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OPTICAL SPECTRA OF METAL-DIELECTRIC NANOCOMPOSITES WITH A LAYERED SUBWAVE STRUCTURE

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The results of theoretical and experimental investigations of the optical spectra of layer-periodic nanocomposites consisting of alternating tightly packed monolayers of silver nanoparticles and separating KCl layers of subwave thickness are presented. The characteristic features of the spectral dependence of the transmission and reflection coefficients of this type of nanocomposites have been analyzed for the case where the photon forbidden bands are located near the plasmon-absorption band. Experimental samples were prepared by successive thermal evaporation of silver and KCl in vacuum. Theoretical calculations were carried out using the quasi-crystalline approximation of the theory of multiple scattering of waves. It is shown that the spectral position, shape, and intensity of absorption and reflection bands can be regulated by changing the optical thickness of the intermediate dielectric films in a layered metal-dielectric composite.

Keywords: *metal-dielectric nanocomposites, resonances of plasmon absorption, photon forbidden bands, optical spectra.*

Introduction. Composites based on metal nanocrystallites inserted into a transparent matrix are promising materials for developing the elemental base of laser physics and opto- and microelectronics. The unique linear and nonlinear optical properties of such nanostructures is based on the fact that, in the visible and UV regions of the spectrum, resonance bands of plasmon-polariton absorption are present whose characteristics depend on the material of the particles and matrix, on the size and shape of nanocrystallites and their volume concentration, and also on the morphology of the composite material [1].

In [2, 3] it is shown theoretically that ordering in space of an ensemble of metallic nanoparticles may serve as an additional means of monitoring the spectral dependence of their coefficients of transmission and reflection, e.g., formation of a stack of tightly packed monolayers of metallic nanoparticles separated by continuous intermediate films whose thickness is comparable with the light wavelength. Such layer-periodic structures can be considered as 1D-photon crystals in which the forbidden photon band is being formed under the conditions of simultaneous electron and photon limitation.

In the present work, the optical spectra of such metal-containing structures with subwave periodicity in one of the dimensions were investigated theoretically and experimentally using as an example layered nanocomposites containing silver nanoparticles.

Theory. The localization of states and formation of forbidden photon bands in the transmission spectra of spatially-ordered systems of mesoscopic particles (photon crystals) is possible due to the coherence and interference of multiply scattered waves. The method of calculation of the optical characteristics of such systems must allow for the electrodynamic interaction of individual scatterers. From this viewpoint the approach in the context of the statistical theory of multiple scattering of waves (STMSW) seems promising [4].

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The STMSW-related approach presupposes that during interaction of incident electromagnetic radiation with an ensemble of particles the resulting field at a certain point of the space represents the sum of the fields of all kinds of multiply scattered waves with allowance for their phase relationships. In this case, each particle is located not in the field of an incident wave $\mathbf{E}_0$, but rather in a certain effective field formed as a result of summation of all the waves multiply scattered in the region of location of the isolated particle. Then the field at any point both outside the disperse medium and inside it can be written in the form

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \sum_j \int d\mathbf{r}' \overleftrightarrow{\Gamma}(\mathbf{r}, \mathbf{r}' + \mathbf{R}_j)\, \mathbf{E}(\mathbf{r}' + \mathbf{R}_j)\,. \tag{1}$$

Integration is carried out over the volume of the jth particle, whereas the summation is made over all the particles of the system, the location of the centers of which is defined by the vectors $\mathbf{R}_j$ lying in the plane XOY; $\overleftrightarrow{\Gamma}(\mathbf{r}, \mathbf{r}')$ is the Green tensor function.

