  $p$ - and  $s$ -polarized light

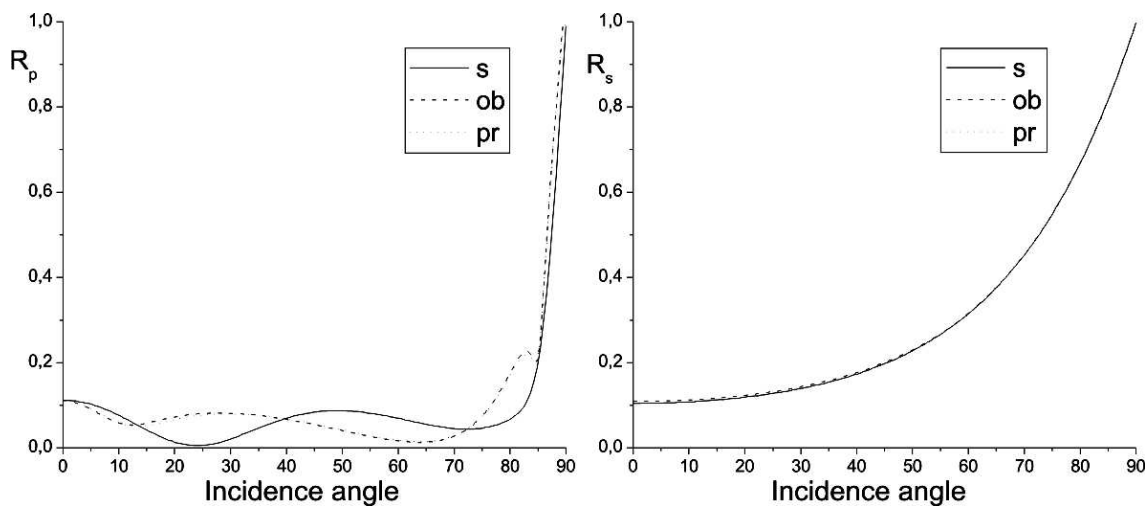


Fig. 3. Dependences of the coefficient of reflection from the system on the angle of incidence at a wavelength of 600 nm for  $p$ - and  $s$ -polarized light and for coatings consisting of spherical ( $s$ ), oblate ( $ob$ ), and prolate ( $pr$ ) particles

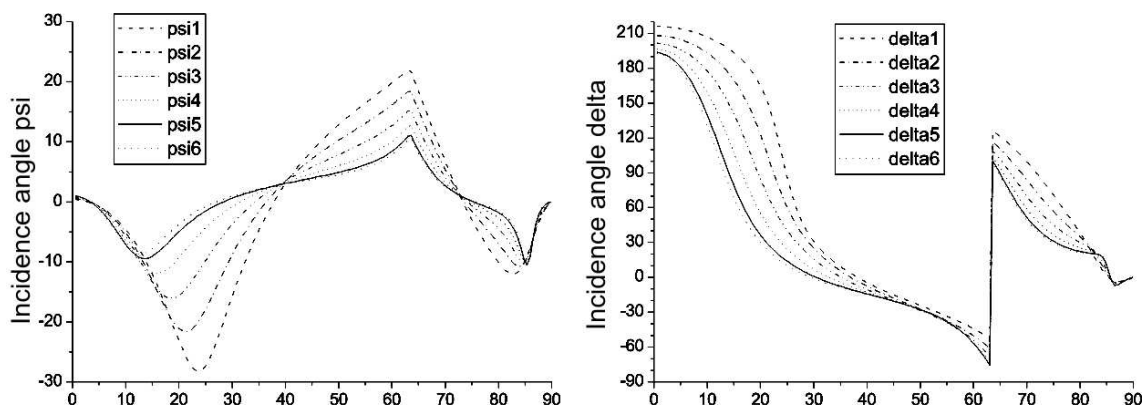


Fig. 4. Difference between the coefficients of reflection from a substrate with particles and a clean substrate versus the angle of incidence at a wavelength of 600 nm for coatings consisting of spherical ( $s$ ), oblate ( $ob$ ), and prolate ( $pr$ ) particles

