POLARIZATION-MODULATION SPECTROSCOPY OF THE SURFACE PLASMON RESONANCE IN GOLD NANOSTRUCTURES OBTAINED BY THE METHOD OF PULSED LASER DEPOSITION

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The anglular characteristics of the internal reflectances for light in rough gold films and composite films of aluminum oxide with gold nanoparticles were measured at wavelengths of 630 and 1150 nm using the method of polarization modulation of radiation. In the range of angles exceeding the critical one, the characteristics of the reflectances for *p*- and *s*-polarizations have wide dips caused by the resonance interaction of both radiation states with surface plasmons. The peculiarities of the surface plasmon resonance and the corresponding structural properties of C films are discussed. The experimental anglular dependences of the internal light reflection for composite films agree with those calculated according to the Fresnel formulas in the approximation of optical indicatrix of the complex refractive index of films. The refractive and absorption indices of films are determined.

1. Introduction

New optical properties of nanostructures of noble metals remain in the focus of the investigators' attention [1]. Those are representative variations of colors, changes in transmission and reflection spectra of electromagnetic radiation with varying the size, shape, and dielectric surrounding of metal nanoparticles, as well as distance between them. In addition, a special attention is attracted by effects related to the resonance absorption of radiation, collective oscillations of electrons in a metal, and manifestation of the surface plasmon resonance (SPR). Investigations of SPR peculiarities represent an effective way of studying the nanostructures of noble metals, first of all, gold. On the other hand, the promising developments for nanoelectronics, biosensorics, optical memory, etc. demand for the use of new optical properties of gold.

The SPR phenomenon is widely used as the most sensitive method of registration of dielectric and optical properties of substances, and it is well investigated by numerous examples of continuous homogeneous media. This phenomenon is observed under the propagation of radiation through a three-layered medium, namely glass (quartz), metal, and air. The SPR in continuous homogeneous films with geometrically flat surfaces is accurately described by the formalism based on the Fresnel equations. At the same time, the peculiarities of the phenomenon in composite media such as island metal films or dielectric films that contain metal nanoparticles remain little investigated.

Among various methods used for the formation of nanostructures including films that contain nanoparticles of noble metals, one of the most attractive ones is the method of pulsed laser deposition (PLD) [2]. It allows one to effectively control the properties of condensates by means of the variation of the parameters of laser ablation, obtain granulated films of specified thicknesses, and form gold nanoparticles in various matrices and on various substrates. These facts determine the choice of the way to obtain samples for the investigation of SPR in the present work.

The surface plasmon resonance represents a polarization-dependent phenomenon observed under the conditions of total internal reflection. It manifests itself as a more or less narrow band on the curve of the internal reflectance for *p*-polarization versus the incidence angle of radiation, which is one of the most widespread ways to register the resonance [3]. But, as was shown earlier [4], the method of polarization modulation of electromagnetic radiation is more informative as for the SPR. The essence of this method lies in the registration of the polarization difference between the reflectances of the intensities of *s*- and *p*-polarized radiations. In the general case, this parameter that represents an independently measured quantity depends on some physical factors. In our case, it is a function of the angle of light incidence on a metal or a composite film. A positive effect of the use of this parameter is ensured by the fact that the subtraction of the *s*- and *p*-functions

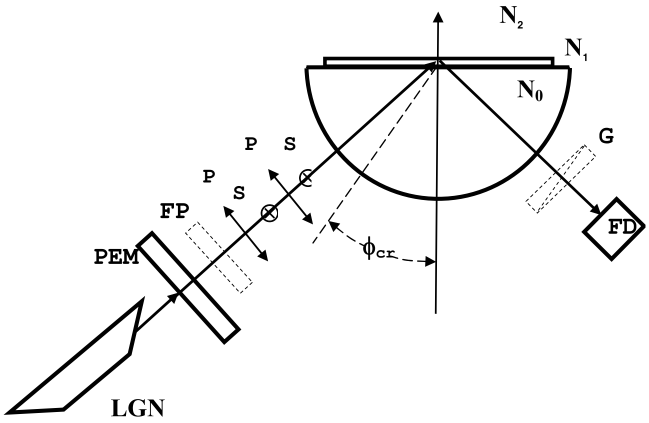


Fig. 1. Diagram of the modulation-polarization optical set-up for the registration of angle characteristics of the internal reflectances of *s*- and p-polarized radiations $\rho_s = R_s^2$, $\rho_p = \mathrm{R}_p^2$ and their difference $\Delta\rho = R_s^2 - -R_p^2$. LGN – helium-neon laser; FP – $\lambda/4$-phase plate; PEM – photoelastic polarization modulator; P, S – linear polarization waves whose azimuths are directed in parallel and in normal to the incidence plane; G – Glan prism; FD – photodetector; ϕ_{cr} – critical angle; N_0, N_1, N_2 – refractive indices for glass, the film, and air, respectively

