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Monitoring of localized plasmon resonance in an inhomogeneous ensemble of silver nanoparticles at the boundary of two media

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Optical properties of an inhomogeneous ensemble of plasmonic silver nanoparticles obtained by thermal vacuum deposition at the interface between two media as this interface moves relative to the nanoparticles themselves have been studied. The movement was carried out due to thermally stimulated diffusion of nanoparticles into the polystyrene layer and due to the deposition of an additional layer of quartz on a granular film with nanoparticles on a quartz substrate. The frequency shifts of the inhomogeneous plasmon resonance of nanoparticles moving through the interface was to about two tens of nanometers.

Keywords: plasmon, nanoparticle, physical vacuum deposition, plasmon resonance.

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Introduction

Currently, noble metal nanoparticles are being actively studied and used in various applications due to the opportunity of forming localized surface plasmons, which are very sensitive to the environment [1]. Depending on the geometry and material, the optical properties of plasmonic nanoparticles can be tuned from the ultraviolet to the near-infrared area of the spectrum, allowing them to find applications in enhanced luminescence [2] spectroscopy and surface enhanced Raman scattering (SERS) [3], development of energy-efficient photonics [4] and sensors [5] devices, as well as in catalysis [6].

At the same time, plasmonic particles are considered as „nanorulers“ , which allow measurements with nanometer resolution when observing in the far field [7,8]. The practical implementation of this is to control the thickness of the sputtered material in vacuum chambers or conduct thermodynamic studies at the interface between two media, for example, when creating glass activated by nanoparticles due to the process of silver diffusion during thermal annealing [9].

Another task is to control the incorporation or diffusion of metal nanoparticles into polymer spheres or thin polymer films that form the basis of composite nanomaterials. Such composites can be used in biomedicine due to the presence of antibacterial, antifungal, antiviral, anti-inflammatory, antiangiogenic and anticancer activities of silver nanoparticles [10]. Depending on their size, shape, size distribution, and surface charge, nanoparticles exhibit low or relatively low cytotoxicity. The matrix for implementation can be the thermoplastic polymer polystyrene, which is used in the production of medical products, such as surgical and dental instruments, dressings, prostheses and many others [11], where it is desirable to have biocidal activity and the opportunity of controlled release of nanoparticles from the composite into the environment [12].

In this paper, we studied the position of the plasmonic resonance of a heterogeneous ensemble of silver nanoparticles obtained by thermal vacuum sputtering in the form of a granular film when moving across the boundary of two media with different refraction indices.

Materials and methods

Studies were carried out for two interface options: air-polystyrene and air-quartz.

Thin films of polystyrene were obtained on SP-7101 glass slides by centrifugation of a solution of polystyrene in toluene. Polystyrene granules (PS, polymer molecular weight $M_w \sim 190\,000$, Sigma Aldrich, USA) were dissolved in toluene (OSCH, JSC „Vekton“, Russia) to obtain a polymer solution with a concentration of 2 weight percent, followed by filtration through an $PTFE$ filter ($0.2\,\mu$m). Thin films were obtained by static centrifugation using a Spin 150 spin coater (SPS, the Netherlands), followed by annealing for 12 h at a temperature of I120°C to remove residual traces of the solvent. AFM images showed that the films were homogeneous with a root-mean-square roughness of the order of 1 nm over a large area ($100\,\mu\text{m}^2$), the thickness was approximately 80 nm.

Silver nanoparticles in the form of a granular film were obtained in a PVD-75 vacuum chamber (Kurt J. Lesker, USA) by physical vacuum deposition of Ag (99.99%) at a residual vapor pressure of $5 \cdot 10^{-7}$Torr [13]. The amount of sputtered material and the deposition rate were controlled using a quartz microbalance.

