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Optical Properties of Thin-Film Metal-Dielectric Nanocomposites

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The method for preparation of metal-dielectric nanocomposites with a layered periodic subwavelength structure is proposed. For systems containing silver and copper nanoparticles monolayers the influence of interlayer parameters on transmission/reflection spectra, as well as their absorbency over the spectral range of the surface plasmon frequency has been established and investigated. The quantitative description of the experimental data is made on the base of the statistical theory of multiple scattering of waves.

Key words: metalline nanocomposite, surface plasmon, photonic crystal.

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I. Introduction

Composite materials consisted of metal nanoparticles embedded in transparent hosts are promising materials for linear and nonlinear optics, laser physics, optoelectronics. Unique optical properties of these nanostructures mainly connect with size effects and resonance surface plasmon-polariton absorption [1]. The bands of surface plasmon resonances (SPR) of metal nanoparticles usually lie in the UV and visible spectral ranges and their characteristics are dependent on particle and matrix materials, sizes and forms of nanocrystals, their volume concentration and nanocomposite morphology [2]. These effects have the collective nature in the case of close-packed nanoparticles. Collective optical excitations in partially-ordered particle array tend to be spatially localized. Localization leads to appearance of “hot” spots and to significant enhancement of a variety of optical processes, such as Raman scattering, four-wave mixing, quadratic electro-optical effect, and nonlinear absorption and refraction [2-5].

The specific case of plasmon-polariton localization is realized when metalline nanocomposites are fabricated with the subwavelength periodicity in one of the dimensions [6-8]. These layer-periodic structures consist of a stack of close-packed metal nanoparticle monolayers stratified by thin solid films of subwavelength thicknesses. They may be regarded as 1D-photonic crystals with electron and photon confinements realized simultaneously. In [6-8] we have shown that when the stack of these monolayers is produced with the matched intermonolayer distances, the multibeam interference leads to the photonic band gap (PBG) appearance. It may increase the attenuation over the range of the surface plasmon resonance. Attractive is to use this effect for an improvement of parameters of light detectors and Q-switchers at the cost of their absorbency growth. The aim of this work is an investigation of the plasmon absorption changing into multilayer metal-dielectric nanocompounds with subwavelength periodicity. In order to realize this we study experimentally and theoretically optical spectra of Ag/KCl and Cu/KCl monolayers and multilayer nanocompounds with a various internal structure.

II. Method

In order to fabricate the multilayer structures we used the thermal evaporation technique with sequent deposition of metal and dielectric materials under conditions of the substrate temperature near the room one, the residual gas pressure about $2\text{-}5\times10^{-5}$ tor and without breaking the vacuum between the evaporation steps. The glass and quartz plates were used as a substrate. The structures grown by this technique consist of a sequence of Ag (or Cu) island films separated by KCl intermediate layers of a subwavelength thickness. The quartz transducer made the thickness control. Optical thicknesses of all separating layers into a nanocompound were made equal to each other. The value of the optical thickness was changed at the range from $\lambda_0/10$ to $\lambda_0/2$, where λ_0 corresponds to the plasmon absorption maximum of a metallic nanoparticle monolayer into KCl environment. The transmission/reflection spectra of monolayer and stack samples were obtained with the use of the spectrophotometer “Cary-500”. Electron-microscope pictures of samples were received on the transmission electron microscope "Hitachi H 800".

III. Calculation scheme

In order to calculate transmission and reflection coefficients of these layer-periodic systems with metallic ultradisperse monolayers we have applied the approach based on the statistical theory of multiple scattering of waves (STMWS) [9]. The approach allows taking into account electrodynamic coupling as an interference of the waves multiply scattered into the partially-ordered particle array both into each close-packed monolayer and between different monolayers too. The efficiency of this approach has been already demonstrated at the description of spectral properties of 3D opal-based PC [10].

The calculation scheme we used consists of two part [11]. The first step is the calculation of the monolayer scattering amplitude as well as transmission and reflection coefficients with the use of the quasicrystalline approximation (QCA) of the STMWS [12,13]. This approximation was proposed for partially ordered particle arrays and contains the procedure of the averaging on the different configurations of the particle ensemble. The statistical properties of the particle array structure are characterized with the use of the radial distributional function [14]. At the second step we regard electrodynamic coupling between different monolayers into the stack by means of a kind of the self-consistent procedure. We have to note, that in the case of layer-periodic systems namely this Intermonolayer interference determines the PBG formation.

