

Ultrathin and Nanostructured Au Films with Gradient of Effective Thickness. Optical and Plasmonic Properties

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Abstract. In present work the results of investigation of optical (transmission spectra) and plasmonic (surface plasmon-polariton resonance) properties of ultrathin and nanostructured Au films are presents. Methods and techniques for the syntheses of samples of ultrathin and nanostructured metallic films, and for the experimental studies of optical and plasmonic properties are representative. Au films on SiO₂ (optic glass) substrates were investigated.

1. Introduction

The interaction of light radiation with the metallic low-dimensional objects (nanofilms, nanoparticles) is determined by the structure of the electronic spectrum of these objects. For the films and nanoparticles with the band type of the energy spectrum, the conduction electrons are the plasma with a specific resonant frequency of its oscillations. The effect of plasmon resonance excitation in nanoislet metallic films can be observed in the optical transmission spectra as the spectral dips at the resonant wavelength. Another method of resonance surface plasmons excitation based on the phenomenon of plasmon and polariton waves phase matching when the effect of total internal reflection of plane-polarized coherent light beam is executed. In this case, the plasmon resonance is observed as an intensity reduction of the reflected light beam when the light is incident under the "resonance angle" [1,2].

2. Experimental technique

The samples of ultrathin and nanostructured Au films were prepared by thermal evaporation and condensation in vacuum. As the substrates were used the plates of optical glass (SiO₂) with a refractive index $n = 1.545$ and the plates of gallium-gadolinium garnet (GGG). Metal evaporation was carried out from molybdenum (Mo) boats at a residual pressure of atmospheric gases not more than $5 \cdot 10^{-4}$ Pa. Before deposition the substrates were annealed in vacuum at $T = 450^\circ\text{C}$ during 30 min. The deposition of Au was carried out on substrates at 150°C . At the deposition process the original technique for obtaining the films with a gradient of thickness along the sample plane was used. [3]. This technique allows one to research films with different thicknesses, which are obtained in a single technological cycle.



So in one cycle the four samples (3 on GGG substrate and 1 on SiO₂ substrate) were obtained. The maximum thickness of the coating was 15 nm, and the minimum approached to zero. The sample length was about 15 mm, so the gradient of effective thickness $grad h \approx 1 \text{ nm} / \text{mm}$.

Then, for the nanoislet structures formation the samples of Au films on GGG substrates were annealed in air at atmospheric pressure at temperatures 750, 850 and 950°C during 10 min. The sample of Au film on the SiO₂ substrate didn't annealed and was used for investigations of plasmon-polariton resonance by Kretschmann's method.

The analysis of surface morphology of nanoislet Au films was made using Scanning Electron Microscope REM-106 (SELM).

The investigation of transmission spectra of ultrathin and nanostructured Au films was carried out using an automated spectrophotometer KFK-3. Spectral range was 400–970 nm.

Surface plasmon resonance (SPR) was excited by the Kretschmann's method using a triangular prism (optical glass, $n = 1,514$). For plasmon excitation normally-polarized light beam (TM mode) with a wavelength $\lambda = 632.8 \text{ nm}$ (He-Ne laser) was used.

3. Results and discussion

Figure 1 shows the results of investigation of the surface morphology of nanoislet Au film on a GGG substrate, annealed at 850°C. The studies were carried in areas with different original thickness of coating, for islet films it is the effective thickness h_{eff} . The step value along the thickness gradient was 1 mm. As it was found the annealing temperature significantly affects to the morphology parameters of nanoislet coatings and, as result, its optical properties. But, the limited scope of this article does not allow us to show the results of morphology investigation of films, who was annealed at temperatures of 750°C and 950°C.

The present images (Figure 1) clearly show that the parameters of nanoislet (size, surface concentration, etc.) significantly depend on the effective thickness of the annealed coating. Table 1 shows the parameters of morphology nanoislet coating in investigated areas.

Table 1. Morphology parameters of nanoislet Au film in different investigated areas.