Table 1. Parameters and results of calculating the frequency shift of plasmonic nanoparticles when immersed from air into polystyrene and fused silica

Diameter nanoparticles, nm	Maximum plasmonic resonance in the air, nm	Media	Indicator refraction resonance	Maximum plasmonic in the medium,nm	Shift, nm	Frequency shift, cm^{-1}
9	355	Polystyrene	1.59	412	57	3897
60	367	Fused quartz	1.46	440	73	4521

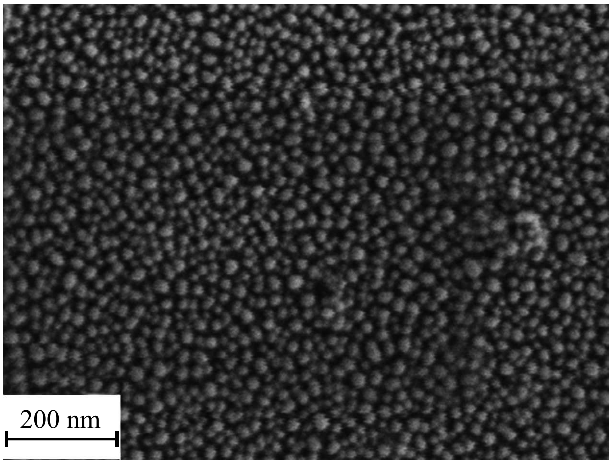

Figure 1. SEM image of a granular silver film with an equivalent thickness of 50 Åsputtered onto a fused silica substrate.

The equivalent thickness of silver sputtered onto a polystyrene film at room temperature was 5 Å at a sputtering rate of 0.1 Å/s. According to the AFM image, the average diameter of silver nanoparticles was 9 nm.

Diffusion of nanoparticles into the polymer film occurred when the polystyrene film was heated to the glass transition temperature $T_g = 95^\circ\mathrm{C}$ [14] on a magnetic stirrer with heating C-MAG HS 7 (IKA, Germany). Temperature setting accuracy 5°C.

The equivalent thickness of sputtered silver onto a polished fused quartz substrate (surface cleanliness class PV) was 50 Å at a sputtering rate of 0.1 Å/s. The average diameter of nanoparticles in such a film was approximately 60 nm according to electron microscopy data (Fig. 1). Sputtering of a quartz layer (99.99%) onto these nanoparticles was carried out in the same vacuum chamber at the same pressure and temperature of the 200°C substrate at a speed of 0.2 Å/s up to a thickness of 100 Å, and then at a speed of 0.5 Å/s. It was noted in the paper [15] that in this case the SiO_2 film on a quartz substrate does not affect the optical properties of the substrate, from which we can conclude that quartz is deposited in a dense, uniform layer. The design of the vacuum chamber and its equipment with a multichannel photonic analyzer PMA-12 (Hamamatsu, Japan) allowed to illuminate the sample directly in the chamber and obtain extinction spectra during the deposition process at certain, predetermined time intervals. Measurements were carried out in steps of 1 nm up to an equivalent quartz thickness of 10 nm, in steps of 2 nm — up to 20 nm, and then in steps of 5 nm — up to a thickness of 50 nm.

Results and discussion

Calculations using Mie theory [16] allow to estimate the frequency shift of the plasmonic resonance of a single spherical silver nanoparticle when the environment changes from air to polystyrene or fused silica (Table 1).

Although the refraction index of polystyrene is higher than the refraction index of fused silica, the frequency shift of the plasmonic resonance is smaller for polystyrene, which is explained by the smaller diameter of its nanoparticles. Let us consider the experimental results and compare them with the calculated data.

Diffusion of nanoparticles into polystyrene

Nanoparticles with a diameter of 9 nm in the form of a granular film were deposited onto a glass substrate with a polystyrene layer 80 nm thick. Such a small diameter of the nanoparticle relative to the thickness of the polystyrene was chosen due to the fact that the mobilities of the polymer chains on the surface and in the bulk of the polymer differ from each other [17]. The increased mobility of the surface layer chains leads to a decrease in the glass transition temperature$T_g = 95^\circ\mathrm{C}$ [18]. Thus, heating to the specified temperature for a certain time leads to partial diffusion of nanoparticles into the surface layer of the polymer (Fig. 2), the thickness of which is less than 50 nm, which is confirmed by the shift of the plasmonic resonance of the heterogeneous ensemble of silver nanoparticles to the long-wavelength area of the spectrum.

