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Influence of Annealing on the Structure of Ultrathin Gold Films on the Surface of Glass and CdS Substrates

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The influence of annealing process on the structure of ultrathin gold films on the surfaces of glass substrates and substrates of CdS is investigated. The formation of nanoparticle arrays as a result of annealing the films on the glass surface was revealed, and analysis of average radii dependence for the formed particles on initial thickness of the film was carried out and shape of the particles analyzed. For annealed Au films on the surface of CdS, the destruction of the film for its initial thickness of 0.5 and 1 nm was noted, and small changes in the surface morphology for thicker films were observed. On the basis of elemental analysis, assumptions about the causes of such temperature behavior of films are made.

Keywords: Thin films, Annealing, Au, CdS, Scanning electron microscopy, Nanoparticles, Distribution by size.

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1. INTRODUCTION

The noble metal usage in modern technologies of thin films as well as in the process of manufacture of nanoparticles and quantum objects, caused by remarkable physical and chemical properties of these metals, which practically do not undergo oxidation, allow to improve the photocatalytic properties of traditional materials [1, 2], provide reliable contacts in integrated circuits [3], and due to the phenomenon of plasmon resonance in thin films and arrays of nanoparticles can significantly increase the light absorption in the working region of the electronic devices [4, 5]. Among the possible methods for ultrathin metal film deposition on the surface of dielectric and semiconductor substrate there is the method of magnetron sputtering [6]. The application of modern precise methods for controlling the thickness of applied coatings makes it possible to form a thin film on this substrate surface with an accuracy of thickness less than 0.1 nm. The disadvantage of the method of deposition is often the amorphous nature of the formed film. Temperature annealing under different atmospheric conditions substantially changes the properties of coatings, promoting the film recrystallization, but, due to the poor adhesion, it can lead to the film exfoliation, local melting and coagulation into separated droplets [7]. Both scenarios can be useful for various film coatings on different substrates. And depending on the initial thickness of the gold films and the temperature conditions as well as the duration of annealing, both a solid film and a film with transition through a percolation barrier can be obtained. There are still a few works devoted to the study of the annealing of ultrathin noble metal films formed on the dielectric and wide bandgap semiconductor substrate [8, 9]. In our paper we investigated the morphology of surfaces of annealed gold films on glass substrate and CdS substrate and analyzed the reasons for the change in the surface structure.

2. DESCRIPTION OF OBJECTS AND METHODS OF INVESTIGATION

Deposition of ultrathin gold films was performed by vacuum magnetron sputtering on the COM-TH2-SP2-ION system of TORR International installation (USA) on glass/ITO/CdS substrates, and optically homogeneous glass substrates. Glass plates with dimensions 16 × 8 × 1.3 mm were immersed into a freshly prepared etchant (1: 1: 1: 1 redistilled water: H_2SO_4 95 %: H_2NO_3 95 %: HF 95 %) for 3 min. It was rinsed repeatedly in redistilled water, and later the plates were rinsed with ethanol and dried under nitrogen flow.

The deposition of Au occurred at the substrate temperature of 423 K. The target-substrate distance was 150 mm. The rate of deposition was 0.1 nm/s. Control of thickness and rate of deposition was carried out by a quartz sensor SQC-330. Four sample series with different thicknesses of the initial gold film (0.5 nm, 1 nm, 2 nm, and 3 nm) were obtained. Thermal annealing of the Au films was carried out in an air atmosphere for 120 minutes at a temperature of 683 K.

CdS films (about 100 nm in thickness) were deposited on an ITO coated glass slides (Nanoes USA) with dimensions of 16 × 8 × 1.1 mm. The thickness of ITO was 320 nm. Again for the formation of CdS thin films, the method of high-frequency (13.6 MHz) magnetron sputtering was used. A single crystal in the form of disk with diameter of 40 mm and with a purity of 99.999 % was used as target. The residual gas pressure in the working chamber was 6.7×10^{-4} Pa. For the substrate heating a tungsten heater with a power of 300 W was used. The thin films were deposited at a substrate temperature of 423 K. The temperature control was carried out by the controller for monitoring the heating speed, cooling rate and release time. The deposition time was 5 minutes, the power of the high-frequency magnetron was about 30 W, and the argon pressure in the working chamber was 1.0 Pa. The distance between the target

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and the substrate was 60 mm. The film thickness was measured with a Veeco Dektak 8 profilometer. The average rate of film deposition was 0.3 nm/s.

