Synthesis of gold nanoparticles by annealing its thin film under a layer of fluoropolymer coating

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Abstract. Gold thin films were deposited on the substrate of silicon and fused silica by method of Vacuum Gas Jet Deposition. Obtained films were coated with a fluoropolymer and annealed in a rarefied inert gas atmosphere at the temperature of 400 °C. The film morphology and composite were studied by the scanning electron microscopy. Optical properties of obtained coatings and composites were investigated. The influence of the fluoropolymer coating on formation of gold nanoparticles in the result of annealing of its thin films is established. The critical gold film thickness coated with fluoropolymer is determined, below which the presence of fluoropolymer lends to the formation of spherical nanoparticles during annealing of the composite in a studied range of parameters.

1. Introduction
Noble metal nanoparticles have a unique optical property – a nonlinear response to the incident radiation of the visible range of the spectrum which is known as Surface Plasmon Resonance (SPR). SPR is attractive for use in various applications, such as photovoltaics, catalysis, chemical and plasmonic sensor, production of biosensors and antibacterial coatings, etc. [1-5]. It is known that the SPR peak position and the absorption intensity strongly depend on a material, nanoparticle size, their shape, distance between them, as well as the dielectric permeability of environment in which they are included [6-8]. In addition, metal nanoparticles are very active and easily interact with the environment, losing their unique properties. One way to protect them is to place them in a matrix of different materials, in particular fluoropolymer. There are several methods for the synthesis of metal-dielectric nanocomposites, which have their own advantages and disadvantages.

The aim of the present work is to study the possibility of the metal nanoparticles formation by annealing thin films (up to 10 nm) under a layer of fluoropolymer. Gold thin films were deposited by method Vacuum Gas Jet Deposition [9]. Fluoropolymer coatings were deposited by Hot Wire Chemical Vapor Deposition (HW CVD) [10-12]. Gold nanoparticles will be isolated from the environment and preserved their unique optical properties.

2. Experimental details
2.1. Deposition of gold films
Thin gold films of different thicknesses were deposited on substrates from silicon and fused silica by method Vacuum Gas Jet Deposition (VGJD) [9]. Deposition process parameters were: the crucible’s temperature – 1300 °C, pressure of the mixture of inert gas (helium) and gold vapor – 10 Torr; helium flow rate – 9.8 sccm, the distance of nozzle-substrate - 300 mm, the nozzle’s critical section diameter 3 mm. Substrates 18 × 18 × 0.5 mm³ in size were made of silicon (100) and fused silica. The thickness of
deposited gold films was regulated by an exposure time. The gold film growth rate is 0.93 nm/min at used deposition process parameters. Thus, it took 129 s for to precipitate gold films with a thickness of 2 nm, 258 s for 4 nm and 387 s for 6 nm, respectively.

2.2. Deposition of fluoropolymer
Fluoropolymer coatings were deposited on the gold films by HW CVD method. It was thoroughly described in paper [12]. Hexafluoropropylene oxide (C₃F₆O) was used as the precursor gas. Deposition process parameters were so chosen that fluoropolymer coatings have a smooth faultless structure at conditions: the activator filament temperature 680 °C, the pressure of precursor gas 0.5 Torr, the precursor gas flow rate 466 sccm, the distance between the activator's grid and the cooled substrate holder with samples 50 mm and the substrates temperature 20 °C, the exposure time - 360 s. The thickness of the deposited fluoropolymer coating was 10 nm.

2.3. Annealing of composites
Samples with gold films and obtained composite coatings were annealed in the vacuum chamber at following conditions: annealing temperature of 400 °C, an argon pressure of 67 Pa, annealing time - 30 minutes.

2.4. Characterization technics
The morphology and elemental composition of gold films, fluoropolymer coatings and composites were examined using a JEOL JSM6700F scanning electron microscope (SEM) in the modes (secondary electrons - SE) and (backscattered electrons - BSE). In SE mode, the sample surface morphology is observed directly, while in BSE mode, the image of the elemental composition of the sample is actually constructed, where the heavy elements (Au) are displayed in light tones, and the light elements (C, F) in darker. This approach allows to study composites consisting from heavy elements covered with a matrix of light elements, as in our case. The microscope is equipped with a Quantax 200 analyzer for element composition determination by the energy dispersive X-ray spectrometer (SEM-EDS). Resulted EDX spectra were analyzed using the Esprit 2.1 software.

Optical properties of the obtained coatings and composites were investigated by optical spectrometry on using a SF-2000 device manufactured by OKB Spektr LLC (Russia). The measured spectral range is 190-1100 nm with a resolution of 1 nm.