Step (mm)	Effective thickness h_{eff} (nm)	Islands concentration (μm^{-2})	Islands size dispersion (nm)	Maximum of dispersion (nm)
1	14.4	3.6	100–450	230
2	11.5	4	100–400	225
3	10.3	4.4	100–300	215
4	9.1	5.4	50–300	200
5	7.6	6.5	50–300	185
6	5.9	7.1	50–200	148
7	5.2	9	50–200	127
8	4.6	8.5	50–200	125
9	4.2	7.9	50–200	122
10	3.9	8	50–200	120
11	3.1	7.2	50–200	105
12	2.7	8.3	50–200	100
13	2	10.3	50–200	90
14	1.6	12	50–150	84

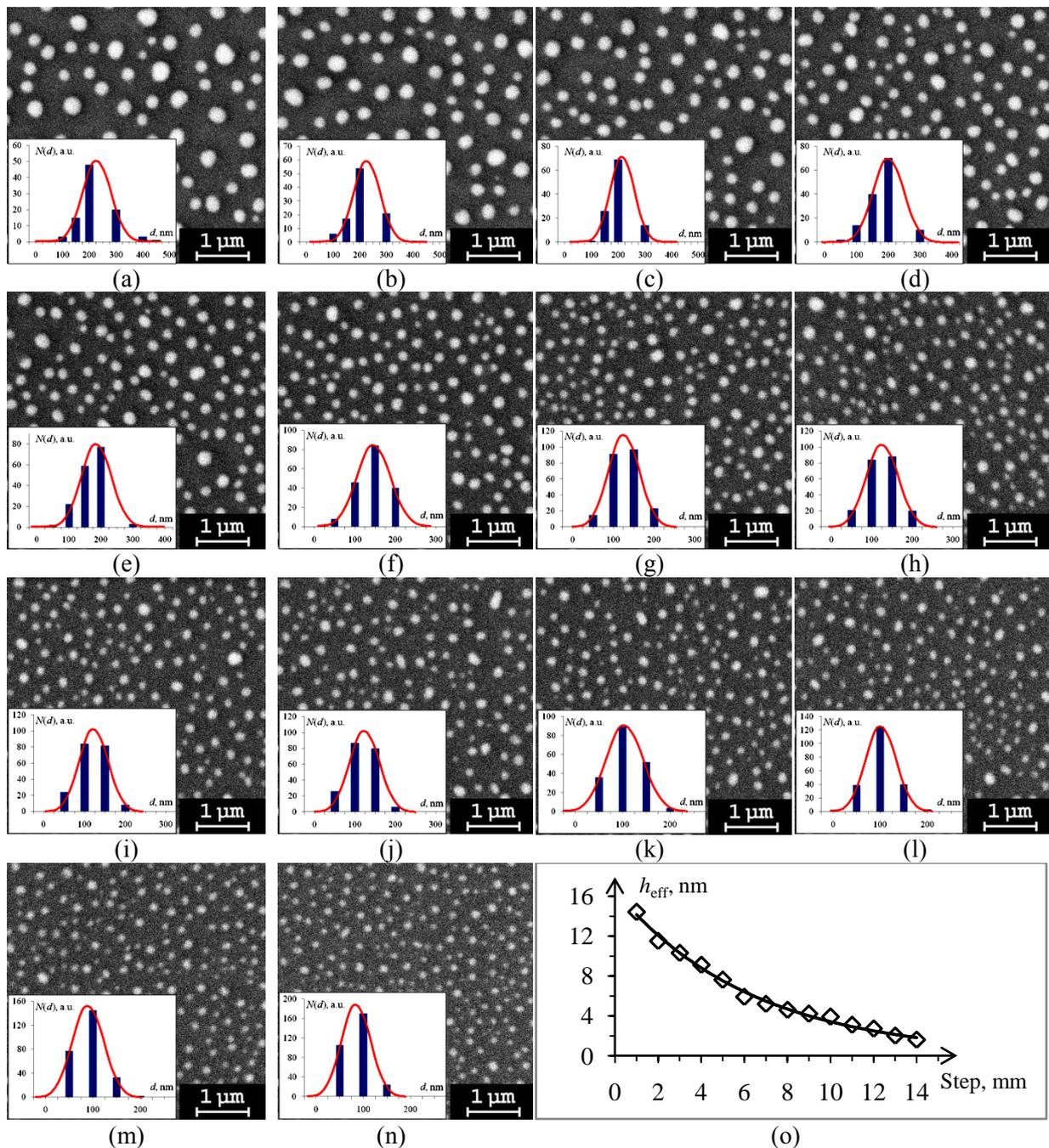


Figure 1. SEM-study of surface morphology in different areas of nanostructured Au film with gradient of the effective thickness. Film was annealed at 850°C, 10 min. Insets shows the dispersion of islands size: columns are experimental data, line is Gaussian approximation. (a–n) – the different areas of thickness gradient, step is 1 mm; (o) – change of h_{eff} along thickness gradient)

The researches of transmission spectra of Au gradient films in areas with different effective thickness are gave the next results. Figure 2 shows the transmission spectra of unannealed Au film on GGG substrate. The legend shows the values of the film effective thickness in the investigated areas. As one can see, the transmission spectra correspond to the volume absorption of Au, so films are solids [4].

