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Optical properties of nickel nanoparticles in systems with a statistically inhomogeneous structure

O. V. Machulianskyi, Ph.D. Assoc.Prof., ORCID 0000-0003-0057-9844
e-mail machulansky@gmail.com
National technical university of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" kpi.ua
Kiev, Ukraine

***Abstract*—The analysis and further development of the experimental-analytical approach for determining the values of the optical parameters of nanosized particles for a system with a statistically inhomogeneous structure is presented. An improved experimental-analytical method for determining the complex specific electric polarizability of nanosized particles in systems with a statistically inhomogeneous structure is based on spectrophotometric and electron-microscopic measurements on two-dimensional structures and application of analytical solution of Rosenberg's spectrophotometric equations with the consideration of analysis of particle size distribution.**

Experimental spectrophotometric and electron-microscopic studies of nickel islet films with weight thickness from 0.3 nm to 2.0 nm deposited by high-vacuum sputtering on quartz substrates in the range of the spectrum 0.2 ÷ 1, 1 µm are performed. Islands nickel film presented morphological microstructure in the form of monolayers isolated from each other nanoislands spherical surface nickel concentration (0.8 ÷ 2.0) · 10^{12} cm^{-2} and an average particle diameter 2.5 ÷ 7 nm.

The optical characteristics, namely, the complex specific electric polarizability, optical electric conductivity of nanosized nickel particles are determined in the spectral range 0.2 ÷ 1.1 µm with the help of the improved experimental-analytical method. A significant increase to one order of magnitude of the absolute values of complex specific electric polarizability of nickel particles with a decrease in their size and in comparison with absolute values of complex specific electric polarizability of model spheres with refractive index and absorption index of nickel in macroscopic volumes was revealed. It is established that in the spectral dependences of optical electric conductivity of nickel nanoparticles in the range 0.2 ÷ 1.1 µm there is a band that diminishing size is shifted to a high-frequency region. In this case, the value of optical electric conductivity of nickel nanoparticles monotonically decreases with a decrease in the size by 1-2 orders of magnitude. Comparison of the obtained values of optical electric conductivity of particles in the range of the considered interval with the values of optical electric conductivity of macroscopic samples of nickel in the studied range of the spectrum shows that in particles the value of optical electric conductivity is 2-3 orders of magnitude smaller than that of bulk metals. It is shown that in the nanoparticles of nickel absorption of "Drude" type in the near infrared region the spectrum is suppressed. The reason for this phenomenon may be the change of the mechanism of low-frequency electromagnetic response in nanosized metal particles in comparison with macroscopic metals.

The research results are of interest for the development and optimization of nanostructured systems with the inclusion of nanosized nickel particles and functional devices based on them with given electromagnetic characteristics.

Ref. 22, fig. 4.

Keywords* — *electric polarizability; nanosized particles; experimental-analytical method

I. INTRODUCTION

Nanocomposite systems based on nanosized metal particles are of particular interest for integrated technology, optoelectronics, informatics, and energy [1]–[3]. The prospects of using nickel nanoparticles to create: electromagnetic filters, miniature laser emitters, light modulators, photosensitive materials, protective and thermoregulatory coatings, high-speed optical devices, magnetic memory elements, high-sensitivity optical sensors and increasing the efficiency of renewable energy sources were noted in [4]–[6].

These applied and fundamental aspects cause considerable attention to the study of the optical properties of nickel nanoparticles. As a rule [1], [7], when solving problems of developing nanocomposite systems and optimizing their characteristics, the optical parameters of nickel nanoparticles are identified with the optical parameters characteristic for nickel in macroscopic volumes. It is obvious that in this case the optical parameters of nickel nanoparticles should not depend on their size. In the literature, information on experimental optical parameters (complex specific electric polarizability $\alpha = \alpha_1 - i\alpha_2$, complex permittivity $\varepsilon = \varepsilon_1 - i\varepsilon_2$ and optical electric conductivity σ) of metal nanoparticles is extremely limited [8], [9]. The complexity of such experimental studies is that the electromagnetic parameters of nanosized particles are not accessible to direct measurements. They can be determined on the basis of experimental values of various characteristics of the electromagnetic response of ensembles of particles, such as islet metal films or composite metal-dielectric structures.

So in [10] it was established by solving the inverse problem of the well-known Maxwell-Garnett theory [2], [11] that in the spectral range 0.5 ÷ 6 μm in islet nickel films the values of σ (and, hence, ε_2) of an individual nanoparticle-island fall with a decrease in its diameter D_0 (beginning with $D_0 < 25$ nm). It should be noted that in [10] the values of D_0 were estimated indirectly by the weight thickness of the films, and σ are given in relative units.

We note that in the optical range of the spectrum (0.2 ÷ 1.1 μm), the reliability of the available experimental data on the dispersion and size changes in the electromagnetic parameters of particles raises serious doubts: since they were obtained without accurate consideration of the particle size and microstructure of the system, by crude methods involving primitive model representations of their electromagnetic response. An analytical solution of the inverse problem of the spectrophotometric system of equations of the Rosenberg theory was found in [12] for the optical properties of two-dimensional systems (monolayers or island films) [11]. The method for determining the real α_1 and imaginary α_2 part of the complex specific electric polarizability of an individual nanoparticle in a system with a statistically homogeneous structure was developed and justified on the basis of the obtained analytical solution [12]. As a result of the application of this method to nickel islet films with a statistically homogeneous structure on glass substrates, the values α_1, α_2 of nickel spherical particles in the spectral range of wavelengths $\lambda = 0.4 \div 1.1$ μm were determined [9].