In the QCA the coherent transmission (reflection) of a close-packed monolayer consisted of spherical particles is regarded as follows:

$$T = \left| 1 - \frac{\pi}{k^2} \sum_l n_0 (2l+1)(c_l + d_l) \right|^2$$

$$R = \left| -\frac{\pi}{k^2} \sum_l n_0 (-1)^l (2l+1)(c_l + d_l) \right|^2 \quad (1)$$

Here $k = \frac{2\pi}{\lambda}$, n_0 is a surface particle concentration. Coefficients c_l and d_l are calculated numerically from the linear system of equations contained the Mie coefficients and some special functions that connected with interparticle coherent interaction and dependent on the radial distribution function in a complicated manner. The size dependence of the complex refractive index $\tilde{m}$ of a metal nanoparticle has been taken into account in the framework of the model of the electron mean free path limitation [2].

It is worthwhile to note that the formulas (1) reduce to simple analytical expressions when the terms connected with the lateral electrodynamic coupling is omitted:

$$T = 1 - \eta Q_{ext} + \frac{4\pi\eta^2}{\rho^2} x(0) \Lambda Q_{ext} \quad (2)$$

$$R = \frac{4\pi\eta^2}{\rho^2} x(\pi) \Lambda Q_{ext}.$$

Here Q_{ext} is the single particle extinction efficiency factor, $x(\gamma)$ is the phase function, ΛQ_{ext} is the scattering efficiency factor, $\rho = \pi d n_m/\lambda$, n_m is the matrix refractive index, $\eta = n_0 \pi d^2/4$ is the monolayer overlapping parameter. This approximation is usually called as the coherent single scattering approximation (CSSA). Further, the neglect of the interference of single scattering waves in the far field leads to the independent single scattering regime when the light attenuation by a monolayer is determined by addition of single particle extinction efficiency factors (SSA): $T = 1 - \eta Q_{ext}$.

IV. Results and discussion

As it was mentioned above, monolayers produced by the vacuum deposition are island films consisted of close-packed metal nanogranules. In order to study the role of the coherent concentration effects in the surface plasmon attenuation we have firstly compared the spectral characteristics of nanoparticle monolayers calculated with (QCA) and without (CSSA) taking into account the lateral electro-dynamic coupling (Fig. 1). The monolayer overlap parameter $\eta = n_0 \pi d^2/4$ was equal to 0.4 for the Ag nanoparticle (diameter of 3.5 nm) and the Cu nanoparticle (diameter of 10 nm). These values were close to parameters of the samples, fabricated by the thermal evaporation technique. As it is seen from the comparison of numerical data, the enhancement of collective coherent interactions with the particle concentration growth have influence on their spectral position. It is important to note that a strong lateral coupling takes place for arrays of nanoparticles characterized by a low value of a single particle albedo $\Lambda = Q_{sca}/Q_{ext}$. The calculations with the use of the Mie theory show that for metal nanoparticles under consideration the extinction (Q_{ext}) and scattering (Q_{sca}) factors are correspondingly 0.688 and $0.136 \cdot 10^{-3}$ for Ag and 0.403 and $0.43 \cdot 10^{-3}$ for Cu. This allows concluding that the concentration red shift of the SPR predicted by the QCA is a sequence of the nearfield electodynamic coupling. In the case of silver island films the QCA gives a good quantitative description of the experimental data [7].

Transmission spectra of copper island films are shown in Fig. 2. We considered both covered with KCl and uncovered samples. For uncovered samples one can see the red shift of the SPR that usually is explained by the evanescent-wave scattering [2]. However, the SPR for the covered sample is also displaced when compare with the calculation in the frame of the QCA. The possible reason of the additional shift may consist in a rapid oxidation of copper nanogranules. The numerical data in Fig. 3 demonstrate the effect of the oxidation. These data are the result of calculations with the use of the extended Mie theory. We consider two cases: (1) formation of the oxide shell on the copper core and (2) formation of the composite metal-oxide nanoparticle. As one can see, in both cases the oxidation gives rise to the displacement, attenuation and broadening of the SPR. In more details the effect of displacement may be analysed with the use of Fig. 4. Data in Fig. 4 illustrate that the

