AFM microscopy and optical studies for the shape of particles in ultrathin silver films

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Abstract. This work deals with investigations of AFM morphology and optical absorption spectra of ultrathin silver films with the mass thicknesses 0.7–1.4 nm. It is shown that the main structural elements of our Ag films are metallic clusters with the shapes of spheroids. The root mean square height and the correlation length of the film surfaces are determined using correlation analysis. The absorption spectra of the films reveal a characteristic complex band in the region of 400–500 nm, which is associated with the transversal and longitudinal oscillations of surface plasmons. In the framework of the quasi-static approximation, the splitting ΔE of the surface plasmonic bands is calculated as a function of ratio c/a for the spheroids. A comparison of ΔE values obtained experimentally with the calculated ones allows for estimating the c/a ratio for the spheroidal clusters, following from the optical spectra. This estimation agrees well with the AFM data.

Keywords: ultrathin silver films, absorption spectra, surface plasmon resonance, AFM topology.

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1. Introduction

Recently metal–dielectric composites of the type of fractal aggregates of metallic clusters in dielectric media have attracted considerable attention of researchers since their unique optical and electrical properties are significantly different from those of the bulk components of the composites. Ultrathin metallic films belong to that class of the composites and consist of conductive (metallic clusters) and dielectric (voids) phases.

One of the most remarkable optical properties of these composites is related to collective electron resonances often called as Mie surface plasmon excitations [1, 2]. Due to specific geometrical properties, optical excitations associated with the surface plasmons tend to be localised.

Ultrathin films far from the percolation threshold can be referred to as fractal structures, which are formed by metal clusters of different sizes and shapes in a dielectric host. Therefore localisation of the surface plasmons that occurs there can be interpreted as a specific type of Anderson localisation taking place in disordered media [3].

Owing to new possibilities for obtaining films with different levels of filling of the metallic phase and a dependence of their structure upon different technological factors (e.g., substrate temperature and deposition rate), ultrathin metallic films seem to be promising for the studies of interaction of electromagnetic radiation with metallic nanoclusters [4].

In this work we investigate the relation between the structure and optical response of ultrathin silver films, which are most often employed in many recent optical applications of metamaterials, such as negative-index materials [4, 5], near-field superlenses and far-field hyperlenses [4, 6].

2. Experimental

Silver films of various thicknesses far from the percolation threshold were deposited on glass substrates at the room temperature, using a thermal vacuum evaporated system VUP-5. Prior to the evaporation process, the glass substrates were cleaned with potassium dichromate, acetone and distilled water, and dried in a furnace. Then the substrates were loaded into an evaporation chamber, with the initial pressure inside the vacuum chamber being approximately equal to ~ 10^{-6} Torr. The deposition rate and the thickness of the films were monitored with a quartz oscillator. The silver deposition rate for all of our samples was kept in the region of 0.010–0.016 nm/s. A number of silver films with the thicknesses of ~ 0.7–1.4 nm were obtained in different technological cycles. One has to mention that all the films obtained by us are far from the percolation threshold, which occurs at the thickness of about 20 nm [7].

In order to characterise the surface morphology of the samples, we performed extensive atomic force microscopy (AFM) studies of our thin films. The surface morphology was monitored at the room temperature using a NT-MDT Solver Pro AFM. The measurements were carried out in a semi-contact regime, with a scan size of 2×2 μm^2.

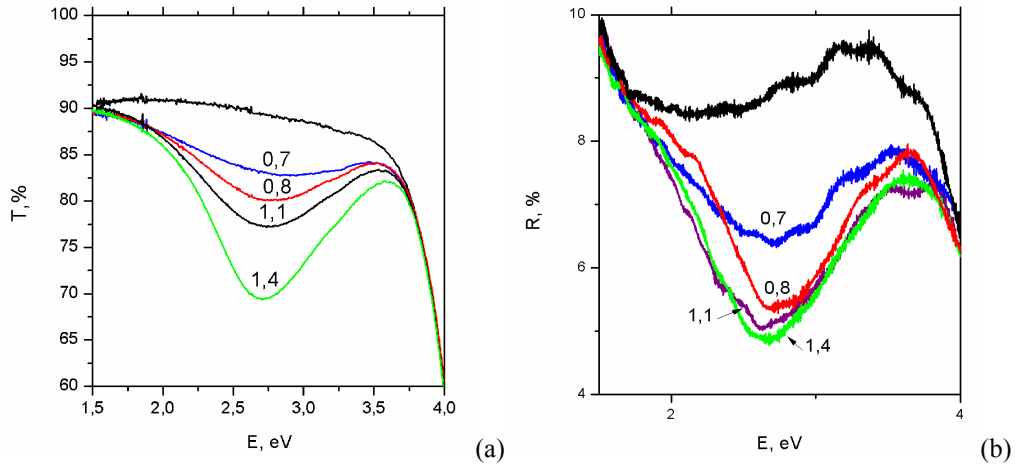

Fig. 1. Transmission (a) and reflection (b) spectra for glass substrate (black curve) and silver films with the mass thicknesses 0.7–1.4 nm (blue, red, pink and green curves) deposited on that substrate.