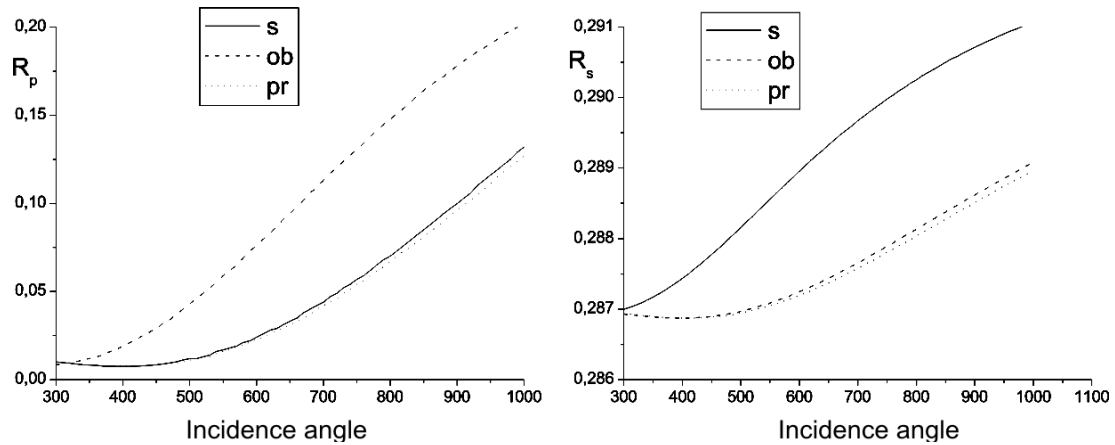


Fig. 5. Dependences of the coefficients of reflection from the system on the wavelength at the angle of incidence  $\vartheta = 60^\circ$  for  $p$ - and  $s$ -polarized light for coatings consisting of spherical ( $s$ ), oblate ( $ob$ ), and prolate ( $pr$ ) particles

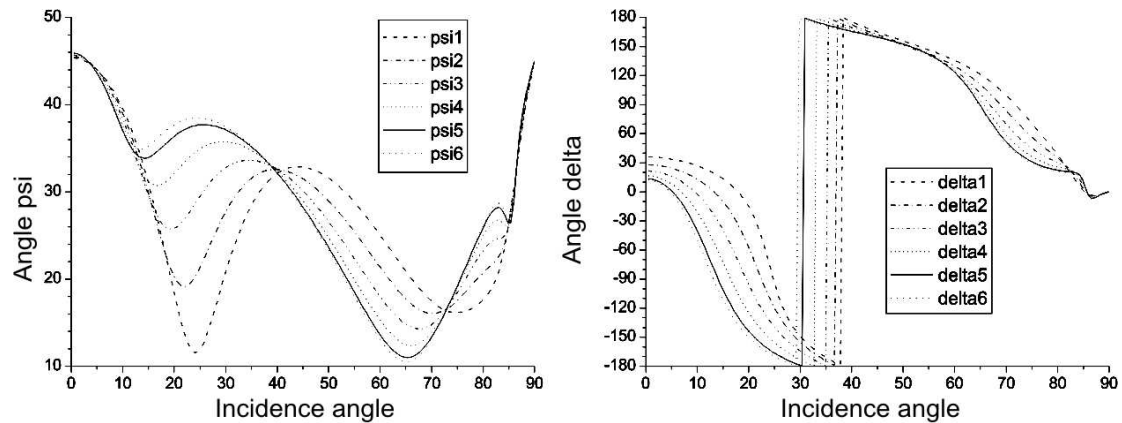


Fig. 6. Angles  $\Psi$  and  $\Delta$  versus the angle of incidence at a wavelength of 600 nm for various particle shapes:  $\psi_1$  and  $\delta_1$  – oblate particles with the ratio of the axes equal to 5;  $\psi_2$  and  $\delta_2$  – oblate particles with the ratio of the axes equal to 4;  $\psi_3$  and  $\delta_3$  – oblate particles with the ratio of the axes equal to 3;  $\psi_4$  and  $\delta_4$  – oblate particles with the ratio of the axes equal to 2;  $\psi_5$  and  $\delta_5$  – spherical particles;  $\psi_6$  and  $\delta_6$  – prolate particles with the ratio of the axes equal to 1/5