Ultrathin films of gold on the CdS surface were deposited by magnetron sputtering again on the same TORR International installation at a substrate temperature of 423 K. The deposition rate was 0.1 nm/c. The film thickness was controlled by a quartz resonator SQC-330 with an accuracy up to 0.5 %. As for the case of gold on glass samples, four different sample series were made on the CdS surface with initial thickness of gold films (0.5 nm, 1 nm, 2 nm, and 3 nm). The sample annealing was carried out for 2 hours at a temperature of 683 K and at normal atmospheric pressure.

The study of the surface morphology for the samples with arrays of gold nanoparticles on the glass substrate and annealed gold films on the surface of CdS was performed by scanning electron microscope Hitachi SU-70 with a built-in microanalyzer and by a field emission scanning electron microscope JEOL JSM-6700F. Analysis of the distribution of gold particles on the surface of the glass substrate was carried out in the software package ImageJ. Only particles with an ellipticity of 0.6 to 1 were taken into account. In addition, individual particles that merged as well as the parts of images with distortions related to accelerating voltage jumps were excluded from the analysis.

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

For all samples with different thicknesses of gold films, deposited both on glass and on CdS, the films were homogeneous and without ruptures. The annealing significantly changed the surface morphology and revealed the dependence of its results on the initial thickness of the films.

3.1 Analysis of Gold Films on Glass After Aannealing

After annealing, as a result of film destruction and coagulation, the arrays of gold nanoparticles formed on the surface of glass substrates. Similar results we already have obtained for thicker gold films [7].

The images of gold nanoparticles on the surface of glass substrates obtained with an electron microscope are characterized by a sufficiently high quality, with a clear distinction between individual nanoparticles (Fig. 1), but in some photographs there are streaks due to charge accumulation on the surface of the samples and voltage jumps.

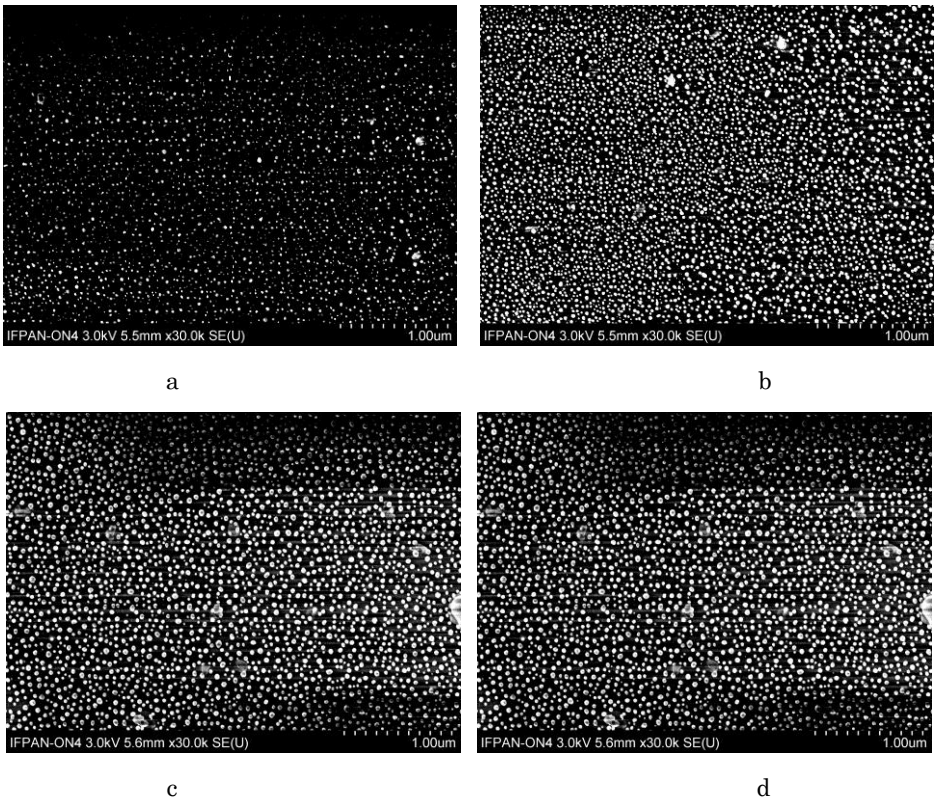

Fig. 1 – SEM images of gold nanoparticles on the surface of glass substrate for samples with initial thickness of the deposited film (a) 0.5 nm, (b) 1 nm, (c) 2 nm, and (d) 3 nm