Averaging (1) over different configurations of the medium, we obtain the chain of equations

$$\begin{gathered}\langle \mathbf{E}(\mathbf{r})\rangle = \mathbf{E}_0(\mathbf{r}) + n_0 \int d\mathbf{R} \int d\mathbf{r}' \overleftrightarrow{\Gamma}(\mathbf{r}, \mathbf{r}' + \mathbf{R})\, \langle \mathbf{E}(\mathbf{r}' + \mathbf{R})\rangle_{\mathbf{R}}', \\ \langle \mathbf{E}(\mathbf{r} + \mathbf{R})\rangle_{\mathbf{R}} = \mathbf{E}_0(\mathbf{r} + \mathbf{R}) + \int d\mathbf{r}' \overleftrightarrow{\Gamma}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R})\, \langle \mathbf{E}(\mathbf{r}' + \mathbf{R})\rangle_{\mathbf{R}} + \\ + n_0 \int d\mathbf{R}' g(|\mathbf{R} - \mathbf{R}'|) \int d\mathbf{r}' \overleftrightarrow{\Gamma}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R})\, \langle \mathbf{E}(\mathbf{r}' + \mathbf{R}')\rangle_{\mathbf{R},\mathbf{R}'} \text{ etc}.\end{gathered} \tag{2}$$

Here, $\langle \mathbf{E}(\mathbf{r})\rangle$ is the coherent field; $\langle \mathbf{E}(\mathbf{r})\rangle_{\mathbf{R}}$ is the averaged field with one fixed particle at the point $\mathbf{R}$;$\langle \mathbf{E}(\mathbf{r})\rangle_{\mathbf{R},\mathbf{R}'}$ is the averaged field with two fixed particles; n_0 is the number of particles per unit area; and $g(\mathbf{R} - \mathbf{R}')$ is the radial distribution function which characterizes the probability of location of two particles at the points $\mathbf{R}$ and $\mathbf{R}'$ and depends only on the module $|\mathbf{R} - \mathbf{R}'|$ for statistically homogeneous media.

To obtain a closed system of equations from (2), a variety of approximations were suggested by various researchers (see, e.g., [4]). In the present work, to calculate the coefficients of coherent transmission and reflection of a multilayer metal-dielectric nanocomposite with subwave periodicity, we applied the method described in [5]. The method is based on the assumption of statistical independence of the structure of individual monolayers, which undoubtedly is implemented in the case considered by us. We shall give a brief description of this approach.

For a system of statistically independent monolayers the coherent transmitted and reflected field is defined by the following system of equations:

$$\begin{gathered}\langle \mathbf{E}^{+}(\mathbf{z})\rangle = \exp(ik|\mathbf{z}|)\left[\mathbf{e} + \sum_{j=1}^{N} \mathbf{G}_j^{+}\right], \\ \langle \mathbf{E}^{-}(\mathbf{z})\rangle = \exp(ik|\mathbf{z}|) \sum_{j=1}^{N} \mathbf{G}_j^{-} \exp[2ikl_m(j-1)]\,,\end{gathered} \tag{3}$$

where the superscript "+" refers to the transmitted wave and "–" to the reflected one, $\mathbf{z}$ is the unit vector in the direction of the z axis, and l_m is the distance between the centers of neighboring monolayers.

To determine the amplitudes of scattering of the jth monolayer that enter into the above equations in the presence of the remaining monolayers ($\mathbf{G}_j$) the procedure of a self-coordinated field is used. In this procedure $\mathbf{G}_j$ is determined in terms of the amplitudes of scattering of isolated monolayers $\mathbf{F}^{\pm} \equiv \mathbf{F}(\pm\mathbf{z})$ in the following way:

$$\mathbf{G}_j^+ = \mathbf{F}^+ + \mathbf{F}^+ \sum_{m=1}^{j-1} \mathbf{G}_m^+ + \mathbf{F}^- \sum_{m=j+1}^{N} \mathbf{G}_m^- \exp\left\{2ikl_m (m-j)\right\},$$

$$\mathbf{G}_j^- = \mathbf{F}^- + \mathbf{F}^- \sum_{m=1}^{j-1} \mathbf{G}_m^+ + \mathbf{F}^+ \sum_{m=j+1}^{N} \mathbf{G}_m^- \exp\left\{2ikl_m (m-j)\right\}. \tag{4}$$