dependences of the coefficients of reflection from a surface covered with a layer of spherical particles are shown for  $p$ - and  $s$ -polarized light. One can see that the dependences of the reflection coefficient for  $p$ -polarized light on both the wavelength and the angle of incidence are rather complicated. At the same time, analogous dependences for  $s$ -polarized light do not reveal noticeable deviations from the behavior of the coefficient of reflection from a clean substrate. It should be noted that, since the substrate is considered as dispersion-free, its reflection coefficients do not depend on the wavelength. The spectral peculiarities in the behavior of the coefficient of reflection from a system of nanoparticles for  $p$ -polarized light correlate with the positions of transverse and longitudinal optical phonons. On the other hand, the corresponding angular dependences demonstrate a

transverse anisotropy induced by the two-dimensionality of the surface-coating particle system, which becomes more pronounced, when the angle of incidence increases.

In Fig. 3, the cross-sections of those dependences at a wavelength of 600 nm are demonstrated for the coating films consisting of particles with different shapes. As we see, the different shapes of coating particles result in almost identical behaviors of the reflection coefficients for  $s$ -polarized light, whereas for  $p$ -polarized light, the reflection in the case of oblate particles considerably differs from those in two other cases. To emphasize the existing difference, Fig. 4 shows the difference between the coefficients of reflection from a substrate covered with a particle layer and from a clean substrate.

Now, it is obvious that the reflection in the case of oblate particles is different for  $s$ -polarized light as well.

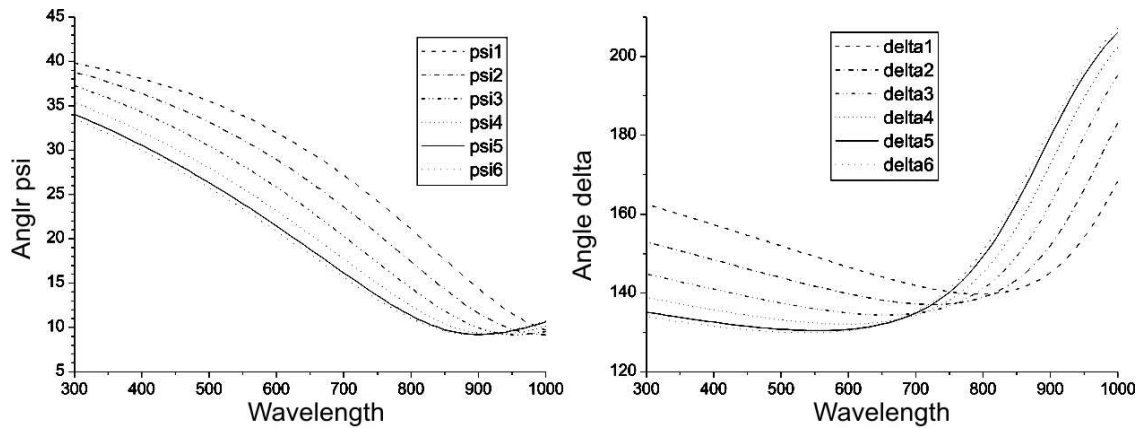


Fig. 7. Angles  $\Psi$  and  $\Delta$  versus the wavelength at the angle of incidence  $\lambda=60^\circ$  for different shapes of particles:  $\psi_1$  and  $\delta_1$  – oblate particles with the ratio of the axes equal to 5;  $\psi_2$  and  $\delta_2$  – oblate particles with the ratio of the axes equal to 4;  $\psi_3$  and  $\delta_3$  – oblate particles with the ratio of the axes equal to 3;  $\psi_4$  and  $\delta_4$  – oblate particles with the ratio of the axes equal to 2;  $\psi_5$  and  $\delta_5$  – spherical particles;  $\psi_6$  and  $\delta_6$  – prolate particles with the ratio of the axes equal to 1/5