The analysis of size distribution for gold particles was carried out in the ImageJ program, and then the distribution histograms were constructed and their maxima determined. For all sample series, the size distribution is close to normal (Fig. 2). With the increase

in the initial thickness of the film, the maxima of the distributions move toward larger particles and, in general, particles of increasingly large size appear on the surface.

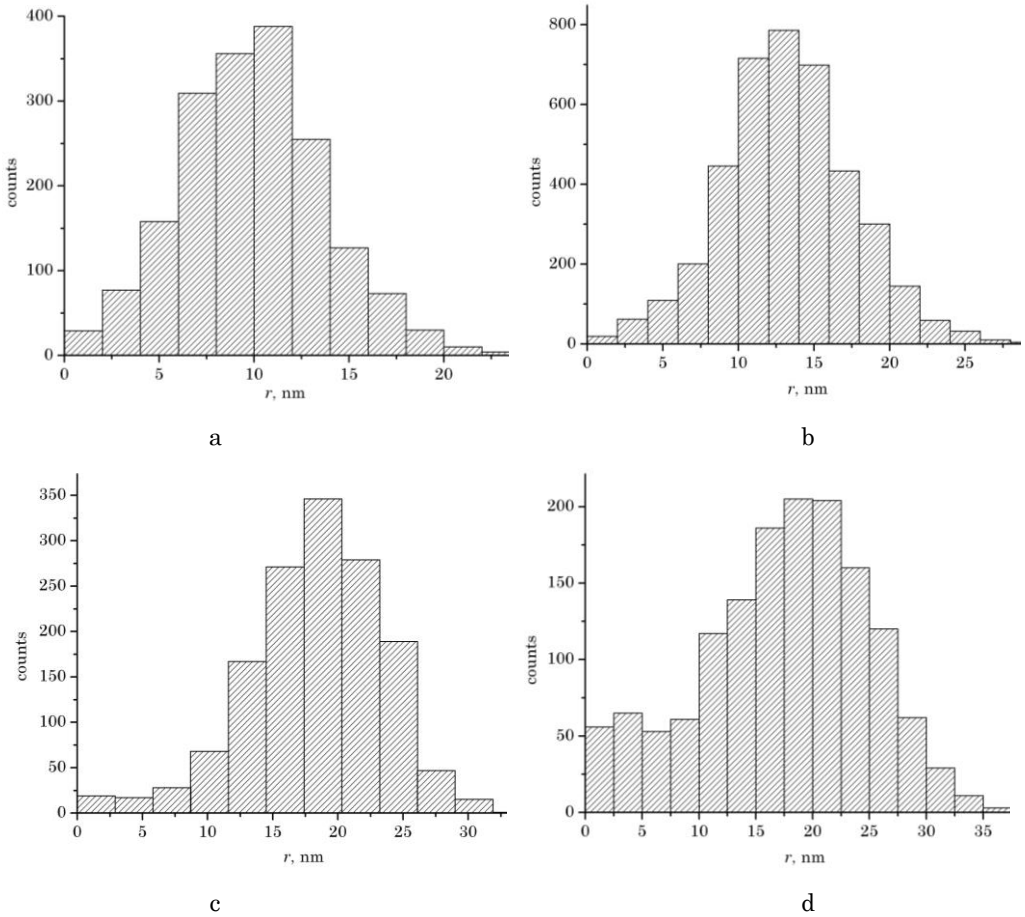

Fig. 2 – Distributions by size of gold nanoparticles on the surface of glass substrate for samples with initial thickness of the deposited film (a) 0.5 nm, (b) 1 nm, (c) 2 nm, and (d) 3 nm

After the heat treatment of the thinnest films, the particles in the distributions have the smallest dimensions. The largest number of particles per histogram has a radius of about 11 nm. The obtained distribution has the shape close to the Gaussian curve. According to the data of ImageJ, the average particle radius was 9.8 nm. Error of computing was 10 %.