results in the decrease of their common dependences, whereas even inessential differences between them can be considerably intensified. The increased (as compared to the usual technique) signal together with the enhanced signal/noise ratio result in the growth of the resolving power in the determination of the angle position of the SPR. In this case, the results of the SPR measurements include not only more accurate information on dielectric and optical properties of an object but also additional data unavailable for methods that do not use the polarization modulation, for example those concerning the shape of metal nanoparticles. In [4], it was reported on the use of the polarization-modulation spectroscopy for studying the SPR in mirror films of gold obtained by means of thermal evaporation. The use of this method in the course of investigations of the plasmon-polariton interaction in other metal nanostructures will be another demonstration of its information possibilities and will favor obtaining the new data on peculiarities of the plasmon resonance and the structure of the investigated objects.

This work is aimed at the investigation of the SPR regularities using the method of polarization modulation in gold films with rough morphology and in dielectric films of aluminum oxide that include Au nanoparticles obtained by means of the pulsed laser deposition.

2. Experiment

2.1. Investigation objects

Thin gold films were obtained on quartz substrates with the help of the PLD method. A beam of a YAG:Nd^{3+} laser (with a wavelength of 1.06 μm, pulse energy of 0.2 J, pulse duration of 10 ns, and pulse repetition frequency of 25 Hz) scanned a target in a vacuum chamber in the argon atmosphere at a pressure of 10–20 Pa. We obtained two kinds of films. The first ones were thin gold films formed using an Au-target and deposited from a direct high-energy flux of erosion torch particles. The substrate was located in normal to the torch axis at a distance of 20–25 mm from the target. The density of the irradiation energy amounted to 5 J/cm^2. The thicknesses of the films did not exceed 50 nm. The films of the other kind represented composite nanostructures including Au nanoparticles in the $\mathrm{Al_2O_3}$ matrix. They were formed from the reverse low-energy flux of erosion torch particles. The substrate was placed in the target plane at a distance of 5–10 mm from the torch axis. The target consisted of gold and aluminum bits. The concentration of gold was varied from 20 to 50%. The density of the irradiation energy was changed from 5 to 20 J/cm^2. Some of these films were subjected to heat treatment at a temperature of 400 °C during 10 min.

The investigations of the morphology of the film surfaces performed with the help of scanning atomic-force microscopy in the periodic contact mode testify to the fact that the surface morphology of the films of the first kind is rough and consists of nanoparticles with different lateral dimensions and a considerable height dispersion. The films of the second kind are much more homogeneous, without clusters on the surface. They are characterized by smaller dimensions of grains. The films of the first kind are single-phase with low porosity, whereas the porosity in the films of the second kind is significant (20–40%). The films of the second kind represent three-phase systems including Au nanoparticles in $\mathrm{Al_2O_3}$ matrices. and air.

2.2. Polarization-modulation method of investigating the SPR

The measurements of the polarization difference $\Delta\rho$ of the internal reflectances of *s*- and *p*-polarized radiation were performed on the set-up, whose optical scheme is presented in Fig. 1. As a source of linearly polarized radiation, we used an LGN-113 helium-neon laser with fixed wavelengths of 0.63 and 1.15 μm. The azimuth of the linearly polarized radiation coming from the laser was established at an angle of 45° with respect to the axes of the polarization modulator. The PEM polarization modulator [5] represented a dynamic phase plate, where the alternating-sign phase incursion took place due to a compression/tension deformation. The resonator part of the modulator is supplied by the alternating voltage, whose magnitude determines one of the two modes of its operation. In the first mode, where the modulator becomes a half-wave phase plate at the corresponding voltage, it changes the azimuth of a linearly polarized wave from that parallel to the plane of light incidence to the normal one twice during the period of the supply voltage. In the second one – the mode of quarter-wave phase plate – it transforms the linear polarization to right- and left-circular once during the period. In this case, locating a stationary quarter-wave phase plate after the modulator, one obtains such a state of polarization, at which the azimuth of the linear polarization changes its position to the orthogonal one once during the period.