It should be noted that in [8], [9] the microstructure of the nanodispersed system and the particle sizes are estimated formally under the condition of a normal particle size distribution. This approach is fully justified for systems with a statistically homogeneous structure, for example, for islet films with a weight thickness of up to 1 nm and a low concentration of nano-islands and depends on the type of substrate [13]. For systems with a statistically heterogeneous structure, which, as a rule, is typical in most island metal films [13], determining the particle size without taking into account the statistical analysis of their microstructural parameters leads to a large error [14].

However, with further development of the experimental-analytical approach, we improved the method for determining the values of α nanoscale particle for systems with a statistically inhomogeneous structure on the basis of spectrophotometric and electron-microscopic measurements on two-dimensional systems and the application of Rosenberg's spectrophotometric equations taking into account the analysis of particle size distribution. It was shown in [14] that the use of an improved experimental-analytical method made it possible to increase the accuracy of obtaining experimental values of α_1 and α_2 nanosized particles.

In addition, in order to study the nature of the dimensional changes in the optical parameters of nickel nanoparticles, it is of interest to expand the spectral range of their experimental values. For this, it is necessary to determine the values of α_1 and α_2 of nickel nanoparticles in an islet nickel film on a fused quartz substrate with a transparency band at electromagnetic radiation frequencies from near infrared to near ultraviolet regions of the spectrum. We note that nanoscale islet nickel films on quartz substrate have a statistically inhomogeneous structure with a significant size fluctuation [15]. Therefore, it is expedient to determine the experimental values of the optical characteristics of nanosizeds nickel particles using advanced experimental-analytical techniques for systems with a statistically heterogeneous structure.

The present work is devoted to the determination of the experimental spectral and size dependences of the optical parameters α, σ of nanosized nickel particles in systems with a statistically inhomogeneous structure in the spectral range $\lambda = 0.2 \div 1.1$ μm.

II. METHODOLOGY OF EXPERIMENT

An experimental analytical approach is used to analyze the electromagnetic properties of composite nanostructured systems and to determine their electromagnetic parameter which establishes the relationship between the electromagnetic parameters of the individual components of the composite system and its response to external electromagnetic effects. The general methodology for analyzing the electromagnetic parameters of the components of a nanostructured system in the framework of the approach under consideration consists of an experimental and an analytical block. The block of experimental metrological support is based on the use of standard methods for studying the microstructure and electromagnetic parameters of materials. The analytical block is based on solving the inverse problem of the equations systems of a mathematical model describing the electromagnetic properties of the corresponding nanostructured system.

To determine the experimental optical parameters of nickel nanoparticles in a system (nanoscale islet film), the model of the electromagnetic response of a two-dimensional nanostructured system based on the use of Rosenberg's spectrophotometric equations taking into account the analysis of the particle size distribution is preferred for use in the optical spectral range [14].

The model establishes the relationship between the energy characteristics (transmission coefficient T, the reflection coefficient from the film side R and the substrate R'), the phase shift in the reflection and transmission of radiation in the system, with the microstructure parameters (concentration, particle size) and the electromagnetic parameter of the nanoparticle (electric polarizability) using Rosenberg's spectrophotometric equations [11].

The model is considered under the following assumptions:

- the normal angle of the electromagnetic wave λ falling on the surface of the nanostructured system;
- the surface concentration of particles N_0 with diameter D_0 is sufficiently large, so that the distance between them is much smaller than the length of the electromagnetic wave;
- particles are spherical and randomly distributed on the surface of substrate with refractive index n_0. The orientation of their dipole moments is arbitrary;
- the effective electric field in the film is determined by the sum of the external field of the incident wave and the wave scattered by all the particles, taking into account the separation of the wave scattered by the layer into a straight and reverse wave;
- the electromagnetic properties of an individual particle are determined by the specific (volume) electric polarizability of the particle α, which is characterized by the ratio $a + b = \frac{1}{\alpha}$, where a and b are dimensionless parameters [11].

Specific electric polarizability is determined by the ratio $\alpha = \frac{4\pi\alpha'}{V}$, where V is the volume of a particle; α' is the electric polarizability of a particle.

Spectrophotometric systems of Rosenberg's equations have the form:

$$\begin{cases} T = (1 - r_0^2)\frac{1+2P_1+\left(P_1^2+P_2^2\right)}{1+2r_0(P_1+2P_2kR_0)+r_0^2\left(P_1^2+P_2^2\right)^2}, \\ R = \frac{r_0^2-2r_0^2(1-2r_0)P_1+4r_0P_2kR_0+\left(1-2r_0^2\right)\left(P_1^2+P_2^2\right)}{1+2r_0(P_1+2P_2kR_0)+r_0^2\left(P_1^2+P_2^2\right)^2}. \end{cases} \qquad (1)$$

$$\begin{cases} P_1 = -\frac{\left\{b+\left(\frac{3}{2}\right)kt_0\right\}\left(\frac{3}{2}\right)kt_0}{\left\{b+\left(\frac{3}{2}\right)kt_0\right\}^2+\left[a-\left\{\frac{3}{4\sqrt{2}}\right\}\sqrt{\eta}kt_0\right]^2}, \\ P_2 = -\frac{\left[a-\left\{\frac{3}{4\sqrt{2}}\right\}\sqrt{\eta}kt_0\right]\left(\frac{3}{2}\right)kt_0}{\left\{b+\left(\frac{3}{2}\right)kt_0\right\}^2+\left[a-\left\{\frac{3}{4\sqrt{2}}\right\}\sqrt{\eta}kt_0\right]^2}. \end{cases} \qquad (2)$$

where $k = \frac{2\pi}{\lambda}$; $\eta = \frac{2\pi N_0}{k^2}$; $t_0 = \frac{4\pi N_0 R_0^3}{3}$; $r_0 = \frac{n_0-1}{n_0+1}$; $R_0 = D_0/2$ is the particle radius.