3. Result and discussion

3.1 Morphological analysis of gold films and composites
Analysis of the morphology of gold thin films (2 nm) showed that the average size of nanostructures had not changed and was about 10 nm (figures 1a, 1b) before and after annealing. However, when annealing composites consisting of the same gold film thickness and a fluoropolymer layer, becomes average size with in of the formed nanostructures equal to 5 nm (figure 1c). This result contradicts the generally accepted experimental data namely during annealing of the nanoparticle should either increase or not change if the annealing temperature is not sufficient [8]. This result can be explained by assuming that the gold films before annealing consist not from spherical nanoparticles, but from flat discs lying on the surface. For gold films uncoated by fluoropolymer, the annealing temperature was not enough to turn the flat discs into spherical nanoparticles. However, in the case of a composite, fluoropolymer promotes the movement of gold particles between each other and spherical nanoparticles are formed. Disks with an average size of 10 nm are turned into spheres with an average size of 5 nm. This assumption was confirmed by measuring and analyzing the optical properties of obtained samples and composites presented in section 3.2.

Analysis of the morphology of thicker gold films (4 nm) showed that the sizes of nanoparticles annealed without fluoropolymer coating are slightly larger than those formed under it (figure 1e – gold film and figure 1f - composite). Similar patterns are observed in annealed gold films with a thickness of
6 nm (figure 1h - gold film, figure 1(i) - composite). The structure of films is the same and does not depend on the presence of fluoropolymer coating.

Thus, fluoropolymer coatings contribute to the formation of spherical nanoparticles during annealing of thin gold films with a thickness 2 nm. When gold films thickness is 4 nm or more this effect is not almost observed.

![Figure 1](image-url)

**Figure 1.** Morphology of gold film different thicknesses: 2 nm (a, b, c), 4 nm (d, e, f), 6 nm (g, h, i); the gold film (a, d, g); the annealed gold film without fluoropolymer coating (b, e, h) and under fluoropolymer coating (c, f, i).

3.2 Optical properties of thin gold films and composites

Optical transmission spectra of deposited gold films and obtained composite coatings are presented in figure 2. On spectra the peak of surface plasmon resonance (SPR) in the wavelength range from 500 to 800 nm are observed. For gold films with the thickness 2 nm, the peak is at a wavelength equal 600 nm, for 4 nm – 650 nm, for 6 nm – 630 nm, respectively. These peak positions are typical for thin gold films of a specified thickness [13–15]. After annealing of the gold film, the SPR peak is shifted to the shortwave region of the spectrum to 560 nm for the gold film with the thickness 2 nm (figure 2a), 600 nm for 4 nm (figure 2c) and 640 nm for 6 nm (figure 2e), correspondingly. New peak positions correspond to spherical gold nanoparticles [13, 14]. Thus, this shift can be explained by the change in the shape of nanostructures from flat disks to spherical nanoparticles during annealing.
After deposition of the fluoropolymer coating on thin gold films practically there is no shift of SPR peak to the longwave region of spectrum (figure 2c, figure 2d). However, according to results obtained in [7], the shift of SPR peak for such composites should be 10-20 nm in the longwave region of the spectrum. This behavior of optical properties is characteristic of gold films having a structure as flat discs on the dielectric surface. In this case, the fluoropolymer layer has no significant effect on SPR peak position of the gold film.

As a result of the composites annealing, the SPR peak of is shifted to the shortwave region of the spectrum by 20 nm (figure 2c and figure 2d). This shift is less than at the annealing of pure gold films. This behavior of the optical properties can be caused by the formation of gold spherical nanoparticles from flat discs in the fluoropolymer matrix. In this case, the SPR peak position is influenced by two factors: the first - the formation of the spherical nanoparticles and the second - the presence of a fluoropolymer matrix around the nanoparticles. Thus, the SPR peak shift due the formation of spherical
gold nanoparticles is compensated by the opposite shift caused by the presence of a fluoropolymer matrix around nanoparticles. Annealing of the composites consisting of gold film with a thickness 6 nm, there is a shift of the SPR peak only in the longwave region of the spectrum. This indicates that the gold film already consists of more spherical nanoparticles. In this case, the SPR peak shift is caused by the presence of a fluoropolymer around the gold nanoparticles, as shown in the work [7]. The obtained data are in the good agreement with results of the SEM analysis presented in section 3.1.

Conclusions
The possibility of nanocomposites reformation of gold nanoparticles with fluoropolymer matrix by annealing thin films was shown.

It is found that fluoropolymer coatings determine the formation of spherical nanoparticles during annealing of thin gold films with a thickness of about 2 nm. Annealing of thicker gold films (4 nm or more), changes the size of the formed nanoparticles are insignificantly.

It is confirmed that the obtained composites have SPR peak with position in the wavelength range 500-800 nm.

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