Figure 3 shows the change in the plasmonic resonance of an heterogeneous ensemble of silver nanoparticles sputtered on a polystyrene layer during sequential heating of the sample at a temperature of 95°C for 5. 10 and 30 min. There is a shift of the plasmonic absorption band to the long-wavelength region of the spectrum and a slight increase in absorbance. If the first feature, as expected, is explained by the immersion of nanoparticles in polystyrene

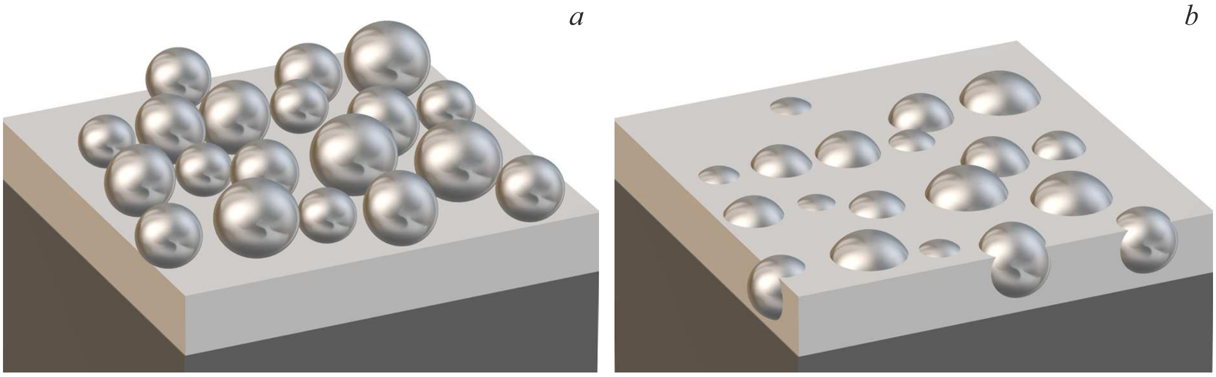

Figure 2. Thermally stimulated diffusion of a heterogeneous ensemble of silver nanoparticles into a polystyrene film: before (*a*) and after (*b*) passing the boundary.

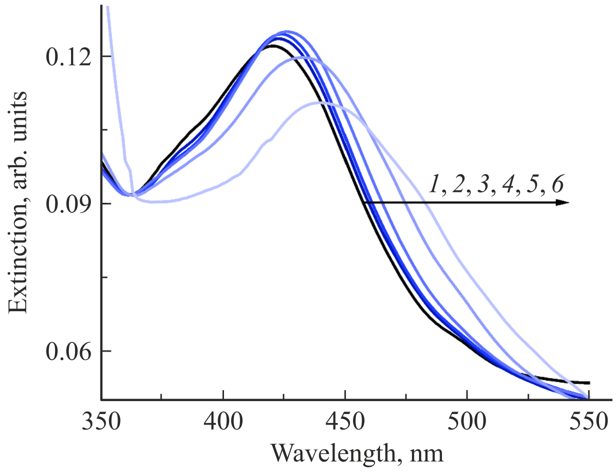

Figure 3. Extinction spectra of a granular silver film deposited on a polystyrene layer. Intervals: before heating (*1*), after heating to 95°C for 5 (*2*), 10 (*3*) and 30 (*4*) min, 12 h after heating (*5*) and subsequent coating with a layer of polystyrene (*6*).

Table 2. Maxima, half-width and shift of the plasmonic resonance of a granular silver film sputtered on a polystyrene layer

Interval	Maximum, nm	Half-Width, cm^{-1}	Shift, cm^{-1}
Before heating	420	3567	—
Heating 5 min	422	3452	113
Heating 10 min	424	3374	225
Heating 30 min	426	3524	335
After 12 h	433	3950	715
Coating with polystyrene	440	3988	1082

and the corresponding change in the average dielectric constant of the environment, then the second is associated with a decrease in the influence of the ionic core of the nanoparticle [19,20].

It was noted that even without heating, the process of further diffusion occurs due to an increase in the mobility of the polymer chains, which lasts approximately 12 h. This process also leads to broadening of the plasmonic resonance (Table 2).

In order to determine the degree of immersion of silver nanoparticles into the polymer during thermally activated diffusion, a polystyrene film was applied on top of them using spin-coating [21], which completely covered the nanoparticles, onto a sample with nanoparticles embedded in polystyrene. This resulted in a further long-wavelength shift of the plasmon resonance of the heterogeneous ensemble of nanoparticles. Thus, we can conclude that heating did not lead to complete immersion of the ensemble of nanoparticles into the polymer. Meanwhile, the maximum frequency shift of the plasmonic resonance for an heterogeneous ensemble of silver nanoparticles when immersed from air into polystyrene turned out to be 3.6 times less than the calculated value.

