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Experimental examination of films of gold nanoparticles on Si/SiO_2 substrate by ellipsometry

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Abstract. We have investigated optical properties of films of gold nanoparticles on Si/SiO_2 substrate by using the method of spectroscopic ellipsometry in dependence on morphology of the films. Different morphology of the films was obtained by flash-annealing at various temperatures of identical sputtered thin gold layers. Ellipsometric spectra were compared with account of pictures of the films obtained by scanned electron microscopy. Remarkable dependence of depolarization of the reflected light with the frequency of localized plasmon resonance versus the film morphology was found.

Keywords: spectroscopic ellipsometry, nanoparticles, annealing, depolarization, plasmon.

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Layers of metallic particles on a surface have been attracting attention of researchers for a long time due to their peculiar optical properties [1-3]. Considerable interest to such systems is defined by the remarkable dependence of optical properties of such layers versus parameters of constituting particle and surface coverage. The former defines the individual resonant plasmonic response of constituting particles while the latter defines the collectivization of those individual properties due to interparticle interactions.

This work is aimed at investigation of layers of gold nanoparticles on Si/SiO_2 substrate. To prepare these samples, a layer of gold with the mass thickness of about 3 nm was deposited on the substrate by using magnetron sputtering. The substrate was a silicon wafer with the silica film of the thickness near 100 nm. These samples were flash-annealed at temperatures from 500 up to 800 ºC for 90 s. Films of separate gold nanoparticles were prepared using similar annealing, as it was shown by atomic force microscopy. The AFM microscope Veeco Dimension 3000 was used. The image of one film is shown in Fig. 1.

It should be noted that the lateral size of particles visible in Fig. 1 is bigger than their real size. The reason is the standard deficiency of AFM where the visible picture is the result of the convolution of the real structure of scanned object with the shape of the probe. To avoid ambiguous process of the deconvolution as well as to obtain the information about the transverse size and shape of particles, scanning electron microscopy of these samples was additionally performed.

Electron microscopy of our samples was made on the ZEISS 1540XB CrossBeam electron microscope. The cut of the sample perpendicularly to the surface is shown in Fig. 2. It demonstrates that the thickness of silicon dioxide layer is practically 100 nm, and the size of particles along the perpendicular to the surface plane is about 20-30 nm.

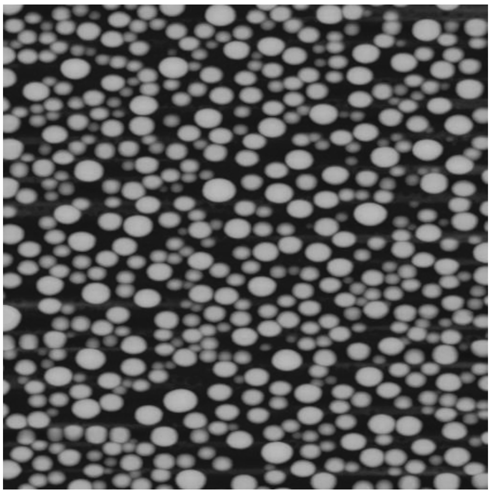


Fig. 1. AFM image of the surface with gold nanoparticles of one of annealed samples.

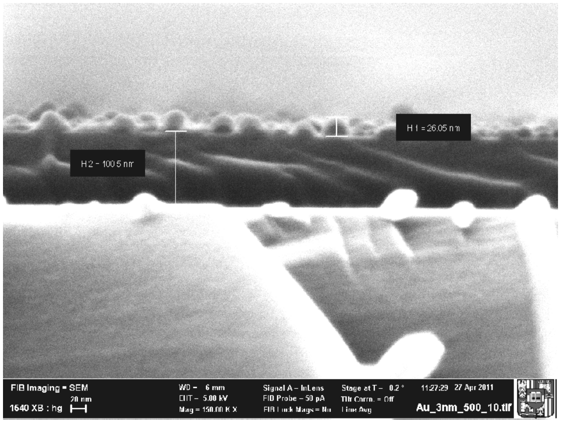


Fig. 2. Image of the profile of the sample annealed at the temperature 500 °C.