The second variant is better firstly due to a decrease of the supply voltage and secondly due to a higher sensitivity of the photodetector as compared to that at the double modulation frequency. In the both cases, rotating the modulator about the optical axis of the measuring set-up, one chooses its such position, at which the azimuths of polarization of the radiation coming from it take, in turn, the parallel and normal positions with respect to the incidence plane (p- and s-polarizations, respectively). The constant-intensity radiation modulated with respect to the polarization state was directed to the investigated sample.

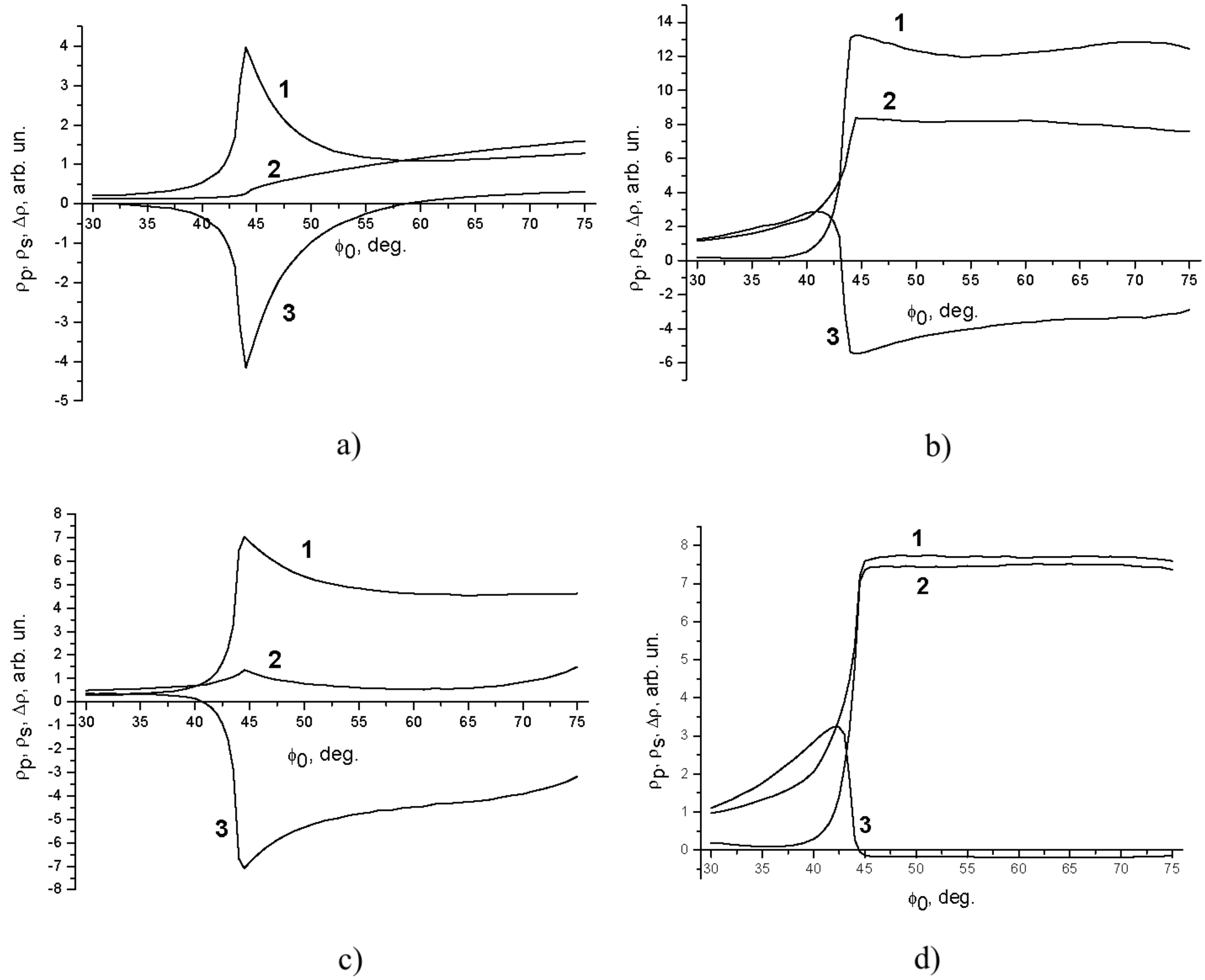
The investigated film was deposited onto a substrate made of fused quartz. The free surface of the substrate that contacts a segment of the same material on an immersion liquid (glycerin) represented a half-cylinder. In this way, a multiple change of the investigated samples provided both the reproducibility of the position of the half-cylinder with respect to the beam and the angle reading. After the interaction with the half-cylinder and the resonance-sensitive film on its working surface, the radiation was directed to a photodetector FD (silicon or germanium photodiode). The radiation absorbed by the latter generates a signal that includes a variable component at the double frequency in the first case and that equal to the frequency of the resonator part of the modulator in the second one. Its magnitude proportional to the difference of the reflectances for p- and s-polarizations $\Delta I = (R_s^2 - R_p^2)\sin\omega t$ was registered with the help of a selective nanovoltmeter with a synchronous phase detector, in which the polarization difference $\Delta\rho = (R_s^2 - R_p^2)$ became positive due to the fitting of the phase of the reference signal.