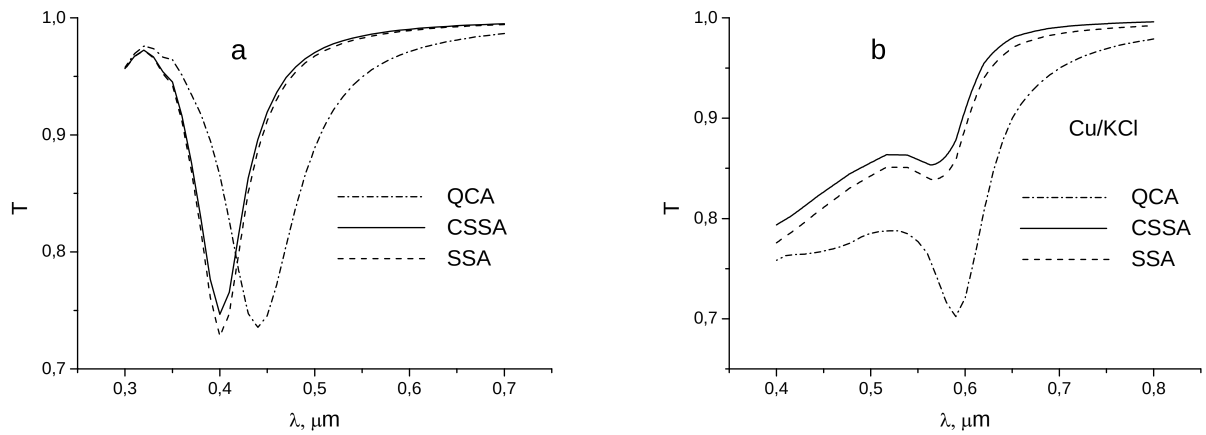

Fig. 1. Transmittance of close-packed (η = 0.4) monolayers of (a) Ag (d = 3.5 nm) and (b) Cu (d = 10 nm) homogeneous spherical particles embedded in KCl film (n_m = 1.5). Spectral dependences are calculated in the QCA, the CSSA and the SSA.

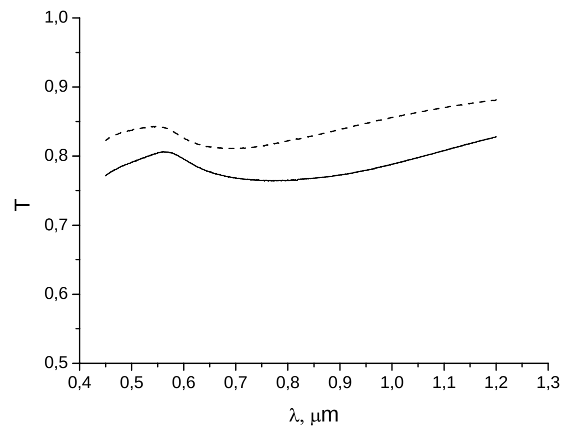

Fig. 2. Transmittance of Cu nanoparticle (d = 10 nm) monolayers (η = 0.4) deposited directly on a glass substrate (solid line) and between KCl films (dash line).