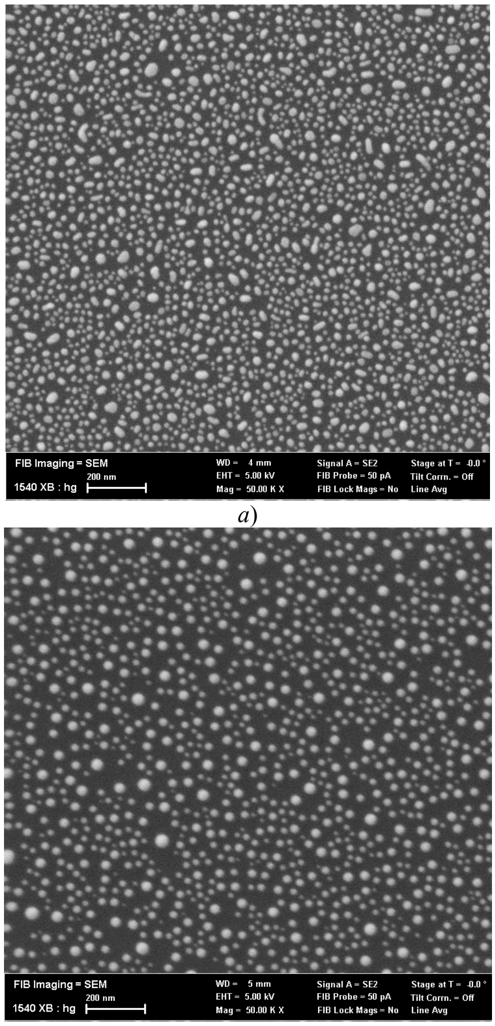
Images of the surface of samples annealed at different temperatures are shown in Fig. 3 for the magnification 50000. It is seen that the samples are heterogeneous by size of particles, which varies from few up to 50 nm.

To analyze the size and shape distribution shown in Fig. 3, 2D Fourier transformation of those images was made. The respective results are displayed in Fig. 4.

It is clearly seen that increase in the annealing temperature results in decrease of the size dispersion for the resulted particles. At the same time, the average size of particles increases.

The most of particles produced by annealing at 800 °C have the lateral size close to 20…25 nm. This size is very close to the transverse size shown in Fig. 2. It means that flash-annealing at 800 °C for 90 s produces almost spherical gold particles. The interparticle distances in this case are close to the particle sizes, as it is clear from Fig. 3. Particles produced at 500 °C have a smaller average size as seen in Figs 3 and 4. It is also noticeable in Fig. 3 that many of those particles, especially with bigger sizes, have nonround irregular forms. However, the circular symmetry of the Fourier transformation in Fig. 4 indicates that asymmetry of individual particles is random and has no preferential orientation. These facts together with bigger number of small close particles mean that formation of particles from sputtered gold layer is not yet finished for the samples annealed at lower temperatures. Films with intermediate annealing temperatures of 600 and 700 °C have particles with intermediate parameters of shape, size and location in comparison with the ones shown in Figs 3 and 4.

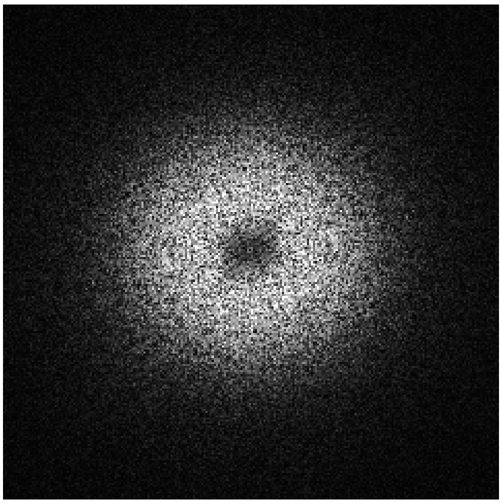
The mass thickness for all of these films is equal, so the density of particles on surface is defined only by the size of particles. As we can see, the used annealing temperatures are enough to form island films from the sputtered ones and morphology of resulted films strongly depends on the annealing temperature.



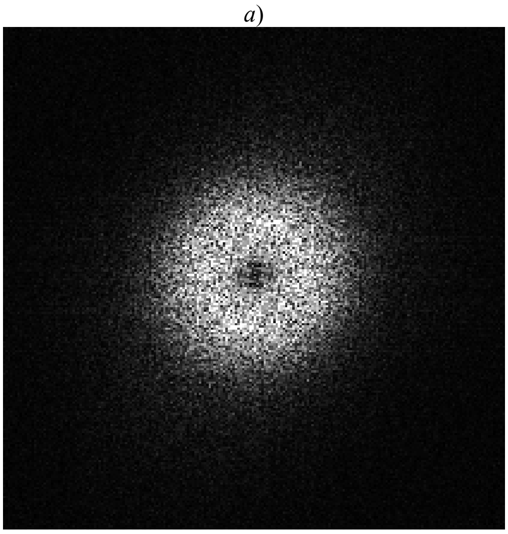
a)

b)

Fig. 3. Images of the surface of samples annealed at the temperature 500 °C (*a*) and 800 °C (*b*).



a)



b)

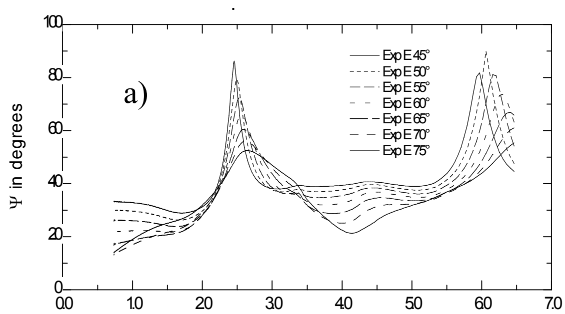
Fig. 4. 2D Fourier transformation of images of samples annealed at the temperature 500 ºC (*a*) and 800 ºC (*b*).