In this variant of the scheme, the arrangement of the linear polarizer **G** before the photodetector results in the modulation of the intensity for the only s- or p-polarization, with respect to which the polarizer is adjusted for transmission. Thus, the addition of one element allowed us to obtain separately the angle dependences of the reflectances for s- and p-polarizations, $\rho_s = R_s^2$, $\rho_p = R_p^2$.

3. Results and Their Discussion

Figure 2 presents the internal reflectances of the s- and p-polarized radiations (ρ_s and ρ_p) and their difference $\Delta\rho$ depending on the angle of light incidence ϕ_0 for the gold film (type I). From Fig. 2,*a,b,c*, one can see that the amplitude of the dependence ρ_p (ϕ_0) (curves *1*) in the angle range from the critical one to the angle of total glancing of the beam has a wide dip. The dependences ρ_s (ϕ_0) (Fig. 2, curves *2*) cross ρ_p (ϕ_0) in the neighborhood of the critical angle. In this case, there appear regions with alternating sign at the characteristic of the polarization difference $\Delta\rho$ (ϕ_0) (Fig. 2, curves *3*). The comparison of Figs. 2,*a,b* testifies to the fact that, after the thermal treatment, the dispersion in the curve ρ_s (ϕ_0) becomes more intense, and the magnitude of the extremum in the curve $\Delta\rho$ (ϕ_0) respectively decreases. Though the observed regularities of the SPR conserve in the case of measurements at wavelengths of 0.63 and 1.15 μm, the form of the dependences somewhat differs (see Fig. 2).

The dependences ρ_p (ϕ_0) for thick mirror films had a form of curves with a narrow dip 1–2 degrees in half-width at an angle somewhat larger than the critical one [4]. A wide dip characteristic of the ρ_p (ϕ_0) curves for the films investigated in this work is associated with their special morphology. By definition, if metal particles have a spherical form, then the condition of the SPR initiation must be fulfilled in the whole range of angles exceeding the critical one. It becomes possible, because, for any angle of incidence on the prism surface, there always exists an angle with respect to the surface of Au nanoparticles that satisfies the condition of resonance interaction of the wave with surface plasmons. Whereas the films obtained by means of the evaporation in vacuum had a mirror surface, those deposited from the direct beam of the erosive torch were characterized by a rough relief caused by different dimensions of separate granules, crystallized drops, and nanoparticles with a



a) b)

c) d)

Fig. 2. Experimental dependences of the reflectances ρ_p and ρ_s of p- and s-polarized radiations and their difference $\Delta\rho$ for an Au film 20 nm in thickness (curves *1, 2* and *3*, respectively): *a* – λ=630 nm and *c* – λ=1150 nm before the thermal treatment; *b* – λ=630 nm and *d* – λ=1150 nm after the thermal treatment. All relative values on the Y-axis are given on the same scale

shape varying from spherical to ellipsoidal and spheroidal one.