In these expressions the sums take into account coherent irradiation of the jth monolayer from the side of other monolayers. Having solved the system of equations (4) for $\mathbf{G}_j^{\pm}$ and substituted them into (3), it is possible to represent a coherent field and, consequently, the coefficients of coherent transmission $T \equiv \left|\langle \mathbf{E}(\mathbf{z})\rangle\right|^2$ and reflection $R \equiv \left|\langle \mathbf{E}(-\mathbf{z})\rangle\right|^2$ in terms of the amplitude functions of isolated monolayers $\mathbf{F}^{\pm}$. To calculate $\mathbf{F}^{\pm}$, we use the quasi-crystalline approximation (QCA) suggested in [6] for tightly packed media. The radial distribution function entering into (2) is calculated in the approximation of solid incompressible spheres [7]. The dimensional dependence of the optical constants of nanoparticles was taken into account in the model of limitation of the free path of electrons. The calculations were performed for silver nanoparticles. The size of the particles, their surface concentration in the monolayers, and the number of monolayers, and also the refractive index and the thickness of intermediate continuous films were varied.

Experimental Procedure. Multilayer metal-dielectric nanocomposites were produced experimentally on a VU-1A vacuum installation by successive evaporation of the metal and dielectric material at temperatures of the substrate close to room temperature. The process of evaporation was conducted at a pressure of the residual gases of $2 \cdot 10^{-5}$ torr. The thickness was controlled by a quartz probe. Plates from glass and quartz were used as substrates. Tightly packed monolayers from metallic nanoparticles represented peninsular silver films. Electronic-microscopic pictures were taken on a Hitachi H 800 electronic translucent microscope.

In multilayer metal-dielectric structures with subwave periodicity the tightly packed silver nanoparticles were separated by subwave KCl interlayers. The optical thickness of the subwave interlayers was evaluated relative to the wavelength λ_0 that determines the maximum of plasmon resonance for a monolayer of silver nanoparticles having the corresponding surface concentration and placed between KCl plates, since for the silver monolayers facing the air the plasmon resonance band is shifted to the longwave region of the spectrum by 30–40 nm. The transmission and reflection spectra were recorded on a Cary 500 spectrophotometer.

Discussion of Results. Figure 1 presents an electronic-microscopic picture of one of the specimens with a silver monolayer. The average size of the silver granules was ~3–4 nm. The parameter of the monolayer overlapping, which is equal numerically to the ratio of the area occupied by metallic nanoparticles to the area of the substrate, was $\eta = 0.4$. The transmission spectra of the same monolayer located in the KCl film are presented in Fig. 2. As is seen, the spectra have an attenuation band with a maximum at $\lambda_0 = 440$ nm. The transmission at the band maximum is equal to ~65%. There is good correspondence between the experimental and calculated data.

Control of the technological regimes of application of a monolayer of metallic nanoparticles (the pressure of residual gases, temperature of the substrate, rate of evaporation, and the geometry of the position of the evaporator and substrate) allows one to obtain optically identical monolayers with the transmission and halfwidth differing by 2–3%. Thus, a high reproducibility of the optical characteristics for the monolayer is attained.

Having adequately selected the distance between the monolayers in a multilayer system, in the region of plasmon resonance it is possible to create conditions for interference leading to the amplification of the dip in the transmission or to an increase in the maximum in the specimen reflection. It is shown theoretically in [2, 3] that the most appreciable suppression of passing radiation with simultaneous minimization of reflection is attained at an optical thickness of the separating films equal to $\lambda/4$. For the separating films with optical thickness $\lambda_0/2$ the plasmon resonance band is split and the reflection in this region increases substantially. By changing the thickness of the intermediate films it is possible to monitor the spectral position of the additional minima in transmission and of the maxima in reflection that correspond to these minima. This is possible, however, only in a certain spectral region with appreciable transmission and significant reflection of the monolayer. We note that formation of the doublet attenuation band

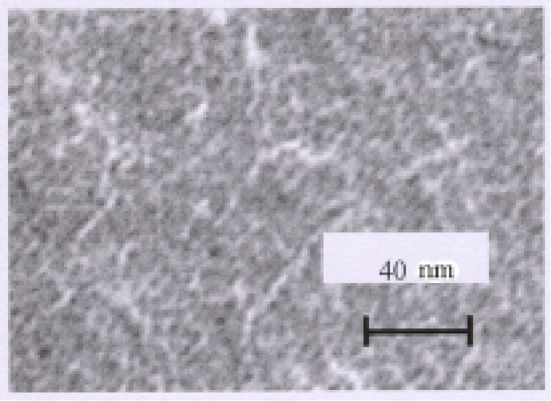

Fig. 1. Image of a monolayer of silver nanoparticles on a glass substrate taken with the aid of an electronic microscope.

