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Frequency shifts of surface plasmon resonances in calculating the absorption coefficient of a composite based on bimetallic 1d-systems

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In this paper analyzes the electromagnetic radiation absorption by a composite based on bimetallic nanowires. Using the Drude-Lorentz theory it was obtained the relationship for the polarizability frequency dependences, as well as real and imaginary parts of the dielectric function of layered 1D-systems was obtained. It is shown that the structure in the form of a metal core covered with a layer of another metal leads to splitting and the appearance of two maxima in the frequency dependence of the absorption coefficient. The positions of the maxima are determined by the composition of bimetallic nanowires and the volume content of metals. The influence of the dimensionality of the systems has been established by comparing the frequency dependences of the composite absorption coefficient based on bimetallic nanowires and nanoparticles. Calculations were performed for Ag@Au and Au@Ag nanowires immersed in Teflon.

Keywords: bimetallic nanowire, surface plasmon resonance, polarizability, dielectric function, absorption coefficient.

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Introduction

The widespread use of metal 1D-systems is due to their unique optical features associated with the regulation of electromagnetic radiation absorption by changing the size, shape and material of the studied samples [1]. Modern technologies allow experimentally obtaining and measuring the optical properties of metal nanowires in various spectral ranges. The theoretical study of the mentioned nanostructures is of interest in connection with the possibility of explaining the position and magnitude of the optical absorption maximum. The ability to adjust the energy and optical characteristics of 1D structures is a promising task from the point of view of using the latter in the form of high-speed switches in the creation of information transmission and processing systems, optical photosensors [2,3], etc.

Recently, studies of composite materials based on two-layer nanostructures have attracted considerable attention. The formation of an oxide layer on the metal wire surface makes it possible to regulate more effectively the position of the surface plasmon resonance (SPR) by changing both the oxide layer thickness and the metal core radius [4]. In turn, the application of a metal layer on the dielectric core leads to the appearance of two frequency maxima of optical absorption due to the surface plasmons hybridization [5]. An intuitively simple model (which is easily extended to multilayer structures) allows to explain the emergence of two resonance maxima due to the plasmon resonance splitting into low-energy symmetric and high-energy antisymmetric modes caused by the interaction of the dielectric core (hollow) with the metal shell inner wall on the one hand and, due to the connection of the metal layer outer wall with the surrounding dielectric medium on the other side. It is obvious that the plasmons interaction with each other directly depends on the metal shell thickness.

In contrast to the above-mentioned types of two-layer structures, bimetallic systems are characterized by a wide spectral range of the SPR shift due to the difference in the scattering and absorption of light by different metal fractions. Au and Ag are usually used as metals for bimetallic wires due to the ease of obtaining and controlling the parameters of such structures. Experimental growth of Ag@Au nanowires with adjustable optical properties is presented in works [6,7]. A theoretical study of the light wave absorption cross-section of the Ag@Au and Au@Ag 1D-systems using the quasi-static theory is given in [8]. Along with Au and Ag, noble metals Pd and Pt are widely used as photocatalysts. In [9], the oxidase-like properties of Pd@Pt nanowires were experimentally studied. The chemical synthesis of Pt@Ag nanowires and their subsequent use as electrocatalysts are discussed in [10].

In connection with the broad prospects of using bimetallic 1D systems as light-stable color filters, polarizers, optical sensors [11], for biological labeling and surface Raman scattering [12], the study of their optical parameters is a relevant task. The purpose of this work is to calculate the composite absorption coefficient based on bimetallic nanowires and analytical estimates the plasmon resonance maxima shifts depending on the composition and sizes of the core and shell metal fractions.

I. Basic relations

Let's consider a composite that consists of a dielectric matrix with permeability ε_m and cylindrical bimetallic inclusions with a total radius of $R = R_c + R_{sh}$ (the length of the wire L is assumed to be much greater than R), where R_c is the radius of the metal core covered with a layer of another metal with a value of R_{sh}. The absorption coefficient of the composite is determined by the ratio [13]:

$$\eta(\omega) = \frac{\omega}{3c}\beta\varepsilon_m^{3/2}\sum_j \frac{1}{P_j^2}\frac{Im\,\varepsilon_{c-sh}}{\left(Re\,\varepsilon_{c-sh}+\frac{1-P_j}{P_j}\varepsilon_m\right)^2+Im\,\varepsilon_{c-sh}^2}, \qquad (1)$$

where ω is the frequency of the incident electromagnetic wave; c is the speed of light; β is the volume content of cylindrical layered systems; P_j is the depolarization factor; $j = x, y, z$; $Re\,\varepsilon_{c-sh}$ and $Im\,\varepsilon_{c-sh}$ are the real and imaginary parts of core-shell system dielectric function.

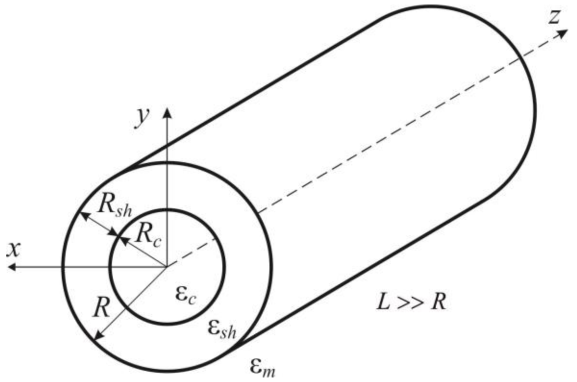

Fig.1. – Geometry of the problem.