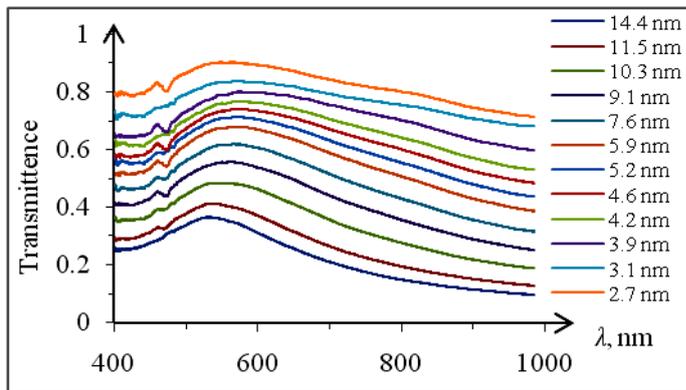


Figure 2. Transmission spectra of unannealed Au nanofilm on GGG substrate, which are measured in different areas along the gradient of thickness.

Figure 3 shows the transmission spectra of the Au film after annealing at 750°C, 10 min in areas with different effective thickness h_{eff} . The spectrum analysis has led to the following conclusions. At first, at the present spectra the peaks of plasmon resonance clearly defined [5]. At second, at the thick coating two peaks are observed: the first "blue" peak (500–540 nm) corresponds to quadrupole resonance, the second "red" peak – to dipole [6]. It is noted that the peak position of the dipole resonance strongly depends to h_{eff} . When the thickness of the coating is decrease the dipole resonance is not always shifts to the blue region of the spectrum, there is a sector with the "red" shifting of the resonance peak (figure 3(b)). This effect may be related to a change of islands size in the normal direction to a plane of the substrate, namely with the formation of islands with spheroidal form and with a different aspect index. The position of the quadrupole resonance peak of almost does not change with h_{eff} , and for the thinner areas of nanoislands Au film the quadrupole resonance is not observed.

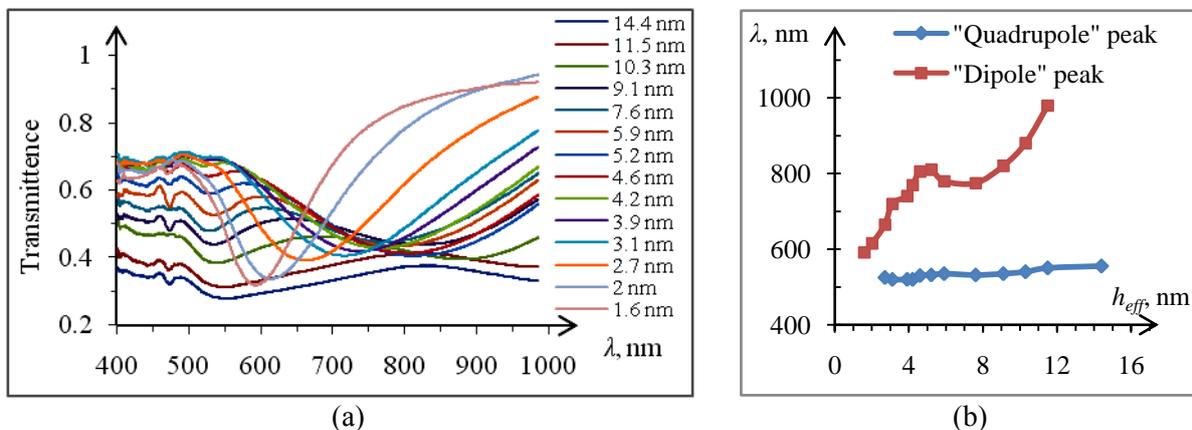


Figure 3. (a) Transmission spectra in different areas of Au nanofilm on GGG substrate with gradient thickness. Film was annealed at 750°C during 10 min. (b) Shift of plasmon peaks for different effective thicknesses of Au nanoislet film.

The transmission spectra of Au film on GGG substrate, annealed at a temperature of 850°C, are shown in Figure 4. The difference from the previous sample is the changes in position of the dipole resonance peak in the thicker areas of coating. (figure 4(a)), and the relocation of sector of "red" shifting of dipole resonance into a region with smaller thickness (figure 4(b)).