The optical transmittance (Fig. 1a) and reflectance spectra (Fig. 1b) were measured with a Shimadzu UV 3600 spectrophotometer in the region of 300–900 nm. The reflectance spectra were studied for the incidence angle of 5^o using an attachment ASR 3105. The optical absorbance A was calculated as $A = 1 - R - T$, with T and R being respectively the transmittance and the reflectance.

3. Results and discussion

Fig. 2 shows the surface morphology of silver thin film with the mass thickness $d_m = 1.1$ nm, which reveals a presence of metallic particles with different shapes and sizes. In order to characterise the surface roughness, the root mean square height δ and the correlation length σ are widely used as quantitative parameters [8]. They can be derived from the correlation function

$$G(r) = \frac{1}{S}\int_S \xi(r')\xi(r'+r)dr', \qquad (1)$$

where $\xi(r)$ denotes the height distribution of roughness, $r = (x, y)$ the coordinate, and S the area of the rough surface. In a computational implementation, $G(r)$ may be numerically calculated as

$$G(r) = F^{-1}\{F^{-1}\{\xi(r)\}F\{\xi(r)\}\}, \tag{2}$$

where F and F^{-1} represent the discrete Fourier transform and the inverse Fourier transform, respectively. Assuming that the correlation function should statistically follow the Gaussian distribution, one can represent this function as $G(r) = \delta^2 \exp\left(-r^2/\sigma^2\right)$.

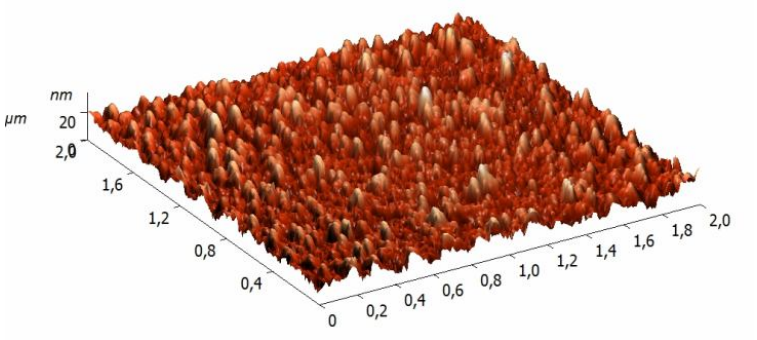

Fig. 2. ASM morphology of a silver film with d_m = 1.1 nm.

By fitting the numerical data with the Gaussian function, one can extract both the surface roughness and the correlation length (see Table 1). Fig. 3 plots the correlation function for the surface roughness and the corresponding Gaussian fitting. It is obvious that its peak has different half-widths for the vertical cuts corresponding to different directions (see the insert in Fig. 3a with the central peak in the shape of an ellipse). The form of the autocorrelation function obtained by us gives evidence that the shape of the particles is spheroidal and, moreover, the particles are predominantly oriented.