Let us assume that an electromagnetic wave is incident on a cylindrical two-layer nanowire perpendicular to wire axis (the movement of electrons along the axis of the wire is neglected), as a result of which the wave vector lies in the plane xy and $P_z = 0,\ P_x = P_y = (1 - P_z)/2$. Then

$$\eta_{1D}(\omega) = \frac{8\omega}{3c}\beta\varepsilon_m^{3/2}\frac{Im\,\varepsilon_{1D(c-sh)}}{(Re\,\varepsilon_{1D(c-sh)}+\varepsilon_m)^2+Im\,\varepsilon_{1D(c-sh)}^2} \qquad (2)$$

The expression for the dipole polarizability of a cylindrical monosystem has the form:

$$\tilde{\alpha}_{1D(c-sh)} = \frac{\varepsilon_{1D(c-sh)}-\varepsilon_m}{\varepsilon_{1D(c-sh)}+\varepsilon_m}. \qquad (3)$$

On the other hand, the polarizability of such a system is found by solving the Laplace equation in a cylindrical coordinate system

$$\frac{\partial^2\varphi_i}{\partial r^2} + \frac{1}{r}\frac{\partial\varphi_i}{\partial r} = 0 \quad (i = 1, 2, 3)$$

taking into account the boundary conditions at the boundary of media

$$\varphi_1|_{r=R_c} = \varphi_2|_{r=R_c};\ \ \varphi_2|_{r=R} = \varphi_3|_{r=R};$$

$$\varepsilon_c\frac{\partial\varphi_1}{\partial r}\bigg|_{r=R_c} = \varepsilon_{sh}\frac{\partial\varphi_2}{\partial r}\bigg|_{r=R_c}; \quad \varepsilon_{sh}\frac{\partial\varphi_2}{\partial r}\bigg|_{r=R} = \varepsilon_m\frac{\partial\varphi_3}{\partial r}\bigg|_{r=R},$$

where ε_c and ε_{sh} are the dielectric functions of the metal core and shell, respectively:

$$\varepsilon_c(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_c^\infty - \frac{\omega_{pl(c)}^2\tau_{eff(c)}^2}{1+\omega^2\tau_{eff(c)}^2} + i\,\frac{\omega_{pl(c)}^2\tau_{eff(c)}}{\omega(1+\omega^2\tau_{eff(c)}^2)},$$

$$\varepsilon_{sh}(\omega) = \varepsilon_3(\omega) + i\varepsilon_4(\omega) = \varepsilon_{sh}^\infty - \frac{\omega_{pl(sh)}^2\tau_{eff(sh)}^2}{1+\omega^2\tau_{eff(sh)}^2} + i\,\frac{\omega_{pl(sh)}^2\tau_{eff(sh)}}{\omega(1+\omega^2\tau_{eff(sh)}^2)},$$

$\varepsilon_{c,sh}^\infty$ – the component responsible for the contribution of the ionic backbone of the core and shell metals, $i = \sqrt{-1}$, $\omega_{pl(c,\ sh)}^2 = \frac{\bar{n}_{c,sh}e^2}{\varepsilon_0 m_{c,sh}^*}$ – bulk plasma frequency, ε_0 – electric constant, $\bar{n}_{c,sh} = \left(4\pi r_{s(c,sh)}^3/3\right)^{-1}$ – concentration of conduction electrons, $r_{s(c,sh)}$ – average distance between conduction electrons, $m_{c,sh}^*$ – effective electron mass, $\tau_{eff(c,sh)}^{-1} = \tau_{bulk(c,sh)}^{-1} + \gamma_{1D(c,sh)}(\omega)$ – effective relaxation time, $\tau_{bulk(c,sh)}$ – relaxation time in the bulk metal, $\gamma_{1D(c,sh)}$ is the decrement of the attenuation of the dipole plasma oscillations of the cylindrical metal core and shell, respectively.

For a metal particle in the elongated ellipsoid form of rotation (that is, at $0 \le e_p \le 1$, where e_p is the eccentricity of the spheroid), the parameter γ based on the kinetic approach is calculated as [14]

$$\gamma_{c,sh}(\omega) = \frac{v_{F(c,sh)}}{4R_{c,sh}}\left(\frac{\omega_{pl(c,sh)}}{\omega}\right)^2 \frac{3}{16e_p^3}\left(e_p\left(1+2e_p^2\right)\left(1-e_p^2\right)^{1/2} - \left(1-4e_p^2\right)\arcsin e_p\right), \tag{4}$$

where $v_{F(c,sh)}$ is the Fermi velocity. At the boundary condition, when $e_p \to 1$, the expression for the attenuation decrement of dipole plasma oscillations of a metal nanowire takes the form:

$$\gamma_{1D(c,sh)}(\omega) = \frac{9\pi v_{F(c,sh)}}{128R_{c,sh}}\left(\frac{\omega_{pl(c,sh)}}{\omega}\right)^2. \tag{5}$$

Substituting the solutions of the Laplace equation into the boundary conditions for polarizability, we get

$$\tilde{\alpha}_{1D(c-sh)} = \frac{(\varepsilon_c+\varepsilon_{sh})(\varepsilon_{sh}-\varepsilon_m)+\beta_c^2(\varepsilon_c-\varepsilon_{sh})(\varepsilon_{sh}+\varepsilon_m)}{(\varepsilon_c+\varepsilon_{sh})(\varepsilon_{sh}+\varepsilon_m)+\beta_c^2(\varepsilon_c-\varepsilon_{sh})(\varepsilon_{sh}-\varepsilon_m)}, \tag{6}$$

where $\beta_c = R_c/R = 1 - R_{sh}/R$ is the volume content of the core material. When $\varepsilon_c = \varepsilon_{sh}$ expression (6) turns into a relation for the dipole polarizability of a continuous nanowire.