The thermal treatment of a thin film results in the aggregation of the metal in balls [6]; due to this fact, the film partially or completely turns into an island one at constant mass thickness. This fact results in the violation of not only total internal reflection but also that at angles smaller than the critical one. As one can see from curves *2* in Figs. 2, *a,b,c*, the reflectance of s-polarized radiation is more influenced by the finiteness of the dimensions of gold nanoparticles than the reflection in the case of p-polarization. Together with the dispersion in the curve ρ_s in the form of a sharp bend in the neighborhood of the critical angle, this fact results in the change of the sign of the polarization difference $\Delta\rho$ (ϕ_0).

The observed dependences ρ_p (ϕ_0) and ρ_s (ϕ_0) cross at $\phi_0 = \phi_{\rm cr}$ at the expense of the violation of the conditions of total internal reflection by the metal film. The angle range, for which the polarization difference has the opposite sign, lies between the angle of intersection of the s- and p-dependences and the value corresponding to the beam glancing. Both this angle interval and the amplitude of the region of $\Delta\rho$ with opposite polarity depend on the thickness of the film. The angle dependence of $\Delta\rho$ transforms from that typical of the internal reflection from a metal to a characteristic of the total internal reflection disturbed by the environment.

The analysis of the curve $\Delta\rho$ (ϕ_0) testifies to the fact that there exists a region of negative sign with an extremum at $\phi_0 \geq \phi_{\mathrm{cr}}$ that overlaps that of positive sign related to the resonance interaction of radiation with surface plasmons.

Figure 3 presents all the three characteristics obtained at the wavelength $\lambda = 630$ nm for the samples of the second type – composite nanostructures that include Au nanoparticles in Al_2O_3. One can see that the resonance character of the interaction of s- and p-polarized radiations with electrons of Au nanoparticles is more pronounced in this film, as compared with gold ones. It is unusual that the intensity of the plasmon-polariton interaction in the case of the s-polarized wave is higher than that in the case of the p-polarized one based on their estimation from the ratio of the amplitudes at the critical angle and in the region of the minimum. This could be due to the anisotropy of the dielectric properties of Au nanoparticles, as well as to their shape in the case of their preferred orientation. In addition, as was shown in [7], the role of the substrate appears to be different for two states of the polarized radiation at the expense of the polarization of the substrate by the wave field. In this case, the investigated film is characterized by the anisotropy of dielectric properties not only due to the oblique incidence of light but also due to the macroscopically heterogeneous structural character.

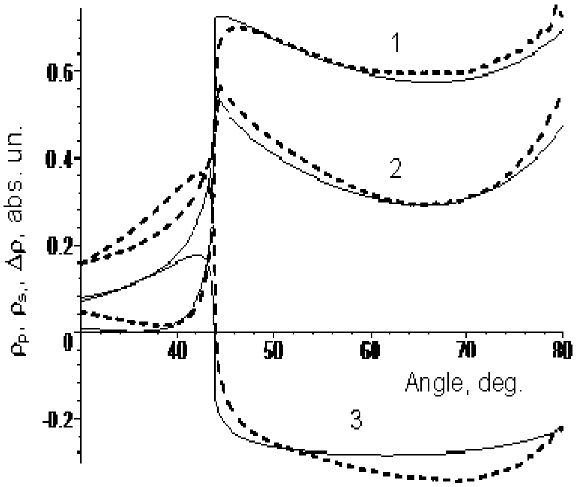


Fig. 3. Dependences of the reflectances ρ_p and ρ_s of p- and s-polarized radiations and their difference $\Delta\rho$ (curves *1, 2* and *3*, respectively) on the angle of light incidence for a composite film of Au nanoparticles in Al_2O_3; dashed line – experiment, solid line – the results of calculations by the Fresnel formulas for the three-layered sample structure in the model of anisotropic complex refractive index of the film for the following parameters: N_0=1.445; N_2=1.003; $N_{1p}=n_p+I\cdot\kappa_p$; $N_{1s}=n_s+I\cdot\kappa_s$; n_p=1.53; κ_p=0.065; n_s=1.51; κ_s=0.08; λ=630 nm; d=100 nm