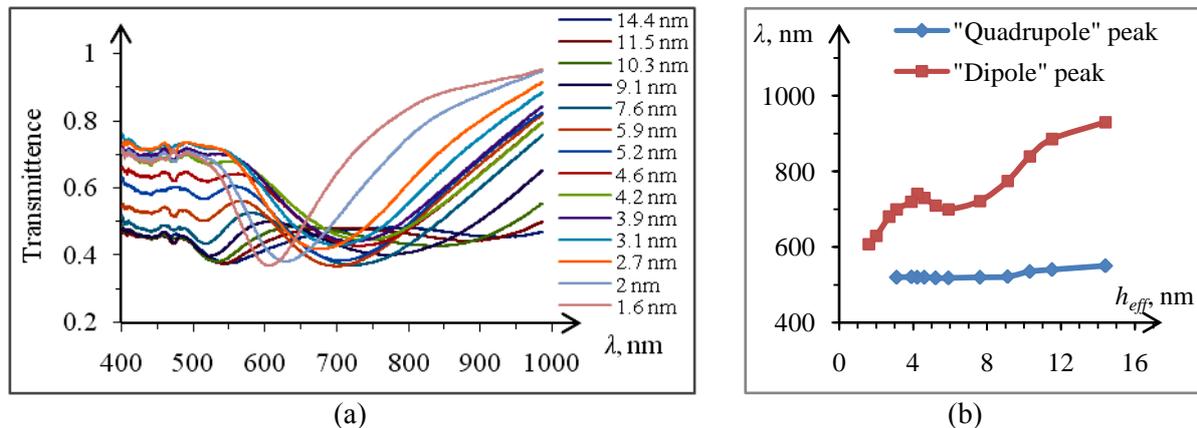


Figure 4. (a)Transmission spectra in different areas of Au nanofilm on GGG substrate with gradient thickness. Film was annealed at 850°C during 10 min. (b) Shift of plasmon peaks for different effective thicknesses of Au nanoislet film.

Figure 5 shows the transmission spectra in different areas of the effective thickness gradient of the nanoislet Au film after annealing at 950°C. Compared to the samples annealed at 750°C and 850°C for this film a "blue" shift of the dipole plasmon resonance peaks is observed, and a small decreasing in the region where for the low annealing temperature "red" shifts are observed (figure 5(b)).

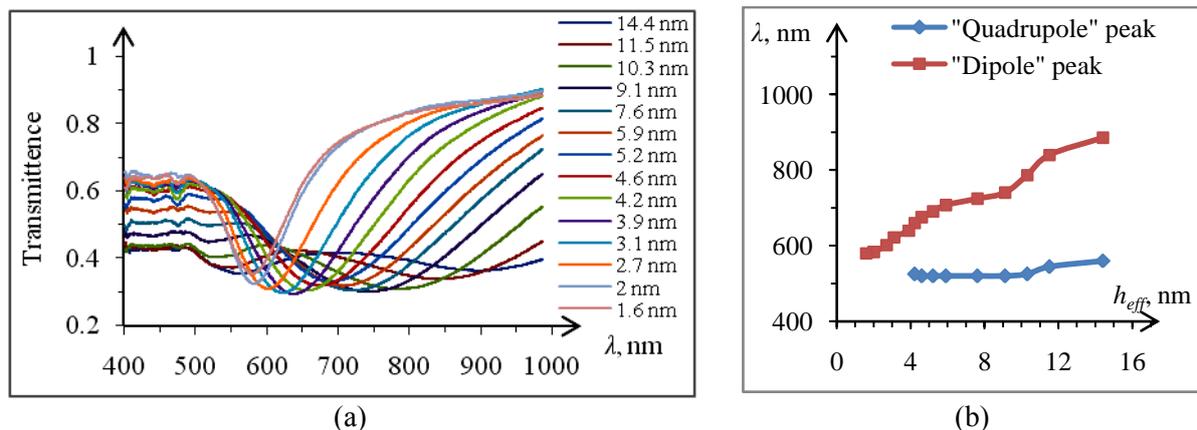


Figure 5. (a)Transmission spectra in different areas of Au nanofilm on GGG substrate with gradient thickness. Film was annealed at 950°C during 10 min. (b) Shift of plasmon peaks for different effective thicknesses of Au nanoislet film.

The investigations of surface plasmon-polariton resonance (SPR) in a gradient Au film on SiO₂ substrate, excited by Kretschmann's method gave the next results. Figure 6 (a) presents the normalized resonance curves of the reflected beam intensity in dependence to incidence angle (in the legend the relocation of investigated area along h_{eff} gradient are shown, the values of the thickness see in table 1). It can be seen that for all studied areas the SPR peak is observed, besides the last three areas [7]. The absence of the resonant peak for the most thin parts of Au film may be indicative about island structure of coating. The structural heterogeneity of the coating does not allow realizing the SPR [8]. Figure 6 (b-d) shows the main parameters of SPR peaks. It has been shown, that when h_{eff} is decreased, the quality coefficient of the resonant peak is decreased, the resonance angle is increased and the height of peak is decreases (increases the intensity of the reflected beam).