Equating (3) and (6), we have

$$\varepsilon_{1D(c-sh)} = \varepsilon_{sh}\frac{(\varepsilon_c+\varepsilon_{sh})+\beta_c^2(\varepsilon_c-\varepsilon_{sh})}{(\varepsilon_c+\varepsilon_{sh})-\beta_c^2(\varepsilon_c-\varepsilon_{sh})}. \tag{7}$$

By substituting the Drude function and separating the real and imaginary parts, we finally get

$$Re\ \varepsilon_{1D(c-sh)} = \frac{\chi_{(-)}\chi_{(+)}\varepsilon_3\left(\varepsilon_1^2+\varepsilon_2^2+\varepsilon_3^2+\varepsilon_4^2\right)+\chi_{(-)}^2\left(2\varepsilon_2\varepsilon_3\varepsilon_4+\varepsilon_1\left(\varepsilon_3^2-\varepsilon_4^2\right)\right)+\chi_{(+)}^2\varepsilon_1\left(\varepsilon_3^2+\varepsilon_4^2\right)}{\left(\varepsilon_1\chi_{(-)}+\varepsilon_3\chi_{(+)}\right)^2+\left(\varepsilon_2\chi_{(-)}+\varepsilon_4\chi_{(+)}\right)^2} \tag{8}$$

$$Im\ \varepsilon_{1D(c-sh)} = \frac{\chi_{(-)}\chi_{(+)}\varepsilon_4\left(\varepsilon_1^2+\varepsilon_2^2+\varepsilon_3^2+\varepsilon_4^2\right)+\chi_{(-)}^2\left(2\varepsilon_1\varepsilon_3\varepsilon_4-\varepsilon_2\left(\varepsilon_3^2-\varepsilon_4^2\right)\right)+\chi_{(+)}^2\varepsilon_2\left(\varepsilon_3^2+\varepsilon_4^2\right)}{\left(\varepsilon_1\chi_{(-)}+\varepsilon_3\chi_{(+)}\right)^2+\left(\varepsilon_2\chi_{(-)}+\varepsilon_4\chi_{(+)}\right)^2}, \tag{9}$$

where $\chi_{(\mp)} = 1 \mp \beta_c^2$.

At the boundary condition, when the layer thickness $R_{sh} \to 0$, we have $Re\ \varepsilon_{1D(c-sh)} = \varepsilon_1$ and $Im\ \varepsilon_{1D(c-sh)} = \varepsilon_2$; as $R_{sh} \to R$ and $\beta_c = 0$ we obtain $Re\ \varepsilon_{1D(c-sh)} = \varepsilon_3$ and $Im\ \varepsilon_{1D(c-sh)} = \varepsilon_4$.

II. Calculation results

The calculations of the absorption coefficient $\eta_{1D}(\omega)$ were carried out for bimetallic nanowires with the Ag@Au and Au@Ag structure, located in Teflon (ε_m = 2,3). The parameters of the metals are given in Table 1.

Let's trace the dimensional dependence of the composite absorption coefficient based on 1D-systems. Figure 2 shows the frequency dependences of $\eta_{1D}(\omega)$ which are calculated using relation (2) taking into account the formulas of the dielectric function real and imaginary parts (8)–(9) for a bimetallic Ag nanowire covered with a layer of Au (Ag@Au). For clarity, we introduce the following notations: $\hbar\omega_{sp(-)}$, $\hbar\omega_{sp(+)}$ – surface plasma frequencies of the first (low-frequency) and second (high-frequency) resonances. Figure 2 demonstrates the presence of one resonance maximum $\hbar\omega_{sp(+)} \approx 3{,}6$ eV (curve *1*), which corresponds to the Ag monowire R_{sh} = 0 nm. The presence of a Au metal layer at a constant value of the Ag core radius R_c causes the appearance of the second resonance peak $\hbar\omega_{sp(-)} \approx 2{,}8$ eV. An increase R_{sh} (curves *2*→*4*) leads to a slight shift of both maxima towards low frequencies. At the same time $\hbar\omega_{sp(-)}$ shifts slightly faster in contrast to $\hbar\omega_{sp(+)}$, as a result of which there is a "repulsion" of the absorption coefficient maxima. It is obvious when R_{sh} is fixed and R_c increases (curves *1'*→*4'*), a smooth shift of resonance peaks towards high frequencies should be expected.

The absorption coefficient of the composite based on Au@Ag 1D-systems is shown in Figure 3. The results of the calculations also demonstrate the presence of two resonance maxima in the considered frequency range. However, an increase in the R_{sh} value of the Ag shell (curves *2*→*4*), in contrast to the Ag@Au structure, leads to linear shift $\hbar\omega_{sp(+)}$ to the region of lower frequencies, while $\hbar\omega_{sp(-)}$ moves towards high frequencies. Thus, the frequency absorption peaks are "attracted" to each other. A significant increase in the thickness of the shell neutralizes the influence of the core and leads to a gradual merging of the maxima into one, which will correspond to the plasmon resonance frequency of the Ag monowire.

An increase in R_c of the Au core (curves *1'*→*4'*) leads to red shift of $\hbar\omega_{sp(-)}$. At the same time, $\hbar\omega_{sp(+)}$ undergoes a blue shift. The "repulsion" of resonance maxima from each other is observed.

Comparing Figures 2(*a*) and 3(*a*), we can conclude that the low-frequency peak $\hbar\omega_{sp(-)}$, which shifts from 2,76

Table 1.
Parameters of metals (a_0 – Bohr radius; m^* – the electron effective mass is given for a 3D metal; m_e – electron mass; $\hbar = h/2\pi$ – Planck's reduced constant)

Parameters	r_s, a_0 [15]	m^*/m_e [16]	ε^∞ [17]	τ_{bulk}, 10^{-15}s [15]	$\hbar\omega_{pl}$, eV
Au	3,01	0,99	9,84	29	9,07
Ag	3,02	0,96	3,70	40	9,17