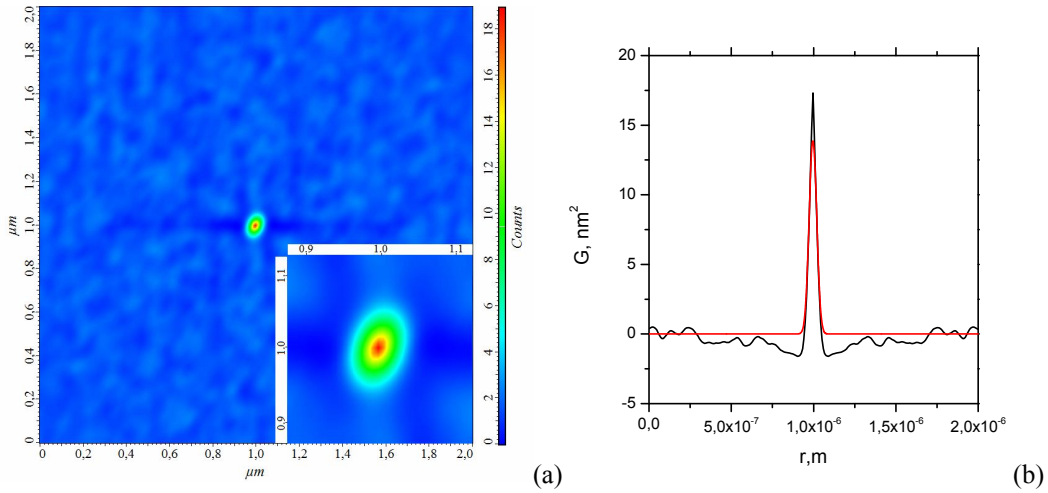

Fig. 3. Two-dimensional autocorrelation image (a) and its vertical cross section with a single-peak Gaussian fitting (b).

To confirm further this hypothesis, we have cut the image at the height of 15 nm. Following from this cut, it becomes obvious that the individual particles are isolated. It allows outlining the bounds of elements by means of a so-called threshold method [9] (see Fig. 4). The particles have an elliptic shape of the cross section, which is also observable visually. To determine the lengths

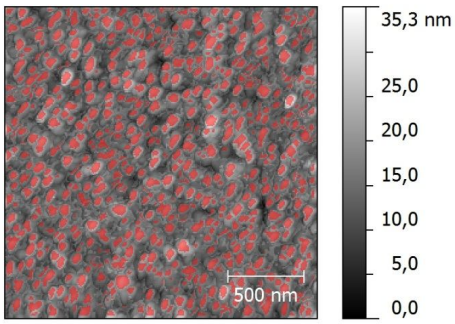

Fig. 4. Separated boundaries of particles as seen in the AFM image.

of principal axes of the ellipsoids, the spot occupied by every particle is described as a rectangle of a minimal size. Then its length and width would coincide with the major axes of the ellipsoid denoted hereafter as a and c. The third axis, b, is determined by the maximal height of the particle related to the cut threshold. The data indicate that the equality $a \approx b$ holds true. The average main axis lengths c of the spheroids obtained for the mass thickness range under study lie in the limits of 47–60 nm.

The optical absorbance spectra for the Ag films with different mass thicknesses are presented in Fig. 5a. The optical spectra, which are characterised by a complex resonance peak at 400–500 nm, should be associated with the surface plasmons [10]. Since the optical properties of plasmonic systems are shape-dependent, a complex structure of the bands observed can be explained assuming that the shape of the metallic particles is nonspherical. In other words, the complex band is due to transversal and longitudinal oscillations of the surface plasmons. The splitting ΔE between these oscillations can be extracted while decomposing the spectra (see Fig. 5b).

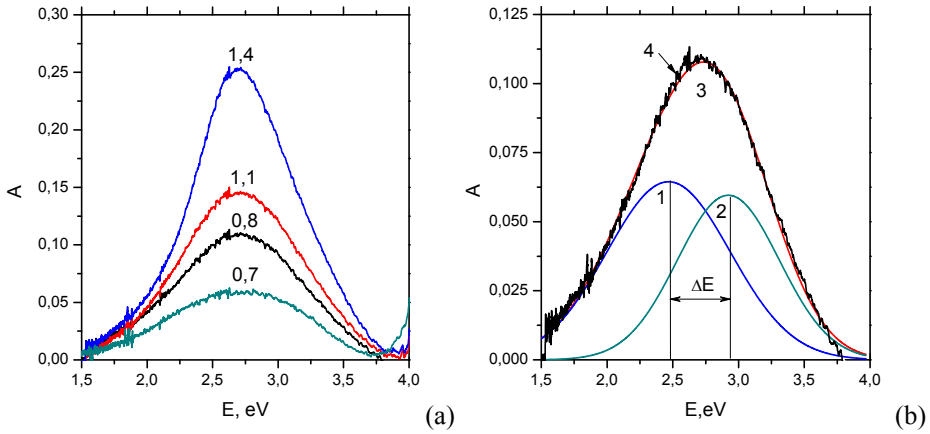

Fig. 5. Absorbance spectra of ultrathin silver films with different mass thicknesses shown in the legend (a) and double-peak fitting of the absorbance curve obtained for the silver film with d_m = 1.1 nm (b): curve 4 corresponds to experimental spectrum, curve 3 to double-peak fitting, and curves 1 and 2 to individual peaks. ΔE is the energy splitting.