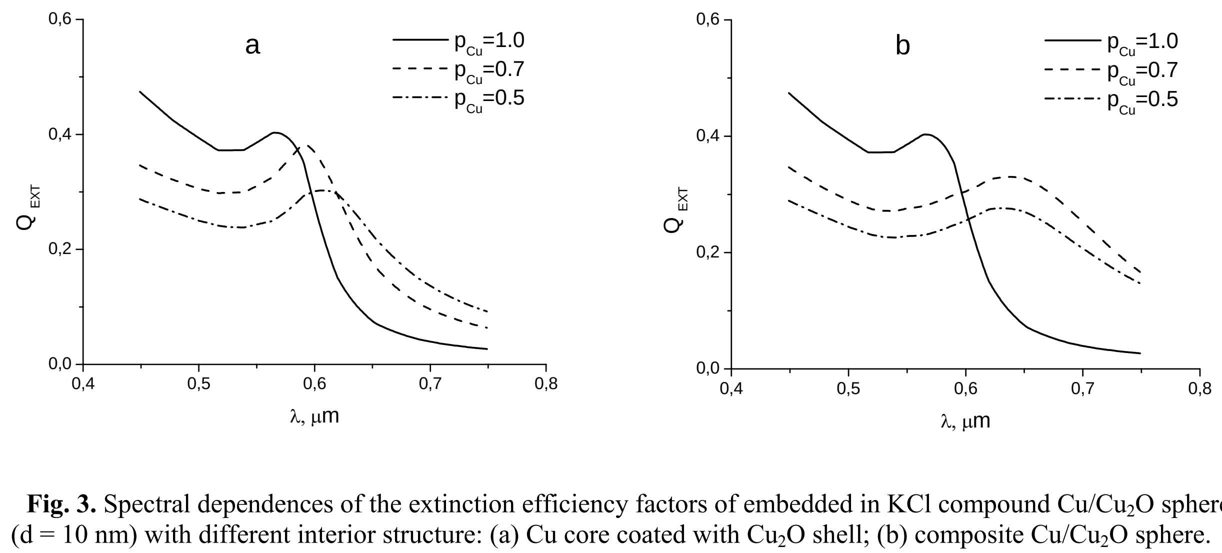

Fig. 3. Spectral dependences of the extinction efficiency factors of embedded in KCl compound Cu/Cu_2O spheres (d = 10 nm) with different interior structure: (a) Cu core coated with Cu_2O shell; (b) composite Cu/Cu_2O sphere. Calculations are performed for various Cu volume fraction p_{Cu} in a compound particle.

dependence of the SPR spectral position on the metal volume fraction into the nanoparticle may in common case be nonmonotonous. At the initial stage of the oxidation process the red shift takes place regardless of the internal structure of the metalline nanoparticle.

To demonstrate the influence of longitudinal coherent interactions we investigated the transmission and reflection spectra of 1D photonic crystals consisted

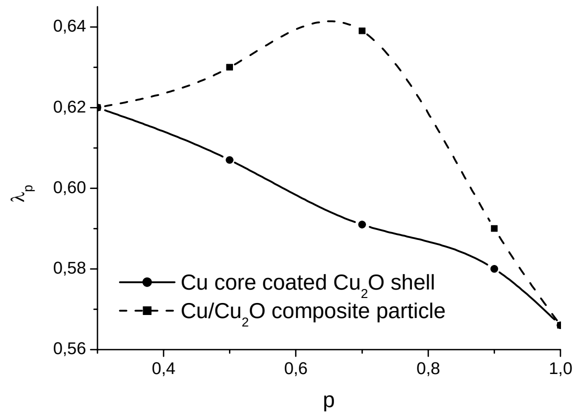

Fig. 4. Dependence of the wavelength in the maximum of plasmon absorption band of embedded in KCl compound Cu/Cu_2O spheres (d = 10 nm) with different interior structure on the Cu volume fraction p_{Cu} in a particle

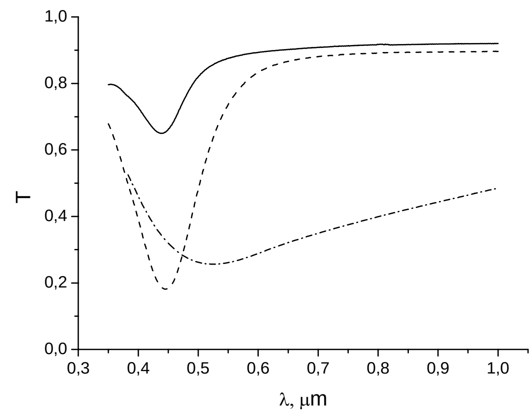

Fig. 5. Transmittance of Ag/KCl multilayer nanostructures fabricated on the base of close-packed (η = 0.4) Ag nanoparticle (d = 3.5 nm) monolayer (solid line): 3 Ag monolayers are separated by quarter-wavelength KCl films (dash line); 6 Ag monolayers separated by KCl films of 1-1.5 nm thickness (dash-dot line)