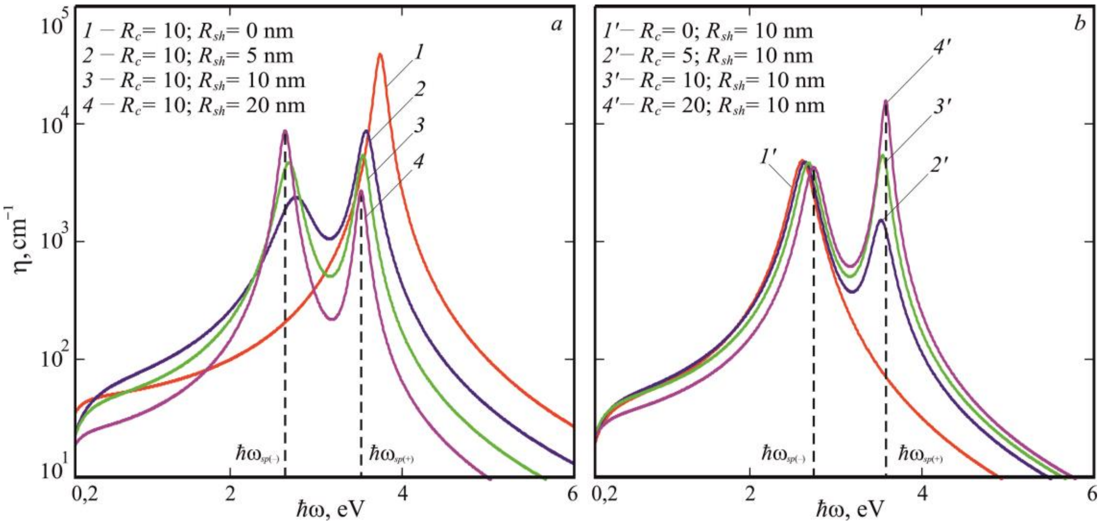

Fig. 2. – Frequency dependence of the absorption coefficient of the composite based on Ag@Au bimetallic nanowires: *a* – R_c = 10 nm; R_{sh} = 0; 5; 10; 20 nm; *b* – R_c = 0; 5; 10; 20 nm; R_{sh} = 10 nm.

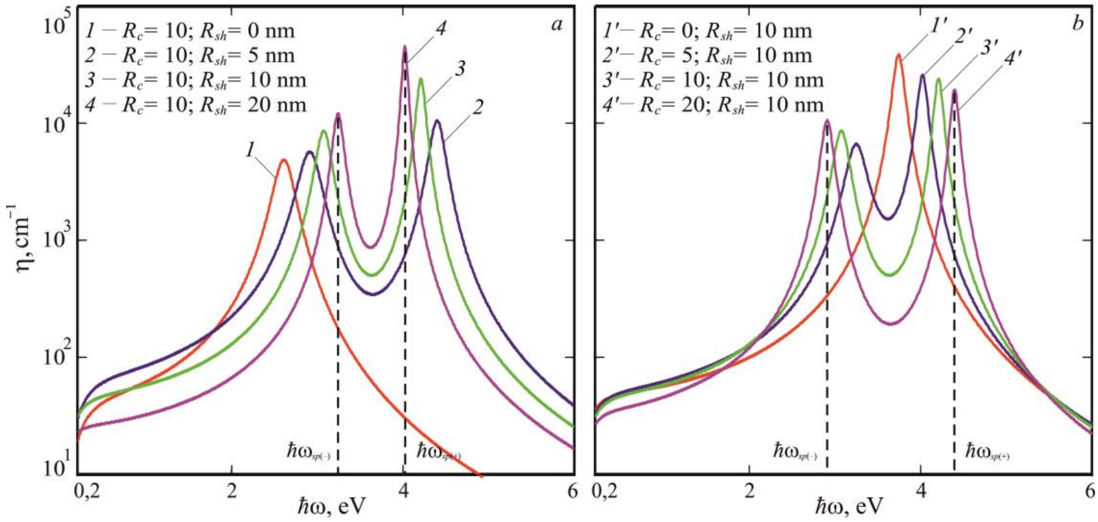

Fig. 3. – Frequency dependence of the absorption coefficient of the composite based on bimetallic Au@Ag nanowires: *a* – R_c = 10 nm; R_{sh} = 0; 5; 10; 20 nm; *b* – R_c = 0; 5; 10; 20 nm; R_{sh} = 10 nm.

to 2,62 eV in the Ag@Au nanowire, has the same origin as the high-frequency maximum $\hbar\omega_{sp(+)}$ in the Au@Ag structure, which shifts from 4,3 to 4 eV. Both maxima are a consequence of the plasmon interaction of the outer shell wall and the dielectric matrix ε_m. In turn, $\hbar\omega_{sp(+)}$ in the Ag@Au nanowire and $\hbar\omega_{sp(-)}$ in Au@Ag also have the same origin, which is the result of the surface charges induction of the inner shell wall and the core.

It is known that resonant oscillations of free electrons, which are weakly connected to the cation lattice, determine the frequency of SPR. As shown in [8], the stronger the bond between electrons is, the greater the energy of the SPR is and the higher the frequency is. On the contrary, weak electron coupling reduces the SPR value and shifts the resonance towards low frequencies. Thus, in the Ag@Au structure, Ag electrons move to the Au shell as a result of the "attraction" of positive charges. This leads to a decrease in electron coupling and a red shift of the maximum ($\hbar\omega_{sp(+)}$ in Figure2 (*a*)). Instead, the blue shift of the maximum of the Au@Ag nanowire ($\hbar\omega_{sp(-)}$ in Figure 3(*a*)) occurs due to the repulsion of the Au core electrons from the negative charges of the Ag shell.