The system of equations (1) connects T and R of a nanocomposite system with effective complex polarization of the entire ensemble of nanoparticles of the system $P = P_1 + iP_2$ and their average size. The system of equations (2) expresses P in terms of the specific electric polarizability α of the nanoparticle, the concentration and size of the nanoparticle.

The microstructure of a nanostructured system is characterized by parameters: particle size distribution function, particle size, concentration which are determined taking into account the nanoparticle size distribution statistics based on the Pearson's consensus criterion χ^2 [16].

The determination of T and R from the known values of the electromagnetic parameters is called the direct problem of spectrophotometry of a two-dimensional nanocomposite system. The solution of the direct problem of the spectrophotometric equations (1) and (2) does not present fundamental difficulties and is unambiguous. The inverse problem of the Rosenberg's spectrophotometric equations is the calculation of the specific electric polarizability of a nanoparticle according to known values of T, R. We obtained analytical solutions of the inverse problems of systems of equations (1), (2) [12].

The choice of the physical solution from two mathematical roots ($P_1 < 0$, $P_2 > 0$ and $P_1 < 0$, $P_2 < 0$) of the solution of the system of equations (1) and (2) was carried out on the basis of the generally accepted principle – according to the conditions of the anomalous dispersion of the effective permittivity $\varepsilon_{eff} = \varepsilon_{1eff} - i\varepsilon_{2eff}$ of a nanostructured system near the dipole (Rayleigh) resonance band in a separate nanoparticle. In accordance with [1], $\varepsilon_{1eff} > 0$, $\varepsilon_{2eff} > 0$ in the region $\lambda > \lambda_R$ and $\varepsilon_{1eff} < 0$, $\varepsilon_{2eff} > 0$ for $\lambda < \lambda_R$, and λ_R is the resonant wavelength. In order to find the conditions for the anomalous dispersion of P_1, P_2 near λ_R, it is expedient to use the relation $\varepsilon_{eff} - 1 = i\frac{\lambda}{\pi D_0}P$ established in [11] between ε_{eff} and P.

It follows from the singularities of the dispersion ε_{eff} in a neighborhood of λ_R that the physical meaning in the domain $\lambda \leq \lambda_R$ has a mathematical root with the values $P_1 < 0$, $P_2 > 0$, and in the range $\lambda > \lambda_R$ the root $P_1 < 0$, $P_2 < 0$ (λ_R is the point of the stitching of mathematical solutions). It should be noted that in the spectrophotometric systems of Rosenberg's equations the concept of ε_{eff} for two-dimensional systems is not introduced. At the same time, comparing the results of investigations [1], [8], [9] of the optical properties of three- and two-dimensional systems, it can be concluded that the obtained conditions for the anomalous dispersion of P_1 and P_2 near λ_R are also preserved in the case of two-dimensional systems. The resonance wavelength λ_R is determined from the conditions [1]:

$$\begin{cases} \varepsilon_1(\lambda_R) = -2\varepsilon_a, \\ \varepsilon_2(\lambda_R) = 0. \end{cases} \qquad (3)$$

where ε_a is the permittivity of the environment surrounding a particle.

Typically [1], when assessing λ_R on expressions (3) is used approximation $\varepsilon = \varepsilon_m$ and ε_m is determined by the values of the refractive indices n and k of the absorption of metals in macroscopic amounts. The data on nickel n and k available in the literature [17], [18] indicate that the dipole resonance in its particles (in the $\varepsilon = \varepsilon_m$ approximation) should take place in the far ultraviolet region. This serves as the basis for choosing in the investigated range $\lambda \geq 0.2$ μm as the physical solution of the root with $P_1 < 0$, $P_2 < 0$ and the corresponding values α_1, α_2.

To determine the optical characteristics of nanoparticles by experimental and analytical methods in experimental software made a series of experimental models of islet nanoscale nickel films and held their spectrophotometric and electron microscopic studies.

Nanoscale islet films of nickel with effective thicknesses of 0.5 ÷ 2.0 nm were obtained by thermal evaporation of nickel (with an initial purity of 99.99%) in a vacuum of 10^{-6} mmHg at a rate of 0.5 nm/s on thoroughly quartz substrates heated to 650 K. The effective thickness of the films and the rate of their deposition were controlled by the quartz resonator method. After spraying and cooling in vacuum to room temperature, the samples were exposed to air.

Coefficients of transmission of T and reflection R films were measured in the range of lengths of waves $\lambda = 0.2 \div 1.1$ microns with an accuracy of 3% at a normal hade of light for a film on the spectrophotometer SF-16 with a special prefix for light reflection measurement.

Microscopic studies of the structural phase composition of nickel films were performed using an electron microscope BS-613. Electron microscopic images showed that nanoscale nickel films possess an island-like statistically inhomogeneous structure, and the shape of the islands is close to spherical.