Sputtering of quartz onto silver nanoparticles

Nanoparticles with a diameter of 60 nm in the form of a granular film were sputtered onto a fused quartz substrate (Fig. 4). The design of the vacuum chamber and its equipment with a multichannel photonic analyzer allowed to record extinction spectra directly during the sputtering process. It should be noted that the extinction spectra of a granular silver film coated with a layer of quartz, taken in a vacuum chamber and in air, completely coincide.

The displacement of the interface relative to the nanoparticles due to the sputtering of quartz leads to a shift in the plasmonic resonance of the granular silver film to the long-wavelength area of the spectrum (Fig. 5, *a*) from 418 nm to 440 nm. Thus, the frequency shift of the plasmonic resonance maximum for nanoparticles in quartz

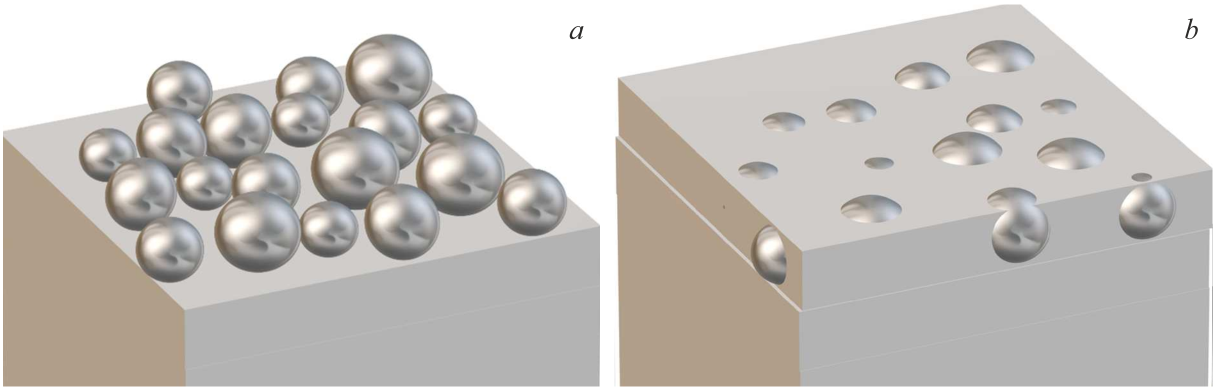

Figure 4. Sputtering of a quartz layer onto a heterogeneous ensemble of silver nanoparticles formed on quartz: before (*a*) and after (*b*) changing the boundary of the quartz layer.

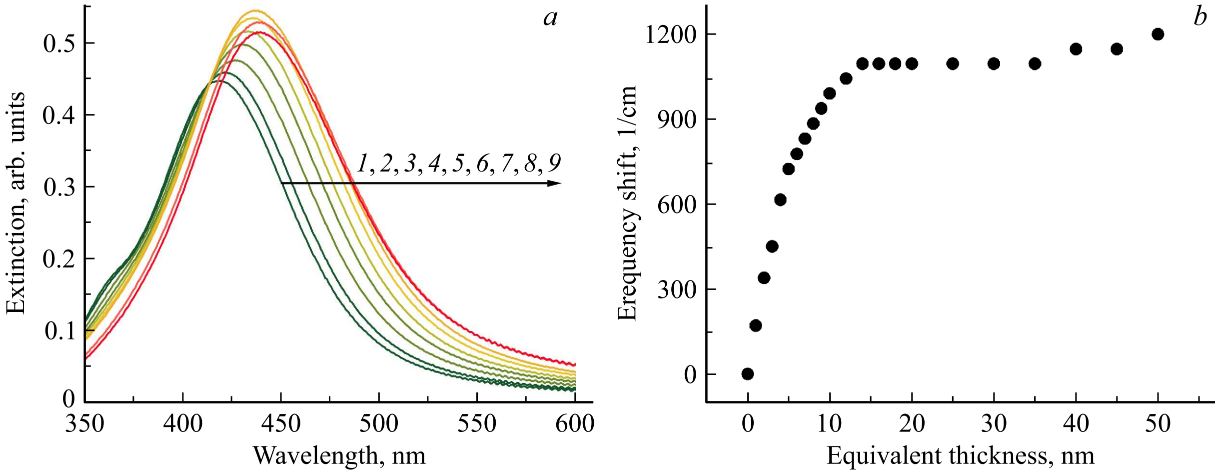

Figure 5. (*a*) Extinction spectra of a granular silver film on quartz before (*1*) and after deposition of a quartz layer with a thickness of: 1 (*2*), 3 (*3*), 5 (*4*), 7 (*5*), 10 (*6*), 14 (*7*), 40 (*8*) and 50 (*9*) nm. (*b*) Dependence of the frequency shift of the plasmonic resonance of a granular silver film on quartz on the thickness of the deposited quartz.