Thus, a characteristic feature of a two-layer bimetallic nanowire is a frequency shift of resonance maxima due to variations in the ratio of the values of the core radius and the shell thickness. However, in order to be able to estimate the SPR position and their frequency shifts, it is possible to go another way. For this, it is sufficient to consider formula (6). It is known that the polarizability of the 1D-system will be zero if the following condition is fulfilled for the numerator in (6):

$$\frac{\varepsilon_m - \varepsilon_{sh}}{\varepsilon_m + \varepsilon_{sh}} = \beta_c^2 \frac{\varepsilon_c - \varepsilon_{sh}}{\varepsilon_c + \varepsilon_{sh}}$$

The fact that polarizability is equal to zero means the invisibility of the wire metal core together with the shell. In the case of equating the denominator (6) to zero, we obtain the condition for the occurrence of plasmon resonance. Due to the large number of parameters, we will perform analytical calculations taking into account some approximations. Let us assume that $\omega\tau >> 1$ and the dielectric constant is also a real value (at the same time, $\varepsilon_m = 1$)

$$\varepsilon_{c,sh}(\omega) \approx 1 - \frac{\omega_{pl(c,sh)}^2}{\omega^2}$$

Substituting the last expression into the denominator (6), we have

$$4\omega_{sp}^4 - \omega_{sp}^2\left(4\omega_{pl(sh)}^2 + 2\omega_{pl(c)}^2\right) + \omega_{pl(sh)}^2\left(\omega_{pl(c)}^2(1+\beta_c^2) + \omega_{pl(sh)}^2(1-\beta_c^2)\right) = 0,$$

where the substitution $\omega = \omega_{sp}$ is introduced.

Then the resonance in (6) occurs at the following frequencies:

$$\omega_{sp(\mp)}^2 = \frac{1}{4}\left(2\omega_{pl(sh)}^2 + \omega_{pl(c)}^2 \mp \left(4\omega_{pl(sh)}^2\beta_c^2\left(\omega_{pl(sh)}^2 - \omega_{pl(c)}^2\right) + \omega_{pl(c)}^4\right)^{\frac{1}{2}}\right) \qquad (10)$$

It follows from (10) the presence of two surface plasmon resonances in the bimetallic 1D-system. Considering boundary conditions $\beta_c = 0$ (absent core) and $\beta_c = 1$ (absent shell), we obtain the following results:

$$\omega_{sp(-)}\Big|_{\beta_c=0} = \frac{\omega_{pl(sh)}}{\sqrt{2}} \text{ and } \omega_{sp(+)}\Big|_{\beta_c=0} = \sqrt{\frac{\omega_{pl(sh)}^2+\omega_{pl(c)}^2}{2}};$$

$$\omega_{sp(-)}\Big|_{\beta_c=1} = \frac{\omega_{pl(c)}}{\sqrt{2}} \text{ and } \omega_{sp(+)}\Big|_{\beta_c=1} = \omega_{pl(c)}.$$

The minus sign "–" leads to the equality of the frequency of the first resonance $\omega_{sp(-)}$ with the frequencies of the localized surface plasmon of the shell and core. As a result, the frequency range for the first resonance at $0 \le \beta_c \le 1$ varies within $\omega_{pl(c)}/\sqrt{2} \le \omega_{sp(-)} \le \omega_{pl(sp)}/\sqrt{2}$. As for the last two results, they testify to the equality of the frequency of the second resonance $\omega_{sp(+)}$ to the value $\sqrt{\left(\omega_{pl(sh)}^2 + \omega_{pl(c)}^2\right)/2}$ and bulk plasma frequency of the shell $\omega_{pl(sh)}$. It is obvious that the solutions $\omega_{sp(+)}$ at $\beta_c = 0$ and $\beta_c = 1$, indicating the absence of a surface plasmon, have no physical meaning, since they are a consequence of the boundary conditions which are used to obtain relation (6). Therefore, the frequency range of the second resonance lies in the region $\omega_{pl(sh)} < \omega_{sp(+)} < \sqrt{\left(\omega_{pl(sh)}^2 + \omega_{pl(c)}^2\right)/2}$.

Let's continue further evaluation judgments for the Ag@Au bimetallic structure. By substituting the value of $\omega_{pl(c,sh)}$ (see Table 1), we obtain for $\omega_{sp(-)}$ a shift towards low frequencies when $\beta_c \to 0$ (increasing R_{sh}), while $\omega_{sp(+)}$ moves towards high frequencies. There is a "repulsion" of maxima from each other. On the contrary, when $\beta_c \to 1$ (increasing R_c), there is an "attraction" of resonance peaks. However, for Au@Ag, when $\beta_c \to 0$, the maxima converge, and when $\beta_c \to 1$, they move away from each other. It is obvious that the fulfillment of the condition $\omega_{pl(c)} > \omega_{pl(sh)}$ at $\beta_c \to 0$ leads to the "removal" of the maxima; $\omega_{pl(c)} < \omega_{pl(sh)}$ is responsible for their "convergence". It can be argued that to determine the SPR shifts depending on the value of β_c, it is sufficient to calculate the bulk plasmon frequencies $\omega_{pl(c)}$ and $\omega_{pl(sh)}$, while neglecting other constants (τ_{bulk}, ε_m and ε^{∞}).

It is interesting to compare the results of the study of the thin bimetallic wires absorption coefficient with similar results for bimetallic spheres. The starting point can be considered the polarizability formula for a layered 0D-system [18]:

$$\tilde{\alpha}_{0D(c-sh)} = \frac{(\varepsilon_c+2\varepsilon_{sh})(\varepsilon_{sh}-\varepsilon_m)+\beta_c^3(\varepsilon_c-\varepsilon_{sh})(2\varepsilon_{sh}+\varepsilon_m)}{(\varepsilon_c+2\varepsilon_{sh})(\varepsilon_{sh}+2\varepsilon_m)+2\beta_c^3(\varepsilon_c-\varepsilon_{sh})(\varepsilon_{sh}-\varepsilon_m)}. \qquad (11)$$