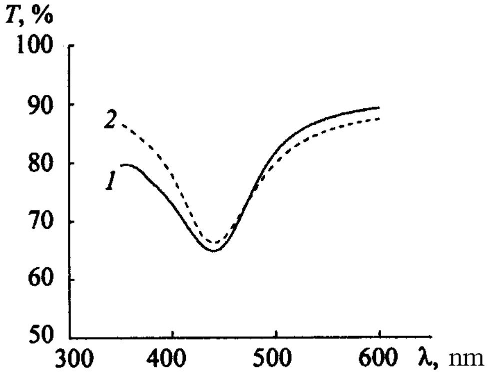

Fig. 2. Spectral dependence of the transmission coefficient of a monolayer of silver particles in a KCl film (d = 3.5 nm, η = 0.4); 1) experiment (specimen made); 2) calculation in QCA of STMSW.

at $I_m \approx \lambda_0/2$, just as simultaneous minimization of transmission and reflection for systems with separating layers $\lambda_0/4$, is a distinctive characteristic feature of the photon forbidden band formed near the band of plasmon absorption.

Figure 3 presents the spectral dependence of the coefficients of transmission T and reflection R of stratified systems made from monolayers of silver nanoparticles with separating KCl films of different optical thickness: 225–230 nm ($\approx\lambda_0/2$) and 110–112 nm ($\approx\lambda_0/4$). The number of layers of metallic nanoparticles N = 7, their average size d = 3.5 nm, and the overlapping parameter η = 0.4. The spectral dependences of T and R calculated by the method described above are shown in the insets. In the calculations the quasihomogeneous system was considered as a stack of tightly packed monolayers of spherical silver nanoparticles separated by transparent continuous films of optical thickness corresponding to experimental values.

Analysis of Fig. 3 shows that the transmission spectra of multilayer systems, irrespective of the thickness of separating dielectric layers, are characterized by a distinct attenuation band in the vicinity of λ_0. In both the experiment and numerical calculations general tendencies can be seen in the dependence of the shape of the plasmon resonance band on the optical thickness of separating layers. For a system with separating layers $\lambda_0/4$ the attenuation band is narrower and the reflection is considerably smaller than the reflection of the system with separating layers $\lambda_0/2$. Moreover, in the transmission spectrum of the system with separating layers $\lambda_0/2$ one can observe an indistinct doublet structure. In comparison with calculated data, the splitting of the band is manifested more weakly in the experiment. The reason for this seems to be the influence of the nonspherical shape, the polydispersity of silver nanoparticles, and