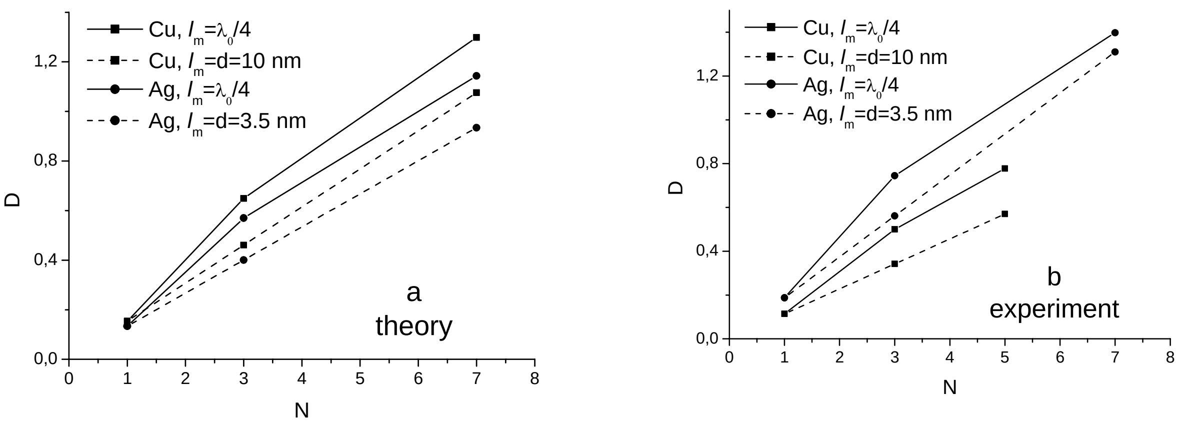

Fig. 6. Dependence of optical densities in the maximum of the plasmon absorption band of Ag/KCl and Cu/KCl multilayer nanostructures for the case of quarter-wavelength separating KCl films (solid lines) and for the case of addition of optical densities for component monolayers (dash lines): (a) calculation in the QCA; (b) experimental data

of the close-packed silver and copper nanosphere monolayers separated by subwavelength dielectric films. We found, that the strongest spectral manifestation of longitudinal electrodynamic coupling takes place in the case of jointed electron and photonic confinements. In order to achieve it we chose intermonolayer film thicknesses so that the photonic band gap and the metal nanoparticle surface plasmon band could be realized at close frequencies in the visible. The optical thicknesses τ of separating dielectric layers were equal about $\lambda_0/4$, where λ_0 corresponds to the plasmon absorption maximum of a metallic nanoparticle monolayer into KCl environment. As an example, the transmission spectrum of the quaterwavelength stack contained three silver monolayers is given in Fig. 5. For comparison the spectrum of the other multilayer system (with τ~1-1.5 nm and six silver monolayers) is shown. As one can see, both systems are characterized by the comparable attenuation at the maxima of the SPR. The broadening of the SPR of the second system is apparently connected with the more dispersion in sizes of metal nanoparticles. The increase of the size dispersion may be connected with the possibility of the aggregation of nanoparticles placed into different monolayers when they are separated by too little amount of a dielectric material.

As it is seen from Fig. 5 one-dimensional subwavelength ordering and connected controlling the interaction between light and metal nanoparticles is a power tool for optical spectra regulation in the vicinity of the surface plasmon resonance.

It is worthwhile to note that for intermonolayer film thicknesses of $\lambda_0/4$ the low value of transmission and reflection are realized simultaneously at the range of λ_0. As soon as the PBG formation is accompanied by the light localization, it may lead to the absorption increasing into a layer. Last fact may be useful for the optical shutter parameters increasing. In order to illustrate it, the optical densities of multilayer systems were calculated with the assumption of the monolayer independent action and compared with the experimental data (Fig. 6). One can see that the absorption over the range of the surface plasmon resonance is sensitive to the internal stack parameters and increases when intermonolayer film thicknesses is equal to $\lambda_0/4$. The effect grows with increasing the number of metal nanoparticles monolayers.

V. Conclusions

In the present paper we considered electrodynamic coupling under the conditions when the BG and the SPR are realized at the nearby frequencies that is when electron and photon confinement are revealed simultaneously. For layered metal-dielectric nanocompounds with the subwavelength periodicity we have established the nonadditive increase of optical density with the growth of the metal monolayer number. Besides, we have shown importance of near-field interactions in the formation of the optical response of a metal nanoparticle monolayer.

This studying is certainly essential for creation of metal nanostructures with a given optical behaviour in the visible as well as for development of express optical methods for these structures diagnostic.

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Оптичні властивості тонкоплівкових нанокомпозитів метал-діелектрик

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Запропоновано метод для приготування нанокомпозитів метал-діелектрик з нашарованою періодичною структурою піддовжини хвилі. Для систем, що містять срібло і мідні моношари nanoparticles вплив параметрів interlayer на спектри передачі/відображення, також як і їх absorbency над спектральним рядом зовнішньої частоти plasmon був встановлений і розслідує. Кількісний опис експериментальних даних робиться на базі статистичної теорії багаторазового розкидання хвиль.