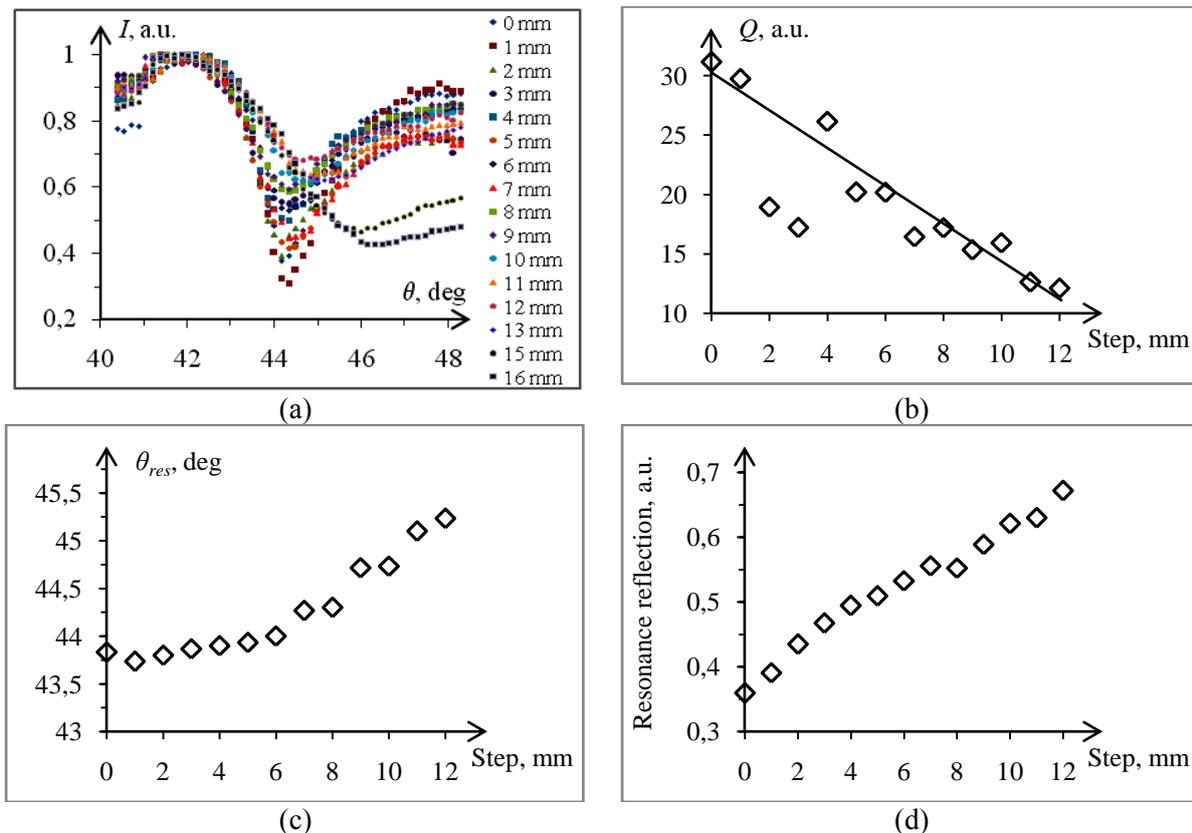


Figure 6. (a) SPR resonance curves for Au nanofilms with different thicknesses (in different areas along thickness gradient) on SiO₂ substrates. In legend the translocation (step in mm) of studied area from maximum film thickness (15 nm) to minimum are specified. Parameters of SPR: (b) quality factor, (c) resonance angle, (d) resonance reflection.

Conclusions

It is shown that the optical and plasmonic properties of ultrathin Au films are strongly depend on the coating structure. So for "thick" nanofilms with continuous structure of the coating the peak of surface plasmon-polariton resonance is observed, while in transmittance spectra the resonance absorption is absent. For ultra-thin films with nanoislet structure of coating the resonance absorption in the transmission spectra is observed, but clearly defined SPR peak is absent. For islet films the presence of a discrete quasi-regular structure leads to the beam energy absorption at incidence angles higher than the resonance SPR angle.

Acknowledgments

This work is supported by the RF Ministry of Education and Science in the framework of the base part of the state task №2015 / 701 (project 3879) and the State Council of Republic Crimea in the framework of the grant for young scientists of the Crimea (resolution № п170-1/16 from 02.02.2016).

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