The parameters of the microstructure of nickel island films: the particle size distribution function, the average particle size D_0 of the island particles, the average surface concentration of N_0 were determined by analysis of the distribution of nickel nanoparticles in size using the Pearson criterion. With an increase in the effective thickness of samples of nanosized films, the values of D_0 grew from 2.5 nm to 7 nm, and N_0 dropped, respectively, within the interval $(0.8 \div 2.0) \cdot 10^{12}$ cm^{-2}.

In addition, in order to compare the size and dispersion characteristics α obtained by the experimental-analytical method with the results given in [5], it is necessary to determine the values of the optical electric conductivity σ of the nickel nanoparticles. Optical electric conductivity of spherical particles is related to α by means of the relation:

$$\sigma = \frac{1}{4\pi}\frac{9\varepsilon_a\alpha_2}{(3-\alpha_1)^2+\alpha_2^2}\,\omega, \tag{4}$$

where ε_a is the permittivity of the environment surrounding a particle. Formula (4) follows from expression [1], [11]:

$$\alpha = \frac{\varepsilon-\varepsilon_a}{\varepsilon_a+f(\varepsilon-\varepsilon_a)}, \tag{5}$$

where f is the particle shape factor.

For a spherical particle f=1/3 [11]. In this case, α_1 and α_2 are determined by the relations [1], [11]:

$$\alpha_1 = \frac{3\left[(\varepsilon_1-\varepsilon_a)(\varepsilon_1+2\varepsilon_a)+\varepsilon_2^2\right]}{(\varepsilon_1+2\varepsilon_a)^2+\varepsilon_2^2}, \tag{6}$$

$$\alpha_2 = \frac{9\varepsilon_a\varepsilon_2}{(\varepsilon_1+2\varepsilon_a)^2+\varepsilon_2^2}, \tag{7}$$

where ε_1, ε_2 are real and the imaginary parts of the complex permittivity, respectively.

The permittivity and the optical constants of the film (index of refractive n and absorption k) are related by the relations [1]:

$$\begin{cases}\varepsilon_1 = n^2 - k^2,\\ \varepsilon_2 = 2nk.\end{cases} \tag{8}$$

The value of ε_a according to [19] was estimated on the basis of the expression $\varepsilon_a = (1+\varepsilon_0)/2$, where ε_0 is the permittivity of the substrate.

The permittivity of the substrate was determined from the measured values of the transmittance of the substrate T_0, taking into account its dispersion dependence from the relationship $T_0 = \frac{2n_0}{n_0^2+1}$, where n_0 is the refractive index of substrate [20].

III. RESULTS AND DISCUSSION

The obtained experimental dispersion dependences of the real α_1 and imaginary α_2 parts of the specific complex electric polarizability of ultradisperse nickel particles are shown in Fig. 1, and the dimensional ones in Fig. 2

For comparison, in Fig. 1 shows the dispersion dependences of α_{1Ni} and α_{2Ni} of a model spherical particle, with properties of "bulk" (in macroscopic volumes) of nickel. α_{1Ni} and α_{2Ni} calculated from the formulas (5-8) and the data on n and k for nickel in the macroscopic volumes contained in [18].

From the above results it can be seen that dispersion changes of α_2 of nickel nanoparticles are monotonic, and their dispersion curves qualitatively coincide in the interval $\lambda = 0.2 \div 0.9$ μm with the corresponding dependences for model particles with the properties of "bulk" nickel. The experimental values of α_1 and α_2 grow to one order of magnitude with decreasing particle size, and in comparison with the absolute values of α_1 and α_2 of the model sphere with refractive index n and absorption index k of nickel in macroscopic samples.

From Fig. 2 it follows that when the size of the nickel nanoparticle decreases from 7 nm to 2.5 nm, α_1 and α_2 increase by more than three times in the blue region of the spectrum, and approximately twice in the red region.

It should be noted that in the range $\lambda \geq 0.9$ μm, the optical constants n and k of "bulk" nickel were determined in [18] with a step $\lambda \sim 0.1$ μm. This probably explains the differences between curves 1-5 and 6 (Fig. 1) for the spectral dependences of α_2 for $\lambda \geq 0.9$ μm. More detailed studies [17] of the dispersion of optical conductivity of continuous ($d \sim 60$ nm) chemically pure nickel films indicate the detection of a weak band near $\hbar\omega \sim 1.4$ eV ($\lambda \sim 0.88$ μm), which is attributed to the long-wavelength interband absorption of nickel.

The presence of this band is confirmed by the spectral dependences of the optical conductivity σ of the nickel particles are shown in Fig. 3. The optical conductivity was determined from the experimental values of α_1 and α_2 obtained on the basis of relation (4). In Fig. 3 also shows the dispersion dependences σ of nickel in macroscopic volumes, contained in [18].

A comparison of the dimensional and dispersion dependences σ obtained by us and in [5] showed that they are qualitatively similar. In both cases (except for small deviations caused by the long-wave band in the dispersion σ), a decrease in σ with a decrease in the size of the nanoparticles is observed.

The significant difference in the dispersion σ of bulk nickel and its particles attracts attention in the spectral range $\lambda = 0.2 \div 1.1$ µm. As is known [21], the absorption of metals in macroscopic volumes is due to intraband transitions of conduction electrons. In accordance with the Drude model [21], σ should increase with decreasing $\hbar\omega$, which is observed on the dispersion relation σ for bulk nickel.