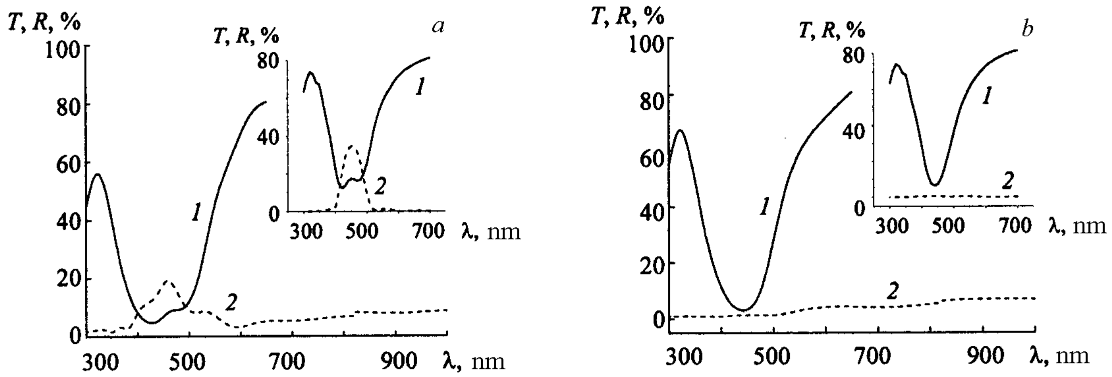

Fig. 3. Spectral dependence of the coefficients of transmission T (1) and reflection R (2) of a stratified system of monolayers of silver particles separated by KCl films of thickness $l_m = \lambda_0/2$ (a) and $\lambda_0/4$ (b); the number of layers of metallic nanoparticles $N = 7$, $d = 3.5$ nm, $\eta = 0.4$; the insets present calculated dependences of T and R in QCA.

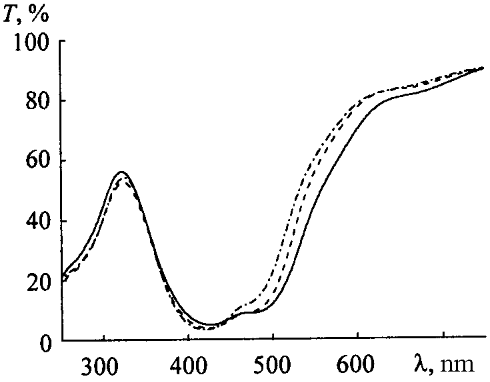

Fig. 4. Dynamics of the attenuation band of a multiplayer system of silver nanoparticles in KCl ($N = 7$, $d = 3.5$ nm, $\eta = 0.4$); the solid curve represents the characteristic of the structure directly after the layer was prepared; the dashed curve, after 24 h after the layer was prepared, and the dot-dashed curve, after 48 h after it was prepared.

a certain scattering in the optical thickness of intermediate dielectric films obtained in the process of thermal deposition.

As is seen from Fig. 3, for systems with quarter-wave separating layers in the region of plasmon resonance there are simultaneous small transmission and very small reflection. This indicates a considerable increase in absorption with the optical thicknesses of intermediate films selected in this way. Thus, by changing the optical thickness of separating dielectric layers in a certain region of the spectrum we can create conditions either for large reflection or for considerable absorption.

It should be noted that in carrying out the experimental investigations we varied the thickness of separating half-wave gaps within small limits, i.e., we "tuned" it out by 3–5% from λ_0 trying to note the manifestation of the doublet structure of plasmon resonance. In this case, the most distinct nonmonotonicity of the spectral characteristic of transmission was observed on small tuning out from λ_0 to the longwave region. This result is presented in Fig. 3. The optical thickness of half-wave layers in the calculations was assigned equal to 225 nm.

Figure 4 presents the transmission spectra of a 7-layer system with half-wave separating gaps recorded in a certain time interval after they were made. It is seen that with time the spectral characteristic undergoes changes manifesting themselves mainly as the narrowing of the band of plasmon attenuation. The main changes are observed in the longwave wing of the band. The probable mechanism of the occurring changes associated with the hygroscopicity of KCl and filling of its pores by atmospheric moisture cannot give a full explanation for them, since in this case the band had to shift to the longwave region of the spectrum because of the increase in the refractive index of KCl. It may well be that these changes are due to the action of several mechanisms, among which processes that are associated with the packing of deposited layers and also with redistribution of local charges can be isolated. The set of processes leading to a change in the properties of the matrix in the regions adjoining metallic nanoparticles and, as a result, to changes in the electrodynamic interactions in the nanocomposite must be studied additionally.

Conclusions. The given theoretical and experimental results point to the fact that electrodynamic interactions in spatially ordered nanostructures exert a substantial effect on the formation of collective surface modes which is manifested in the spectral characteristics of these systems. The creation of quasi-one-dimensional structures based on tightly packed monolayers of metallic nanoparticles may lead to the occurrence of a doublet structure of plasmon resonance. The transformation of the optical spectra of transmission and reflection is carried out by altering the material and thickness of intermediate continuous films.

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