The application of the Fresnel formulas to the description of the experimental results obtained for our media is possible only with regard for the following condition. To the film, we assign a certain indicatrix of dielectric properties based on the complex refractive index separately for s- and p-polarized radiations. Eventually, we managed to satisfactory describe all the three results of measuring the angle characteristics $\rho_p(\phi_0)$, $\rho_s(\phi_0)$, and so $\Delta\rho(\phi_0)$ by means of the Fresnel formulas with the use of the multiparametric fitting of the components of the complex refractive index for two orthogonal polarizations. The fitting procedure appears to be simple as the directions of variation of the curve shapes (the amplitude of the extrema and their position on the angle scale) differ in the case of separate variation of the refractive and absorption indices. In addition, we did not use the dependence of the optical constants on the film thickness, as it was done in [4], because its thickness is much larger than the characteristic parameter of this dependence. The best agreement between the results of calculations and measurements is reached in the case where we assign the only possible combination of the refractive indices n_s=1.51, n_p=1.53 and absorption indices κ_s=0.08, κ_p=0.065 to the film. The obtained optical constants allow us to make a conclusion about the role of gold nanoparticles in the formation of optical parameters of a composite substance. Their presence in the dielectric medium results in a decrease of the effective refractive index of the composite film as compared to the Al_2O_3 matrix (n=1.765 at λ=632 nm). As for the absorption index, its value is lower than that in a homogeneous gold film (κ=3.6 for the same wavelength). In other words, the optical constants of the system take on intermediate values between those they have in the components of the film. Their specific magnitudes are in a certain connection with the “solution concentration”.

4. Conclusions

We have investigated the peculiarities of the surface plasmon resonance in rough gold films and composite films of aluminum oxide with gold nanoparticles obtained using the method of pulsed laser deposition. The measurements were performed with the help of the method based on the polarization modulation of radiation. The angle dependences of the reflectances $\rho_p(\phi_0)$, $\rho_s(\phi_0)$ for p- and s-polarizations and the polarization difference $\Delta\rho(\phi_0)$ are characterized by wide dips caused by the resonance interaction of the both states of radiation with surface plasmons. We have revealed the simultaneous resonance interaction of both polarization states. The peculiarities of the plasmon resonance reflect the structural characteristics of the films, dimensions, size and shape dispersions of gold nanoparticles, as well as the properties of the dielectric environment. The experimental angle dependences of ρ_p, ρ_s, and $\Delta\rho$ for a composite film – gold nanoparticles in Al_2O_3 matrix – agree with those calculated theoretically according to the Fresnel formulas in the approximation of optical indicatrix of the complex refractive index of the film. The calculation allowed us to determine the effective values of the refractive indices $n_{s,p}$= 1.51, 1.53 and the absorption coefficients $\kappa_{s,p}$=0.08, 0.065 for s- and p-polarizations of light, respectively. Thus, using the PLD method, we have obtained gold nanostructures with structural and, respectively, optical properties that expand their functional possibilities.

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ПОЛЯРИЗАЦІЙНО-МОДУЛЯЦІЙНА СПЕКТРОСКОПІЯ ПОВЕРХНЕВОГО ПЛАЗМОННОГО РЕЗОНАНСУ В НАНОСТРУКТУРАХ ЗОЛОТА, ОТРИМАНИХ МЕТОДОМ ІМПУЛЬСНОГО ЛАЗЕРНОГО ОСАДЖЕННЯ

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Резюме

В шорсткуватих плівках золота і в композитних плівках оксиду алюмінію з наночастинками золота методом поляризаційної модуляції випромінювання виміряно кутові характеристики коефіцієнтів внутрішнього відбиття світла при довжинах хвиль 630 та 1150 нм. У діапазоні кутів, що перевищують критичні, виявлено в характеристиках коефіцієнтів відбиття p- та s-поляризацій широкі провали, що зумовлені резонансною взаємодією обох станів випромінювання з поверхневими плазмонами. Обговорено особливості поверхневого плазмонного резонансу та відповідні структурні властивості плівок. Для композитних плівок отримано узгодження експериментальних кутових залежностей внутрішнього відбиття світла з теоретично розрахованими згідно з формулами Френеля в наближенні оптичної індикатриси комплексного показника заломлення плівок. Визначено величини показників заломлення та поглинання плівок.