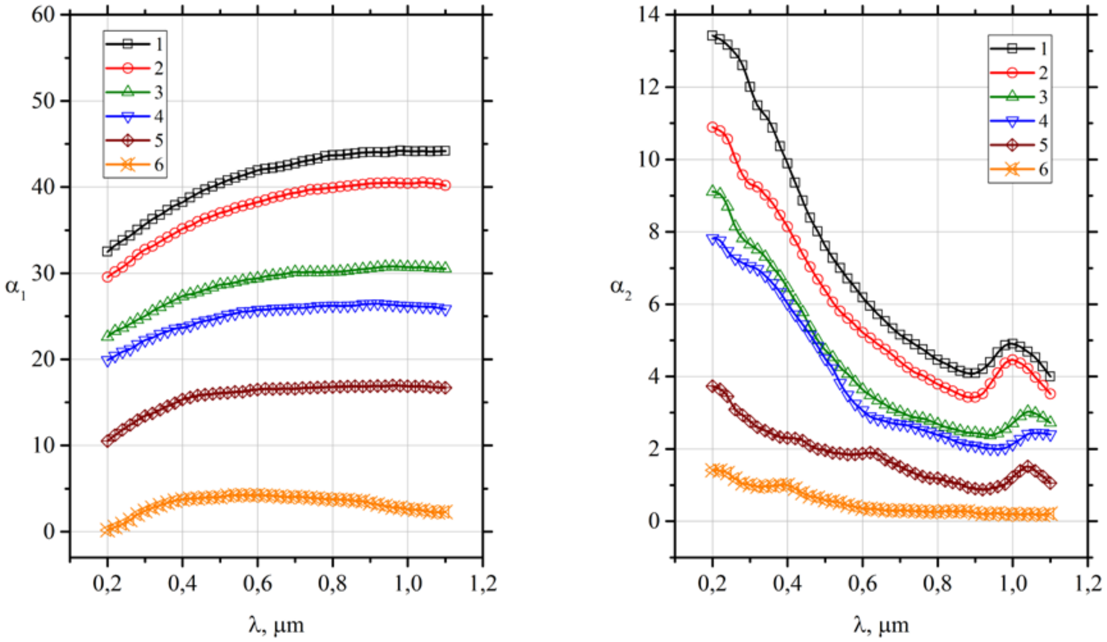
From Fig. 3, we can conclude that in nickel particles, the "Drude" type absorption in the near infrared region of the spectrum is suppressed. The reason for this phenomenon may be a change in the mechanism of the low-frequency electromagnetic response in ultradisperse metallic particles in comparison with macroscopic metals.

From Fig. 3 it follows that the values of σ of the particle fall monotonically with decreasing D_0 by 1-2 orders of magnitude. Comparison of the obtained values of σ particles within the considered range D_0 with the values of σ macroscopic samples of nickel, silver in this spectral range shows that in the particles the values of σ are 2-3 orders of magnitude smaller than in bulk metals. We note that, in order of magnitude, the σ of nickel and silver particles are close to each other, and the degree of decay σ with decreasing D_0 depends little on the type of metal [22].

It seems necessary to compare the results of studies of nickel island nanoparticles on a quartz substrate using the experimental-analytical method developed for systems with a statistically inhomogeneous structure with optical parameter values for nickel nanoparticles in the "island film on a glass substrate" system, obtained earlier in [9]. A comparative analysis of the spectral and size dependences α_1, α_2 (Fig. 1, Fig. 2) with the corresponding values for nickel islands nanoparticles for systems with a statistically homogeneous structure [9] shows that they are qualitatively identical. In quantitative terms, the differences between the experimental values of α_1, α_2 for both indicated cases reach 30%.

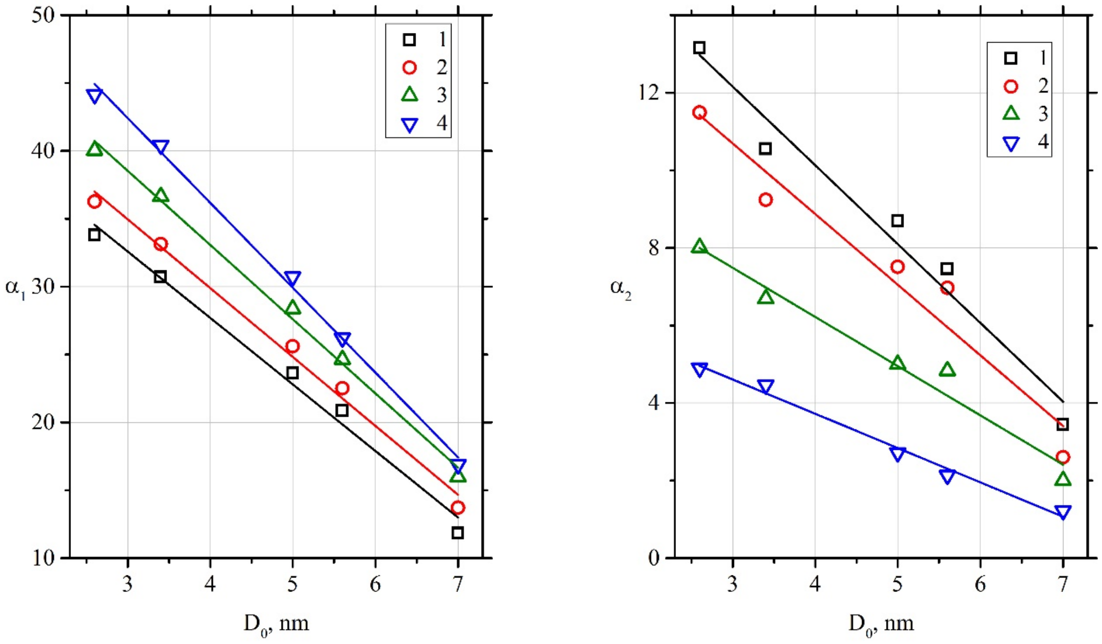
It should be noted that such significant quantitative discrepancies are due to the following aspects:

- In [9], the microstructure of the nanodispersed system and the particle sizes are estimated formally from the corresponding histogram of the particle size distribution for the pre-selected samples. This approach is completely justified for systems with a statistically homogeneous structure, which is typical, for example, for islet films with an effective thickness of up to 1 nm and a low concentration of nanoislands.
- For systems with a statistically heterogeneous structure, which, as a rule, is typical for most island metal films [13] determining the particle size without taking into account the statistical analysis of their microstructural parameters leads to a large error [14].



a) b)

Fig. 1 Spectral dependences of the real α_1 (a) and imaginary α_2 (b) parts of the complex specific electric polarizability of the nanoparticles of nickel at different values of the diameter D_0 of the nanoparticles of nickel: 1 – D_0 = 2.6 nm; 2 – D_0 = 3.4 nm; 3 – D_0 = 5 nm; 4 – D_0 = 5.6 nm; 5 – D_0 = 7 nm; 6 – for a model sphere with values of electromagnetic parameters characteristic of nickel in a macroscopic volume [18]



a)

b)

Fig. 2 Dimensional dependences of the real α_1 (a) and imaginary α_2 (b) parts of the complex specific electric polarizability of the nanoparticles of nickel at different values of λ: 1 – λ = 0.24 μm; 2 – λ = 0.32 μm; 3 – λ = 0.48 μm; 4 – λ = 1 μm

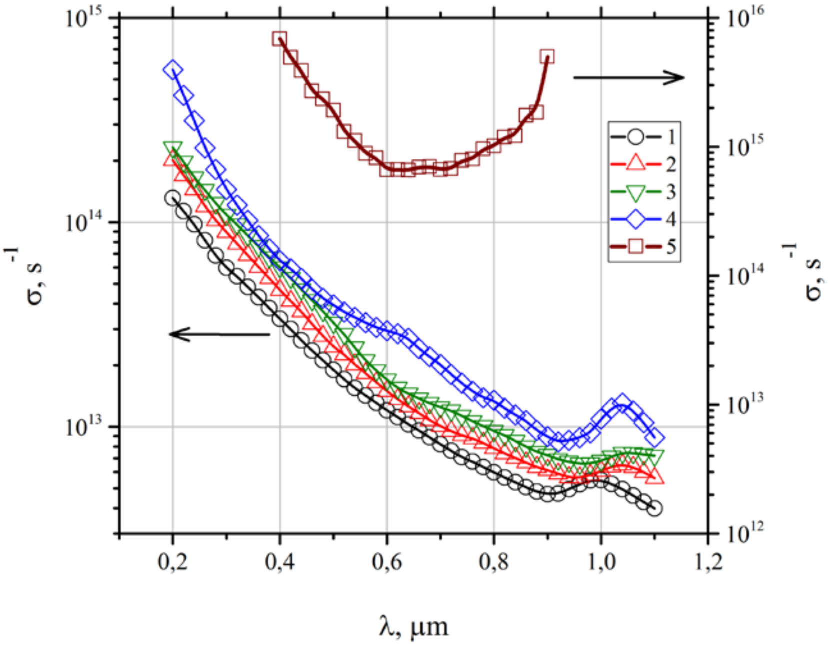
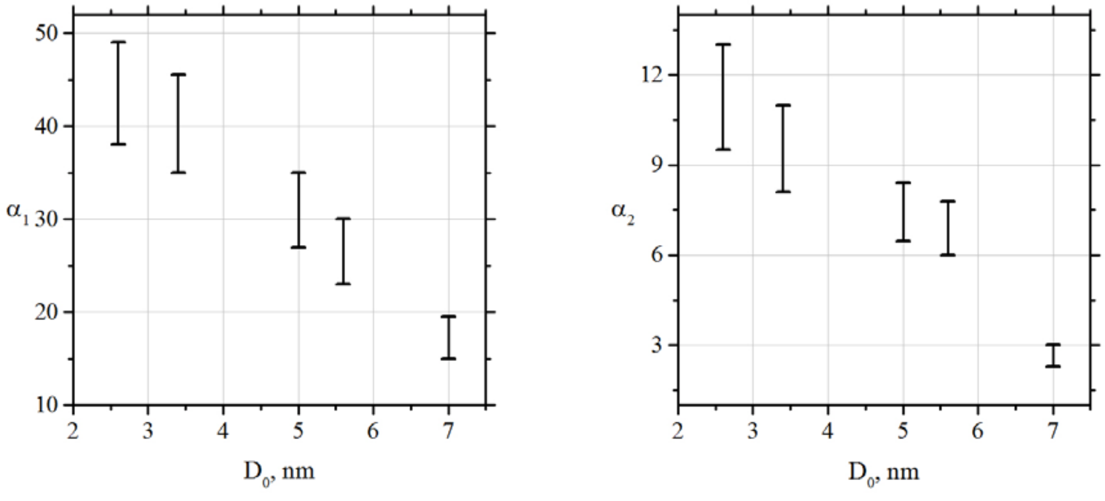