Equating (11) to

$$\tilde{\alpha}_{0D(c-sh)} = \frac{\varepsilon_{0D(c-sh)}-\varepsilon_m}{\varepsilon_{0D(c-sh)}+2\varepsilon_m}$$

we get

$$\varepsilon_{0D(c-sh)} = \varepsilon_{sh}\frac{(\varepsilon_c+2\varepsilon_{sh})+2\beta_c^3(\varepsilon_c-\varepsilon_{sh})}{(\varepsilon_c+2\varepsilon_{sh})-\beta_c^3(\varepsilon_c-\varepsilon_{sh})}. \qquad (12)$$

For the case of a spherical coordinate system ($P_x = P_y = P_z = 1/3$), the absorption coefficient of the composite takes the following form

$$\eta_{0D}(\omega) = \frac{9\omega}{c}\beta\varepsilon_m^{3/2}\sum_j \frac{Im\ \varepsilon_{0D(c-sh)}}{\left(Re\ \varepsilon_{0D(c-sh)}+2\varepsilon_m\right)^2+Im\ \varepsilon_{0D(c-sh)}^2} \qquad (13)$$

and the real $Re\ \varepsilon_{0D(c-sh)}$ and $Im\ \varepsilon_{0D(c-sh)}$ imaginary parts of the bimetallic nanoparticle dielectric function

$$Re\ \varepsilon_{0D(c-sh)} = \frac{\xi\zeta\varepsilon_3(\varepsilon_1^2+\varepsilon_2^2)+2\xi^2\left(2\varepsilon_2\varepsilon_3\varepsilon_4+\varepsilon_1(\varepsilon_3^2-\varepsilon_4^2)\right)+\varsigma(\varepsilon_3^2+\varepsilon_4^2)(\varepsilon_1\zeta+2\varepsilon_3\xi)}{(\varepsilon_1\xi+\varepsilon_3\varsigma)^2+(\varepsilon_2\xi+\varepsilon_4\varsigma)^2}, \qquad (14)$$

$$Im\ \varepsilon_{0D(c-sh)} = \frac{\xi\zeta\varepsilon_4(\varepsilon_1^2+\varepsilon_2^2)+2\xi^2\left(2\varepsilon_1\varepsilon_3\varepsilon_4-\varepsilon_2(\varepsilon_3^2-\varepsilon_4^2)\right)+\varsigma(\varepsilon_3^2+\varepsilon_4^2)(\varepsilon_2\zeta+2\varepsilon_4\xi)}{(\varepsilon_1\xi+\varepsilon_3\varsigma)^2+(\varepsilon_2\xi+\varepsilon_4\varsigma)^2}, \qquad (15)$$

where the following notations are entered: $\xi = 1-\beta_c^3$, $\zeta = 1+2\beta_c^3$ i $\varsigma = 2+\beta_c^3$.

To calculate the attenuation decrement of spherical nanoparticle dipole plasma resonances, we use the expression given in [19]

$$\gamma_{0D(c,sh)}(\omega) = \frac{\nu_{c,sh}}{2}\left(\frac{\omega_{pl}}{\omega}\right)^2\left(1-\frac{\nu_{c,sh}}{\omega}sin\frac{\omega}{\nu_{c,sh}}+2\left(\frac{\nu_{c,sh}}{\omega}\right)^2\left(1-cos\frac{\omega}{\nu_{c,sh}}\right)\right), \qquad (16)$$

where $\nu_{c,sh} = \upsilon_{F(c,sh)}/2R_{c,sh}$ is the frequency of electron oscillations from one potential wall to the opposite one. Note that for the case of a nanoparticle in vacuum at frequencies $\omega = \omega_{pl}/\sqrt{3}$ and $\nu_{c,sh} \ll \omega$ we obtain a well-known result $\gamma_{0D(c,sh)}(\omega) = 3\upsilon_{F(c,sh)}/4R_{c,sh}$.

The differences in the indicators of the bimetallic cylinder and the sphere (Fig. 4) are related to the dimensionality of the systems, which is expressed in a significant difference in the forms of the dielectric function real and imaginary parts. Small low-frequency "stochastic" oscillations $\eta_{0D}(\omega)$ are a consequence of the presence of a parenthesis in expression (16). As for the position of the resonance peaks, it is comprehensively explained by the conditions of the SPR, which follow from the denominators of ratios (2) and (13):

$$Re\ \varepsilon_{1D(c-sh)} = -\varepsilon_m; \quad Re\ \varepsilon_{0D(c-sh)} = -2\varepsilon_m.$$

It should be noted that the maximum $\hbar\omega_{sp(-)}$ in Figs.4(*a*) and 3(*a*) (at $R_{sh} \to \infty$) is the result of the interaction between the shell inner wall and the core, while $\hbar\omega_{sp(+)}$ arises as a result of the induction of surface charges at the separation boundary metal shell and external dielectric medium. However, when $R_c \to \infty$ (Figs.4(*b*) and 3(*b*)), similar regularities are not observed. Indeed, the interaction between the shell and the core is determined by the maxima of $\hbar\omega_{sp(-)}$ for the wire and $\hbar\omega_{sp(+)}$ for the particle. In turn, $\hbar\omega_{sp(+)}$ in the case of a cylinder and $\hbar\omega_{sp(-)}$ in the case of a sphere is responsible for the connection of the shell outer wall and ε_m. It is clear that the given regularities of bimetallic systems are "conditional". Real estimates of the position of the SPR maximum can be made only for monosystems. In the case of two-layer structures, the assessment of the predominance and influence of the shell and core metal fractions is a difficult task due to the consideration of a large number of constants included in the Drude formula and their subsequent "mixing" due to the substitution of the latest equation in the expression for the polarizability of bimetallic systems.