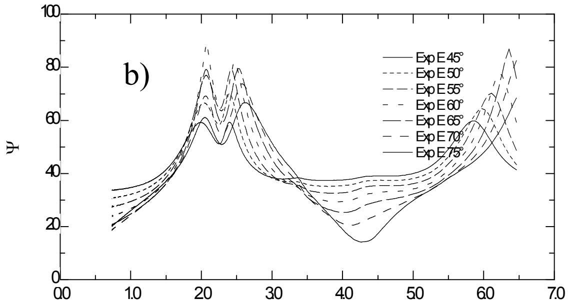
All the samples were investigated using spectroscopic ellipsometry. Ellipsometry is the sensitive method for researches of reflective surfaces and layered structures. This method is based on the analysis of changes in polarization of the incident light at its reflection from the system of interest [4].

Measurements were made on the spectroscopic WVASE and M2000 ellipsometers of Woolam Co. for different angles of incidence. Spectral range of measurements was from 0.75 to 6.5 eV. The obtained spectra have remarkable differences for different films. Fig. 5 exhibits spectra of the angle ψ measured for angles of incidence from 45° to 75° for 3 various samples, namely: initial sputtered film with no annealing and films annealed at the temperatures 500 and 800 ºC.

In all these pictures, the structure corresponding to the features of the dielectric function of Si is located in the region 3.3-4.5 eV and conceal by interference in the thick layer of silica. Both of two high peaks in the first picture correspond to interference in the oxide film, but low-energy peak is modified by the presence of a thin layer of sputtered gold. It is shown in Fig. 6.

It is seen well that the shown experimental spectra as well as spectra measured at other angles of incidence are fitted by the model with the presence of the additional completed gold layer. The thickness obtained for the oxide and gold films from this best fit are 100 nm for the oxide and 4 nm for the gold film, correspondingly. The same oxide thickness is given by the electron microscopy (Fig. 2) as the value for gold matches the thickness grown by sputtering. It is necessary to note that vacuum deposition methods usually do not ensure dense metallic covering, so some larger value given by ellipsometry in comparison to the technological parameters of the gold thickness is reliable. Also, interesting is the notice that the addition of a thing gold film visually "cut out" the low-energy side of the interference peak located within the range 2…2.5 eV.





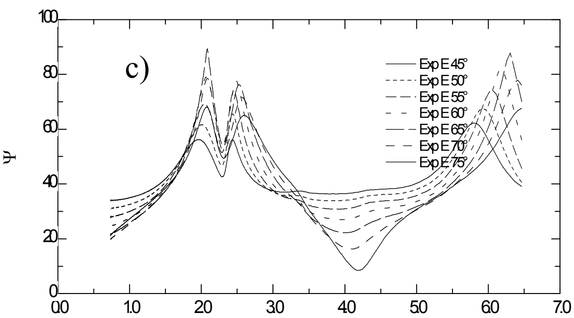


Fig. 5. Spectra of the angle ψ measured for angles of incidence from 45º to 75º for sputtered film without annealing (a); film annealed at the temperature 500 ºC (b); film annealed at the temperature 800 ºC (c).

Fig. 5 demonstrates after annealing that low-energy peak transforms into a doublet. However, the comparison of those doublets with the interference peak for the bare Si/SiO_2 structure with the oxide thickness 100 nm, like the one shown in Fig. 6, and coincidence of the width of that interference peak with the total width of the doublet reveals the other interpretation, namely: it is the one interference peak of 100-nm oxide layer modified by the absorption dip due to the excitation of localized plasmon on the layer of gold nanoparticles made from the dense sputtered gold film by annealing. Decrease in the width of that dip and slight shift of its position with increasing the annealing temperature correspond to increase in the size and shape homogeneity of nanoparticles with temperature, as it was proven by electron microscopy (Figs 3 and 4). The shift is produced by both the change in the average size of constituting particles [5] and change of interparticle interactions along with changes in their separation [6–8].