Fig. 3 Spectral dependences of optical electric conductivity σ of nanoparticles of nickel at different values of their size D_0: 1 – D_0 = 3.4 nm; 2 – D_0 = 5 nm; 3 – D_0 = 5.6 nm; 4 – D_0 = 7 nm; 5 – for a sample of nickel in a macroscopic volume [18]



a) b)

Fig. 4 The scatter of the values of the real (a) and imaginary (b) parts of the complex specific polarizability of nickel nanoparticles (on their dimensional dependencies) determined for different hypotheses of the type of particle size distribution functions at $\lambda = 0.4$ μm

- The results of electron microscopic studies have shown that islet nickel films on glass substrates have a statistically homogeneous structure, and on quartz substrates it is statistically inhomogeneous.
- Experimental information on the optical characteristics of nanoparticles indicates the determining effect of the actual distribution function of nanoparticles on their properties. The development of the experimental-analytical method for determining the values of the complex specific electric polarizability of nanoparticles, taking into account the analysis of the statistics of their distribution by size, made it possible to increase the accuracy of obtaining experimental values of the optical parameters.

Fig. 4 shows the dimensional dependences of α_1 and α_2 of nickel nanoparticles in a statistically inhomogeneous system and shows the possible interval of the scatter of the values of α determined for different hypotheses of the form of the particle size distribution functions. Thus, the accuracy of determining the values of α_1 and α_2 of nanoparticles increases to 30% with using of experimental-analytical method, taking into account the size distribution function of the nanoparticles for the investigated systems, by estimating the particle size ($D_0 < 7$ nm) with a credible probability of 0.95.

CONCLUSIONS

The analysis and further development of the experimental-analytical approach for determining the values of optical parameters of nanosized particles in a system with a statistically inhomogeneous structure is presented.

Experimental-analytical method for determining the complex specific electric polarizability of nanosized particles in systems with a statistically inhomogeneous structure is based on spectrophotometric and electron-microscopic measurements on two-dimensional structures and using an analytical solution of the Rosenberg's spectrophotometric equations, taking into account the analysis of particle size distribution, is proposed.

Experimental spectrophotometric and electron microscopic studies of islet nickel films with weight thicknesses from 0.3 nm to 2.0 nm deposited by high-vacuum deposition on quartz substrates in the spectral range $\lambda = 0.2 \div 1.1$ μm are performed. The island nickel films represented a morphological microstructure in the form of monolayers of isolated nickel nanoislands with a surface concentration $N_0 = (0.8 \div 2.0) \cdot 10^{12}$ cm^{-2} and an average particle diameter $D_0 = 2.5 \div 7$ nm.

Optical characteristics of nanodimensional nickel particles, namely, complex specific electric polarizability, optical electric conductivity, using an improved experimental-analytical method in the spectral range $\lambda = 0.2 \div 1.1$ μm are determined. A significant increase to one order of magnitude of the absolute values of α_1, α_2 nickel particles with a decrease in their size and in comparison with the absolute values of α_1 and α_2 model spheres with refractive indices n and absorption k of nickel in macroscopic volumes was found.

It is established that in the spectral dependences of σ of nickel nanoparticles in the range $\lambda = 0.2 \div 1.1$ μm, a band is observed which, with decreasing size, is shifted to the high-frequency region. At the same time, the values of the nickel nanoparticle decrease monotonically with decreasing size by 1-2 orders of magnitude. Comparison of the obtained particle values σ within the interval D_0 with the values of σ macroscopic samples of nickel and silver in the investigated spectral range shows that in the particles the values of σ are 2-3 orders of magnitude smaller than in bulk metals. It is shown that in nickel nanoparticles the absorption of the “Drude” type in the near infrared region of the spectrum is suppressed. The reason for this phenomenon may be a change in the mechanism of the low-frequency electromagnetic response in nanosized metal particles in comparison with macroscopic metals.

Research results are of interest for the development and optimization of nanostructured systems and functional devices based on them with specified electromagnetic characteristics.

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Оптичні властивості наночастинок нікелю в системах зі статистично неоднорідною структурою

Мачулянський О. В., к.т.н., доцент, ORCID 0000-0003-0057-9844
e-mail machulansky@gmail.com
Національний технічний університет України
“Київський політехнічний інститут імені Ігоря Сікорського” kpi.ua
Київ, Україна

***Реферат*—Представлений аналіз та подальший розвиток експериментально-аналітичного підходу для визначення значень оптичних параметрів нанорозмірних частинок в системі зі статистично неоднорідною структурою. Вдосконалений експериментально-аналітичний метод визначення комплексної питомої електричної поляризованості нанорозмірних частинок в системах зі статистично неоднорідною структурою засновано на спектрофотометричних і електронно-мікроскопічних вимірах на двовимірних структурах і застосуванні аналітичного рішення спектрофотометричних рівнянь Розенберга з урахуванням аналізу розподілу часток за розмірами.**

Проведено експериментальні спектрофотометричні та електронно-мікроскопічні дослідження острівкових плівок нікелю з ваговою товщиною від 0,3 до 2,0 нм, нанесених методом вакуумного розпилення на кварцові підкладки в діапазоні спектра 0,2 ÷ 1,1 мкм. Острівкові плівки нікелю представляли морфологічну мікроструктуру у вигляді моношарів ізольованих один від одного сферичних наноострівків нікелю з поверхневою концентрацією (0,8 ÷ 2,0) · 10^{12} см$^{-2}$ і середнім діаметром частинок 2,5 ÷ 7 нм.