Figure 4 demonstrates the "merging" of $\eta_{0D}(\omega)$ maxima with increasing R_{sh}, while increasing R_c leads to their "repulsion". It is quite obvious that the given nature of shifts of the 0D-systems SPR is similar to that presented

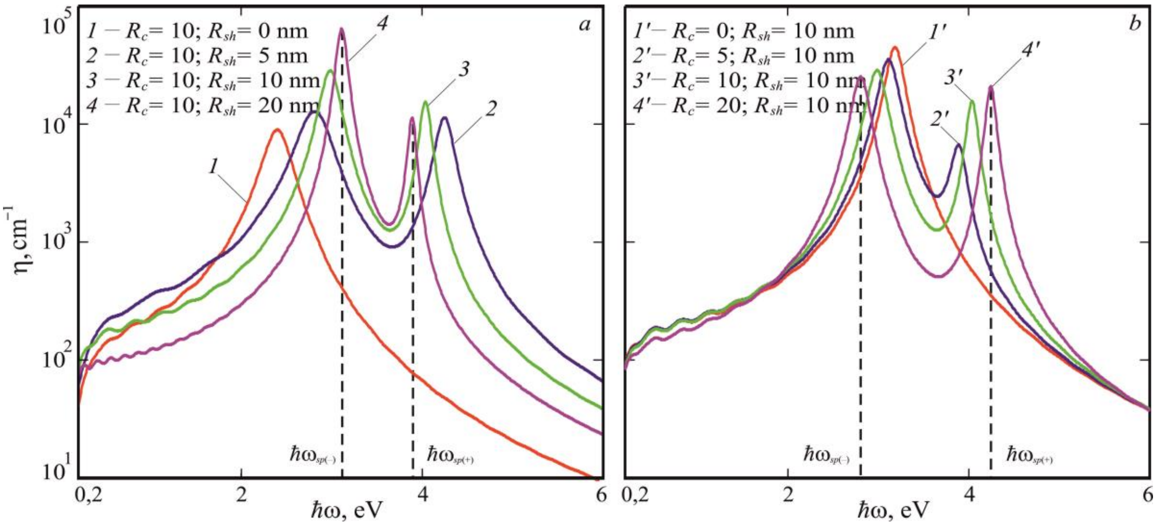

Fig. 4. – Frequency dependence of the absorption coefficient of the composite based on bimetallic Au@Ag nanoparticles: *a* – R_c = 10 nm; R_{sh} = 0; 5; 10; 20 nm; *b* – R_c = 0; 5; 10; 20 nm; R_{sh} = 10 nm.

in Figure 3 for the case of 1D-systems. Again, using the previous judgments and equating the denominator (11) to zero, we obtain the equation for the plasmon frequencies for a bimetallic nanoparticle

$$\omega_{sp(\mp)}^2 = \frac{1}{6}\left(3\omega_{pl(sh)}^2 + \omega_{pl(c)}^2 \mp \left(8\omega_{pl(sh)}^2\beta_c^3\left(\omega_{pl(sh)}^2 - \omega_{pl(c)}^2\right) + \left(\omega_{pl(sh)}^2 + \omega_{pl(c)}^2\right)^2\right)^{\frac{1}{2}}\right), \qquad (17)$$

whence the conditions of plasmon resonances corresponding to the limiting cases are the following:

$$\omega_{sp(-)}\Big|_{\beta_c=0} = \frac{\omega_{pl(sh)}}{\sqrt{3}}$$

and $\omega_{sp(+)}\Big|_{\beta_c=0} = \sqrt{\frac{2\omega_{pl(sh)}^2+\omega_{pl(c)}^2}{3}}$;

$\omega_{sp(-)}\Big|_{\beta_c=1} = \frac{\omega_{pl(c)}}{\sqrt{3}}$ and $\omega_{sp(+)}\Big|_{\beta_c=1} = \omega_{pl(sh)}$.

Substitution of the values of the shell and core metals bulk plasma frequencies for the case of a bimetallic nanoparticle leads to similar conclusions about the SPR shifts that were obtained for the case of a nanowire. It is obvious that similar regularities in the position of resonance maxima should be expected for multilayer systems when calculating the optical characteristics of the composite.

Conclusions

Based on the Drude-Lorentz theory, the ratio of frequency dependences for polarizability, dielectric function real and imaginary parts of bimetallic 1D-systems was obtained. Taking into account the obtained expressions, the electromagnetic radiation absorption coefficient of the composite based on inclusions in the form of bimetallic nanowires was calculated. The presence of two frequency maxima of the absorption coefficient is shown, which is the result of the interaction of the shell inner wall surface charges and the core on the one hand, and the shell outer wall with the dielectric matrix on the other. The ability to control the composite optical characteristics by changing the core radius and the shell thickness is demonstrated.

The influence of the elemental composition on the optical characteristics of 1D-systems was investigated. When the shell thickness increases, for the Ag@Au structure optical absorption maxima are "repelled", while for Au@Ag the maxima are "converged". The resulting equation for the frequency shift of the surface plasmon resonances of bimetallic nanowires indicates the presence of two limiting cases that determine the position of the optical absorption peaks. Fulfillment of the condition $\omega_{pl(c)} > \omega_{pl(sh)}$ leads to "repulsion" of the maxima with an increase of the metal layer thickness. At the same time, when $\omega_{pl(c)} < \omega_{pl(sh)}$, there is a "convergence" of resonance maxima. As a result, the character of the shift of surface plasmon resonances is evaluated by comparing the values of the core and shell bulk plasma frequencies.

Analogous judgments can be extended to systems of other dimensions. In particular, for 0D-systems, the characters of the calculated dependences are similar to those obtained for the case of bimetallic nanowires.

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[1] N.L. Dmitruk, S.Z. Malinich, *Surface Plasmon Resonances and Their Manifestation in the Optical Properties of Nanostructures of Noble Metals*, Ukrainian Journal of Physics, 9(1), 3 (2014); https://ujp.bitp.kiev.ua/index.php/ujp/article/view/2019664.