In order to describe the absorbance of the system under study, one can use a quasi-static approximation for the particles smaller than the radiation wavelength [11]. According to this approach, the absorption cross section is given by:

$$C_{abs} = k\,\mathrm{Im}(\alpha)\,, \tag{3}$$

where $k = 2\pi/\lambda$ is the wave number and $\alpha = \sum_{i=1}^{3} \alpha_i$ denote the polarisabilities,

$$\alpha_i = 4\pi abc \frac{\varepsilon(\omega) - \varepsilon_m}{3\varepsilon_m + 3L_i(\varepsilon(\omega) - \varepsilon_m)}\,, \tag{4}$$

with a, b and c being the spheroid axes, ε_m the dielectric function of the medium, $\varepsilon(\omega)$ the complex dielectric function of the bulk material, and L_i the geometrical factors ($\Sigma L_i = 1$).

Examination of Eq. (4) reveals that a spheroidal metal nanoparticle should manifest two spectrally separated plasmonic resonances corresponding to the oscillations of its conduction electrons respectively along the directions of its major or minor axes [2]. Fig. 6 shows the calculated splitting of the spectral absorption bands that depends on the ratio of principal axes of the spheroid (here $a = b$ is assumed). This allows for estimating the ratio c/a provided that the splitting of the constituent spectral bands is known.

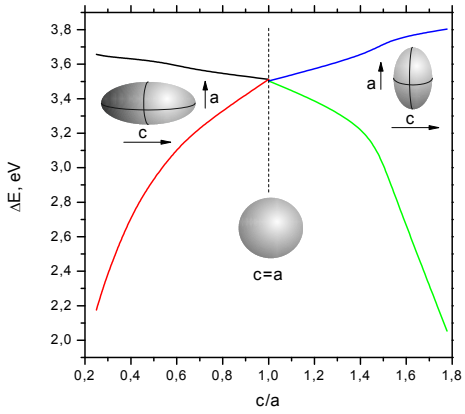

Fig. 6. Dependence of spectral splitting ΔE on the aspect ratio of spheroidal silver nanoparticles with the cross section area 2500 nm^2.

Let us return once again to the absorbance data presented in Fig. 5a for the films with the mass thicknesses 0.7–1.4 nm. The spectrum obtained for the film with the thickness of 1.1 nm and its fitting with the two Gaussian functions are displayed in Fig. 5b. Basing on superposition of these two functions, one can calculate the spectral splitting ΔE and, consequently, the ratio c/a. The resulting geometrical parameters of the particles constituting our ultrathin silver films as evaluated from both the optical and the AFM data are gathered in Table 1

Table 1. Ratios c/a for the spheroidal silver particles as obtained from the optical and AFM data and parameters describing surface morphology for the thin Ag films with different mass thicknesses d_m.

d_m, nm	c/a (AFM data)	c/a (optical data)	δ , nm	σ, nm
0.7	1.38	1.38	0.95	82
0.8	1.40	1.41	2.3	73
1.1	1.41	1.43	2.7	55
1.4	1.44	1.45	4.2	47

4. Conclusion

The AFM microscopy studies have revealed that the ultrathin Ag films with the thicknesses in the region of 0.7–1.4 nm comprise spheroidal particles. Using both the optical spectroscopy and the AFM data, we have determined the aspect ratios for those spheroidal particles, which characterise the structure of the objects under study. The results derived from the optical data and the morphol-

ogy analysis reveal excellent agreement. Moreover, they testify a weak dependence of the corresponding parameters on the mass thickness.

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Анотація. *Дана робота присвячена дослідженню морфології надтонких срібних плівок з масовою товщиною 0,7–1,4 нм методом атомної силової мікроскопії і спектрів поглинання. Показано, що основними структурними елементами срібних плівок є сфероїдальні металічні кластери. Середньо квадратична висота і довжина кореляції поверхні плівок визначена з кореляційного аналізу. Спектри поглинання плівок проявляють характерну складну смугу в області 400–500 нм, яка асоціюється з поперечними і поздовжніми осциляціями поверхневих плазмонів. Розчеплення поверхневої плазмонної смуги ΔE, розраховане в рамках квазістатичного наближення як функція відношення с/а сфероїдів. Порівняння значень ΔE, отриманих експериментально з розрахованими значеннями дозволило оцінити відношення с/а для сфероїдальних кластерів, виходячи з оптичних спектрів. Дана оцінка добре узгоджується з даними атомної силової мікроскопії.*