В спектральному інтервалі довжин хвиль 0,2 ÷ 1,1 мкм отримані експериментальні спектральні та розмірні залежності електромагнітних параметрів, а саме: комплексної питомої електричної поляризованості і оптичної провідності. Виявлено значне зростання до одного порядку величини абсолютних значень дійсної і уявної частин комплексної питомої електричної поляризованості частинок нікелю і при зменшенні їх розміру та в порівнянні з абсолютними значеннями дійсної і уявної частин комплексної питомої електричної поляризованості модельних сфер з оптичними параметрами для макроскопічних об’ємів нікелю. Встановлено, що в спектральних залежностях оптичної провідності наночастинок нікелю в діапазоні довжин хвиль 0,2 ÷ 1,1 мкм спостерігається смуга, яка зі зменшенням розміру зміщується в високочастотну область. При цьому значення оптичної провідності наночастинки нікелю монотонно падають зі зменшенням розміру на 1-2 порядки величини. Порівняння отриманих значень оптичної електронної провідності частинок в межах розглянутого інтервалу зі значеннями оптичної електронної провідності макроскопічних об’ємів нікелю в досліджуваному діапазоні спектра показує, що в частинках значення оптичної електронної провідності на 2-3 порядки величини менше, ніж в масивних металах. Показано, що в наночастицах нікелю поглинання "друдівського" типу в ближній інфрачервоній області спектра придушене. Причиною цього може бути зміна механізму низькочастотного електромагнітного відгуку в нанорозмірних металевих частинках у порівнянні з макроскопічними металами.

Результати досліджень представляють інтерес для розробки та оптимізації наноструктурних систем і функціональних пристроїв на їх основі із заданими електромагнітними характеристиками.

Бібл. 22, рис. 4.

Ключові слова — електрична поляризованість; нанорозмірні частинки; експериментально-аналітичний метод

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Оптические свойства наночастиц никеля в системах со статистически неоднородной структурой

Мачулянский А. В., к.т.н., доцент, ORCID 0000-0003-0057-9844
e-mail machulansky@gmail.com
Национальный технический университет Украины
“Киевский политехнический институт имени Игоря Сикорского” kpi.ua
Киев, Украина

***Реферат*—Представлен анализ и дальнейшее развитие экспериментально-аналитического подхода для определения значений оптических параметров наноразмерных частиц в системе со статистически неоднородной структу-**

рой. Усовершенствованный экспериментально-аналитический метод определения комплексной удельной электрической поляризуемости наноразмерных частиц в системах со статистически неоднородной структурой основан на спектрофотометрических и электронно-микроскопических измерениях на двумерных структурах и применении аналитического решения спектрофотометрических уравнений Розенберга с учетом анализа распределения частиц по размерам.

Проведены экспериментальные спектрофотометрические и электронно-микроскопические исследования островковых пленок никеля с весовой толщиной от 0,3 до 2,0 нм, нанесенных методом вакуумного распыления на кварцевые подложки в диапазоне спектра 0,2 ÷ 1,1 мкм. Островковые пленки никеля представляли морфологическую микроструктуру в виде монослоев изолированных друг от друга сферических наноостровков никеля с поверхностной концентрацией (0,8 ÷ 2,0) · 1012 см-2 и средним диаметром частиц 2,5 ÷ 7 нм.

В спектральном интервале длин волн 0,2 ÷ 1,1 мкм получены экспериментальные спектральные и размерные зависимости электромагнитных параметров, а именно: комплексной удельной электрической поляризуемости и оптической проводимости. Обнаружен значительный рост до одного порядка величины абсолютных значений действительной и мнимой частей комплексной удельной электрической поляризуемости частиц никеля и при уменьшении их размера и по сравнению с абсолютными значениями действительной и мнимой частей комплексной удельной электрической поляризуемости модельных сфер с оптическими параметрами для макроскопических объемов никеля. Установлено, что в спектральных зависимостях оптической проводимости наночастиц никеля в диапазоне длин волн 0,2 ÷ 1,1 мкм наблюдается полоса, которая с уменьшением размера смещается в высокочастотную область. При этом значения оптической проводимости наночастицы никеля монотонно падают с уменьшением размера на 1-2 порядка величины. Сравнение полученных значений оптической электронной проводимости частиц в пределах рассмотренного интервала со значениями оптической электронной проводимости макроскопических объемов никеля в исследуемом диапазоне спектра показывает, что в частицах значения оптической электронной проводимости на 2-3 порядка величины меньше, чем в массивных металлах. Показано, что в наночастицах никеля поглощение “друдевского” типа в ближней инфракрасной области спектра подавлено. Причиной этого может быть изменение механизма низкочастотного электромагнитного отклика в наноразмерных металлических частицах по сравнению с макроскопическими металлами.

Результаты исследований представляют интерес для разработки и оптимизации наноструктурных систем и функциональных устройств на их основе с заданными электромагнитными характеристиками.

Библ. 22, рис. 4.

Ключевые слова — электрическая поляризуемость; наноразмерные частицы; экспериментально-аналитический метод