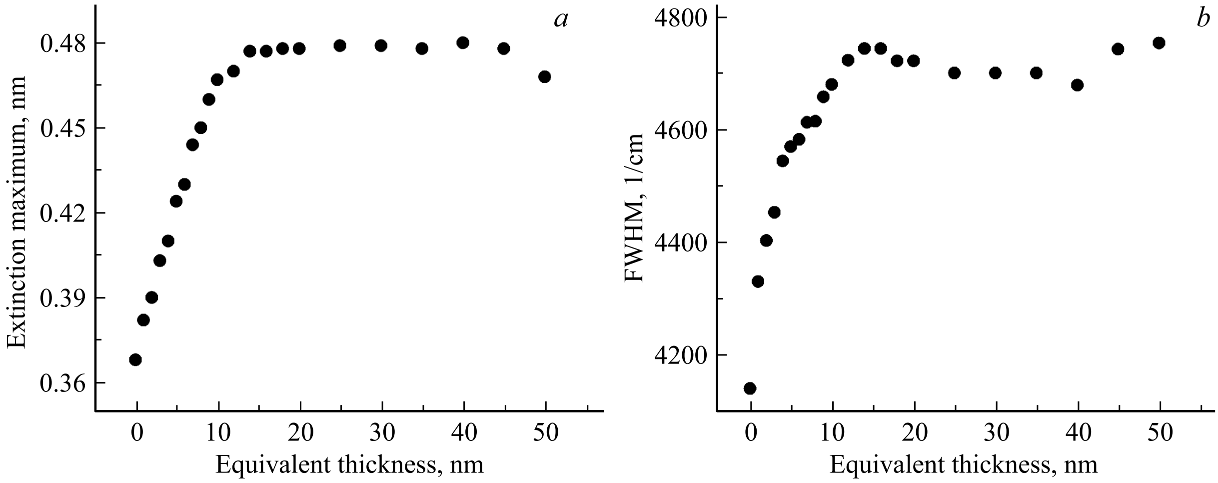

Figure 6. Dependences of the maximum absorbance (*a*) and half-width (*b*) of the plasmonic resonance extinction spectrum of a granular silver film on quartz on the equivalent thickness of the deposited quartz.

was $1196\,\mathrm{cm}^{-1}$, which is 3.8 times less than the calculated shift.

The shift of the plasmonic resonance maximum increases with increasing thickness of the sputtered quartz until a film thickness of 14 nm is reached, after which it stops (Fig. 5, *b*). This indicates that the nanoparticles are completely covered with a layer of quartz and further growth of the layer does not affect the optical properties of the granular film. Similar saturable dependences were obtained for the maximum absorbance and half-width of the extinction spectrum of a granular silver film on quartz on the equivalent thickness of the sputtered quartz (Fig. 6).

Conclusion

A study of the optical properties of a heterogeneous ensemble of plasmonic silver nanoparticles at the interface of two media when this boundary moves relative to the nanoparticles themselves showed that monitoring the spectral position of the plasmonic resonance allows to determine the movement of the interface of two media with different dielectric constants relative to the plasmonic nanoparticles. However, the measured shifts in the plasmonic resonance frequency turned out to be significantly smaller than those calculated in the model of ideal spherical nanoparticles, in which the dielectric constant of the environment changes. This is primarily due to the significant dispersion of nanoparticle sizes, leading to a heterogeneous broadening of the plasmonic resonance. In addition, the shape of nanoparticles formed as a result of growth on the substrate surface according to the Vollmer-Weber mechanism is closer to truncated spheroids than to the ideal spheres for which the assessments were implemented. Therefore, to quantify the position of the interface between media from plasmonic absorption spectra, a more accurate account of the shape of nanoparticles is required.

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Conflict of interest

The authors declare that they have no conflict of interest.

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