[2] N. Lawrence, L. Dal Negro, *Light scattering, field localization and local density of states in co-axial plasmonic nanowires*, Opt. Exp., 18(15), 16120 (2010); https://doi.org/10.1364/OE.18.016120.

[3] K. Mitamura, T. Imae, *Functionalization of Gold Nanorods Toward Their Applications*, Plasmonic, 4(1), 23(2009); https://doi.org/10.1007/s11468-008-9073-z.

[4] J. Zhu, S. Zhao, J.-W. Zhao, J.-J. Li, *Dielectric wall controlled resonance light scattering of coated long gold nanowire*, Curr. Nanosci., 7(3), 377 (2011); https://doi.org/10.2174/157341311795542480.

[5] E. Prodan, C. Radloff, N.J. Halas, P. Nordlander, *A Hybridization Model for the Plasmon Response of Complex Nanostructures*, Science, 302(5644), 419 (2003); https://doi.org/10.1126/science.1089171.

[6] H. Fu, X. Yang, X. Jiang, A. Yu, *Bimetallic Ag–Au Nanowires: Synthesis, Growth Mechanism, and Catalytic Properties*, Langmuir, 29(23), 7134 (2013); https://doi.org/10.1021/la400753q.

[7] S. E. Hunyadia, C. J. Murphy, *Bimetallic silver–gold nanowires: fabrication and use in surface-enhanced Raman scattering*, J. Mater. Chem., 16 (40), 3929 (2006); https://doi.org/10.1039/B607116C.

[8] J. Zhu, *Surface Plasmon Resonance from Bimetallic Interface in Au–Ag Core–Shell Structure Nanowires*, Nanoscale Res. Lett., 4 (9), 977 (2009); https://doi.org/10.1007/s11671-009-9344-4.

[9] L. Jin, Y. Sun, L. Shi, C. Lia, Y. Shena, *PdPt Bimetallic Nanowires with Efficient Oxidase Mimic Activity for the Colorimetric Detection of Acid Phosphatase in Acidic Media*, J. Mater. Chem., B 7 (29), 4561 (2019); https://doi.org/10.1039/C9TB00730J.

[10] X. Cao, N. Wang, Y. Han, C. Gao, Y. Xu, M. Li, Y. Shao, *PtAg bimetallic nanowires: Facile synthesis and their use as excellent electrocatalysts toward low-cost fuel cells*, Nano Energy, 12, 105 (2015); https://doi.org/10.1016/j.nanoen.2014.12.020.

[11] Q. Fu, D.G. Zhang, M.F. Yi, X.X. Wang, Y.K. Chen, P. Wang, H. Ming, *Effect of shell thickness on a Au–Ag core–shell nanorods-based plasmonic nano-sensor*, Journal of Optics, 14 (8), 085001 (2012); https://doi.org/10.1088/2040-8978/14/8/085001.

[12] W. Eberhardt, *Clusters as new materials*, Surface Science, 500 (1-3), 242 (2002); https://doi.org/10.1016/S0039-6028(01)01564-3.

[13] K.Chatterjee, S.Basu, D.Chakravorty, *Plasmon resonance absorption in sulfide-coated gold nanorods*, Journal of Materials Research, 21 (1), 34 (2006); https://doi.org/10.1557/jmr.2006.0032.

[14] P.M. Tomchuk, D.V. Butenko, *Dependences of Dipole Plasmon Resonance Damping Constants on the Shape of Metallic Nanoparticles*, Ukrainian Journal of Physics, 60 (10), 1042 (2015); https://doi.org/10.15407/ujpe60.10.1042.

[15] Neil W. Ashcroft, N. David Mermin. Solid state physics (Saunders College Publishing, 1976).

[16] P. B. Johnson, R. W. Christy, *Optical Constants of the Noble Metals*, Physical Review B, 6 (12), 4370 (1972); https://doi.org/10.1103/PhysRevB.6.4370.

[17] I.I. Shaganov, T.S.Perova, K. Berwick, *The effect of the local field and dipole-dipole interactions on the absorption spectra of noble metals and the plasmon resonance of their nanoparticles*, Photonics and Nanostructures - Fundamentals and Applications, 27, 24 (2017); https://doi.org/10.1016/j.photonics.2017.09.003.

[18] A.V. Korotun, A.A. Koval’, I.N. Titov, *Optical Absorption of a Composite Based on Bilayer Metal–Dielectric Spherical Nanoparticles*, J. Appl. Spectrosc., 87 (2), 240 (2020); https://doi.org/10.1007/s10812-020-00991-7.

[19] N.I. Grigorchuk, P.M. Tomchuk, *Optical and transport properties of spheroidal metal nanoparticles with account for the surface effec*t, Phys. Rev. B, 84 (8), 085448 (2011); https://doi.org/10.1103/PhysRevB.84.085448.

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Частотні зсуви поверхневих плазмонних резонансів при обчисленні коефіцієнту поглинання композиту на основі біметалічних 1d-систем

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В роботі проаналізовано поглинання електромагнітного випромінювання композитом на основі біметалічних нанодротів. З використанням теорії Друде-Лоренца одержано співвідношення для частотних залежностей поляризовності, дійсної та уявної частин діелектричної функції шаруватих 1D-систем. Показано, що структура у вигляді металевого ядра, покритого шаром іншого металу, призводить до розщеплення та появи двох максимумів у частотній залежності коефіцієнту поглинання. Положення максимумів визначаються складом біметалічних нанодротів і об’ємним вмістом металів. Вплив розмірності систем оцінюється шляхом порівняння частотних залежностей коефіцієнту поглинання композиту на основі біметалічних нанодротів та наночастинок. Розрахунки проведені для нанодротів Ag@Au та Au@Ag, занурених у тефлон.

Ключові слова: біметалічний нанодріт, поверхневий плазмонний резонанс, поляризовність, діелектрична функція, коефіцієнт поглинання.