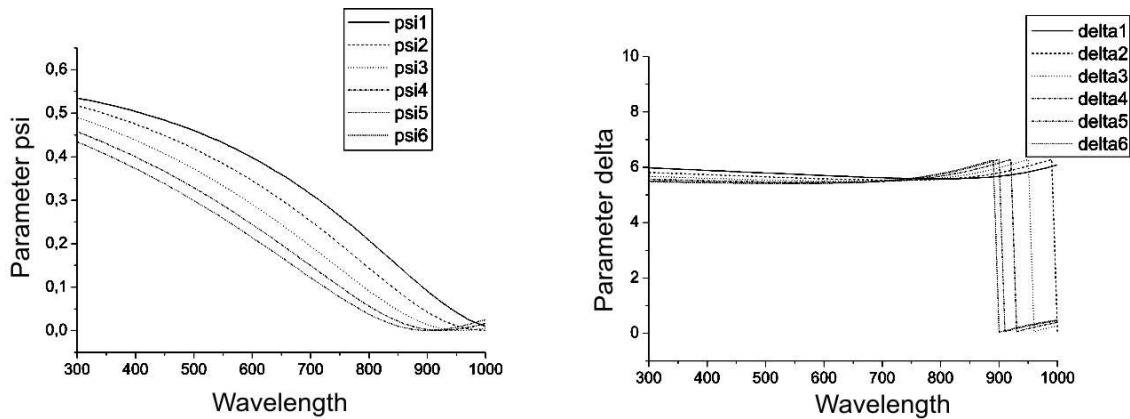


Fig. 8. Difference of the angles  $\Psi$  and  $\Delta$  for the particle-covered and clean substrates versus the angle of incidence at a wavelength of 600 nm for various particle shapes:  $\psi_1$  and  $\delta_1$  – oblate particles with the ratio of the axes equal to 5;  $\psi_2$  and  $\delta_2$  – oblate particles with the ratio of the axes equal to 4;  $\psi_3$  and  $\delta_3$  – oblate particles with the ratio of the axes equal to 3;  $\psi_4$  and  $\delta_4$  – oblate particles with the ratio of the axes equal to 2;  $\psi_5$  and  $\delta_5$  – spherical particles;  $\psi_6$  and  $\delta_6$  – prolate particles with the ratio of the axes equal to 1/5

However, the difference between the coefficients of reflection from a clean substrate and a substrate covered with a particle layer is very small, thus being hardly noticeable in the previous figure. An almost complete coincidence of the reflection coefficients for spherical and prolate particles can be explained by a smaller change of the interaction between a particle and the surface at the particle’s elongation than at its flattening. Since the interaction with the substrate is reciprocal to the cubic power of the distance, it is clear that the largest effect has to be attained in the case of oblate particles, the centers of which are located at shorter distances from the substrate in comparison with other cases. But, in general, the difference between the coefficients of reflection from a clean surface and a surface covered with particles

is rather insignificant. Therefore, it is hard to find the contribution of particles to reflection, which is the subject of our interest, by measuring only the amplitude of the reflected wave.

Figure 5 shows the dependences of the reflection coefficient on the wave frequency at a fixed angle of incidence ( $\vartheta = 60^\circ$ ) for films composed of particles with different shapes. One can see once more that the case of oblate particles considerably differs from the others, and the influence of the particle layer on the reflection of *s*-polarized light is very weak.

In Figs. 6 and 7, the dependences of the ellipsometric parameters  $\psi$  and  $\Delta$  on the angle of incidence and the wavelength, respectively, for coatings with particles characterized by different axis ratios are depicted.



One can see that the ellipsometric parameters strongly depend on the shape of particles that cover the surface. In this case, even the difference between spherical and prolate particles exceeds the standard errors of measurements. The angular dependences of ellipsometric angles reveal the same features that were observed in the behavior of the reflection coefficient for  $p$ -polarized waves,  $R_p$ . The dependence on the wavelength is rather appreciable, being governed just by the presence of particles on the surface, because the substrate is considered as dispersion-free with the parameters  $\psi = 9^\circ 10'$  and  $\Delta = 180^\circ$  at the angle of incidence  $\vartheta = 60^\circ$ .

In Fig. 8, the dependences of the differences between the values of ellipsometric parameters  $\psi$  and  $\Delta$  calculated in the cases of a surface covered with particles characterized by various axis ratios and in the case of a clean surface (all at a wavelength of 600 nm) on the angle of incidence are shown. One can easily see that the largest deviations from the parameters characteristic of the case with a clean substrate are observed in the range of angles of incidence, the vicinity of which contains the peculiarities in the dependences of the ellipsometric angles. At the same time, there exists a region near  $40^\circ$ , where there is almost no difference between the parameters for a clean substrate and a substrate covered with particles, irrespective of the shape of the latter.

All those results evidence a possibility to determine such important characteristics of nanosystems as the shape of particles that form the coating, using just ellipsometric methods.