Behavior of depolarization of the light reflected by the annealed structures with nanoparticles is very interesting. Fig. 7 demonstrates experimental spectra of the angle ψ for the sample annealed at 500 °C together with the spectra of depolarization. The position of the depolarization perfectly matches the position of the localized plasmon resonance. Moreover, pronounced depolarization at that frequency remarkably decreases with increasing the annealing temperature and practically vanishes for the sample annealed at 800 ºC. It means that decrease in inhomogeneity of the system decreases depolarization of the reflected light.

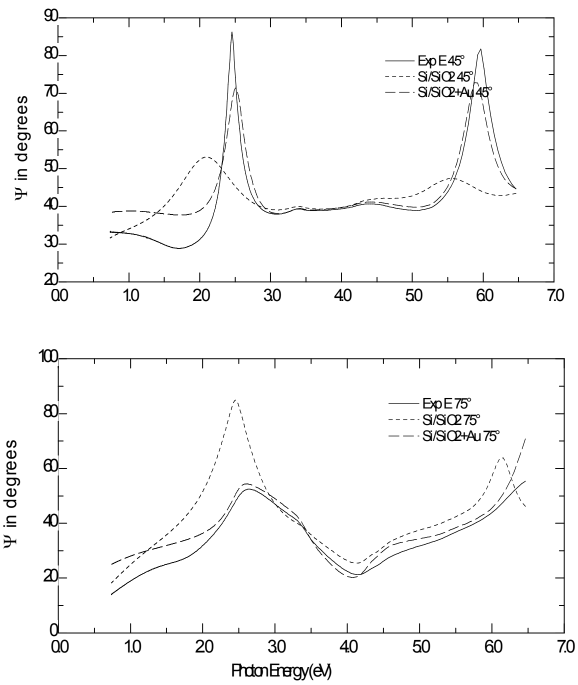


Fig. 6. Experimental spectra of the angle ψ for angles of incidence of 45º and 75º for the sample without annealing (solid) and simulated curves with the best fitting for a bare Si/SiO_2 substrate (dotted) and for Si/SiO_2 substrate with a thin film of gold (dashed).

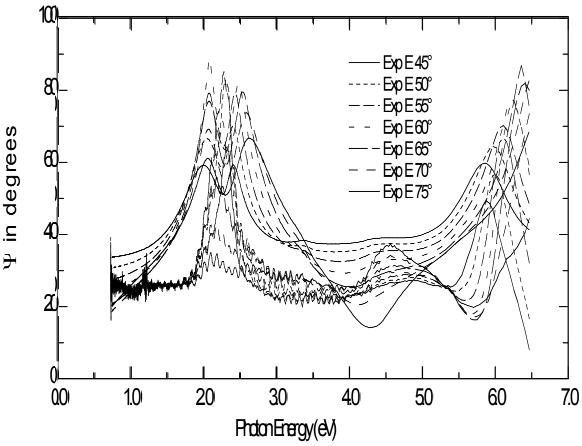


Fig. 7. Experimental spectra of the angle ψ for the film annealed at the temperature 500 ºC with the spectral behavior of the depolarization.

However, heterogeneity of the size and the separation of particles only decrease while the depolarization disappears almost completely. The only visible parameter that behaves in the same way is the shape of particles. All the particles of the film annealed at 800 ºC are practically spherical, while the variety of the particle shape in the film annealed at 500 °C is clearly seen in Fig.3. At the same time, the peak of depolarization is very sharp and coincides with the position of plasmon resonance. It indicates that it is the plasmonic interparticle interactions, which plays the main role in depolarization of the reflected light.

We can suppose that there is a resonance energy transfer between particles like the Förster one [9] due to dipolar interparticle interactions. The strength of this process is in proportion to the involved dipolar moment and in inverse proportion to the sixth power of interparticle separation [9]. It is the resonant plasmonic enhancement of the dipolar moment of constituting nanoparticles, which produces so sharp change in depolarization around the plasmonic resonance. However, in the case of spherical particles dipolar excitation with the same frequency localized on the particle-recipient has the same direction as on the particle-emitter, as it is disoriented in the case of irregular arbitrary shapes of particles. Since this Förster energy transfer process is incoherent, disorientation of the polarization of light reemitted by relaxed plasmons will be recorded as depolarization of the light reflected by the system.

Conclusions

Films of gold nanoparticles prepared on Si/SiO_2 substrate by magnetron sputtering of gold and then flash-annealled at the temperatures between 500 to 800 ºC for 90 s were investigated. As it has been shown, morphology of those films strongly depends on the temperature of annealing. The higher annealing temperature gives almost spherical particles. Ellipsometric measurements demonstrated high sensitivity to morphology of these films exhibiting differences that can be attributed to changes in size, shape and concentration of particles, as it is clearly seen in pictures obtained using scanning electron microscopy. Found depolarization of the reflected light at the frequency of localized plasmon excitation opens the possibility to investigate local interparticle interactions by monitoring macroscopic properties of light in far field.

Acknowledgments

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