## 8. Conclusions

Within the local field method with the use of the idea of effective susceptibility, we have developed the ellipsometric theory for monolayers of nanoparticles that cover the surface of a semiconductor or insulator. For the systems simulated as a substrate with semiconducting particles located on its surface, which have the shape of an ellipsoid of revolution, the effective susceptibility and the dependences of reflection coefficients and ellipsometric parameters on the angle of incidence and the frequency have been calculated. The presence of nanoparticles that cover the semiconductor surface make an appreciable contribution to the values of ellipsometric parameters, which can be measured experimentally.

## APPENDIX

As was shown in work [24], the linear response (polarization) of a separate particle, which has the shape of an ellipsoid of revolution and is so oriented on a surface that its axis of rotation is directed normally to the plane surface of the substrate, can be written in the form

$$\hat{\alpha} = \begin{pmatrix} \alpha_{\parallel} & 0 & 0 \\ 0 & \alpha_{\parallel} & 0 \\ 0 & 0 & \alpha_{\perp} \end{pmatrix}. \quad (D1)$$

The components of this tensor are

$$\alpha_{\parallel, \perp} = \varepsilon_0 \varepsilon_1 V \frac{(\varepsilon_P - \varepsilon_1) L_{\parallel, \perp}}{\varepsilon_1 + (\varepsilon_P - \varepsilon_1) m_{\parallel, \perp}}, \quad (D2)$$

$\varepsilon_0$ ,  $\varepsilon_p$ ,  $\varepsilon_2$ , and  $\varepsilon_1$  are the dielectric constants of vacuum, particles, the substrate, and the external medium, respectively;  $m_{\parallel, \perp}$  are the depolarization factors; and

$$L_{\parallel, \perp} = \left[ 1 + \frac{(\varepsilon_1 - \varepsilon_2)(\varepsilon_p - \varepsilon_1) U_{\parallel, \perp}}{3(\varepsilon_1 + \varepsilon_2)(\varepsilon_1 + (\varepsilon_p - \varepsilon_1) m_{\parallel, \perp})} \right]^{-1}. \quad (D3)$$

For prolate particles, the depolarization factor has the following components:

$$m_{\perp} = \frac{1 - \xi^2}{\xi^3} \left( \frac{1}{2} \ln \frac{1 + \xi}{1 - \xi} - \xi \right), \quad m_{\parallel} = \frac{1}{2}(1 - m_{\perp}).$$

Here,  $\xi$  is a parameter that describes the particle shape and equals  $\xi = \sqrt{1 - \gamma_p^2}$ , where  $\gamma_p = h_x/h_z$  is the ratio between the ellipsoid semiaxes (the eccentricity).

For oblate particles, the depolarization factor has the following components:

$$m_{\perp} = \frac{1 + \xi^2}{\xi^3} (\xi - \arctan \xi), \quad m_{\parallel} = \frac{1}{2}(1 - m_{\perp}), \quad (22)$$

where  $\xi = \sqrt{\gamma_p^2 - 1}$ .

In addition,  $U_{\parallel} = t$  and  $U_{\perp} = 2t$ , where  $t = h_x h_y h_z (2z_p)^{-3}$ , and  $z_p$  is the distance from the particle center to the substrate. In our case,  $z_p = h_z$ , i.e.  $t = \gamma_p^2/8$ .

For spherical particles,  $m_{\parallel} = m_{\perp} = 1/3$ .

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ТЕОРІЯ ЕЛІПСОМЕТРІЇ  
ШАРУ НАПІВПРОВІДНИКОВИХ  
НАНОЧАСТИНОК, ЩО ПОКРИВАЮТЬ ПОВЕРХНЮ

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## Резюме

У рамках методу локального поля побудовано теоретичну модель еліпсометрії субмоношару напівпровідникових наночастинок, що покривають поверхню. Для систем, які моделюються як підкладка з розташованими на ній частинками, що мають форму еліпсоїда обергання, було розраховано ефективну сприйнятливість. Це дало змогу визначити залежності коефіцієнтів відбиття та еліпсометричних параметрів від кута падіння та частоти. Наявність напівпровідникових наночастинок, що покривають поверхню, дає помітний внесок у еліпсометричні параметри, що може бути виміряно експериментально. Знайдено, що ці еліпсометричні параметри залежать від концентрації та форми частинок.