On a histogram for the arrays of nanoparticles formed by the annealing of samples with gold films of thickness $D = 1.0$ nm, there are practically no particles with large radii. The resulting distribution also has a shape close to the Gaussian distribution. According to the ImageJ data, the average particle radius was 15.0 nm. Error of computing was 6 %.

For particles formed by the annealing of films of thickness $d = 2.0$ nm, unlike the two previous series of samples, the number of particles on the histogram with a large radius and their average size increases. According to the ImageJ data, the average particle radius was 18.0 nm. Error of computing was 14 %.

For an array of nanoparticles, obtained by annealing the samples with gold films of thickness $d = 3.0$ nm, the average particle radius was 19.1 nm. Error of computing was 17 %.

The graphic dependence of average radius of a gold nanoparticle on the initial thickness of the film is given in Fig. 3. The resulting graph can be approximated by the Boltzmann curve (shown by solid line in Fig. 3), which corresponds to the equation:

$$R = C_1 + \frac{C_2}{1 + \exp(\frac{d - C_3}{C_4})},$$

where $C_1 = 19.10637$, $C_2 = -305.20621$, $C_3 = -16.55749$, $C_4 = 6.22477$.

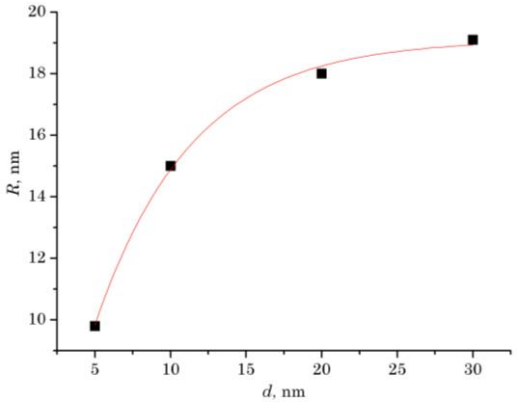

Fig. 3 – Dependence of average radius of gold nanoparticles on the surface of glass substrate on the initial thickness of gold film

The shape of nanoparticles that are formed on the surface after annealing has become the object of our further analysis. We proceeded from the basic assumption that the particles have the shape of oblate spheroid. We calculated the average half-height of the nanoparticles. The volume of the gold film deposited on the surface of glass substrate was calculated by the formula:

$$V_G = xyh, \quad (1)$$

where x, y are the geometric dimensions of SEM image region, h is the height of the deposited gold film.

We believed that gold deposited homogeneously and did not have air gaps. On the other hand, from the analysis of microscope images, the total volume of gold in the region of annealed sample, shown in the image:

$$V_G = NV_1, \quad (2)$$

where N is the number of particles; $V_1 = (4/3)\pi a^2 c$ is the volume of spheroidal particle, a and c are spheroid semiaxes. If we assume that gold does not sublimate, then, taking into account the previous formulas, the final formula for half-height of a nanoparticle will have the form:

$$c = \frac{3V_G}{4\pi R^2 N}, \quad (3)$$

where $R = a$ is the mean particle radius in z-section.

By formula (3), we determined the values of semiaxes of spheroidal particles oblate in z-direction for particles formed by the annealing of gold films with different initial thickness (Table 1).

Table 1 – Parameters of spheroidal particles

Initial gold film thickness	Parameters of spheroidal particles	
***d*, nm**	***a*, nm**	***c*, nm**
0.5	9.8	5.4
1.0	15.0	3.7
2.0	18.0	6.2
3.0	19.1	10.0

3.2 Analysis of Gold Films on CdS After Annealing

Annealing of gold films on the surface of CdS under the same conditions as the annealing of films of similar thicknesses on the glass surface did not allow the formation of arrays of nanoparticles (Fig. 4). For the smallest thicknesses of the films, the annealing results in partial exfoliation and destruction of the films, for films of greater thickness, the appearance of sites with openings is observed, and for films of thickness greater than 2 nm we observed only some distortion of the initially homogeneous deposited films.

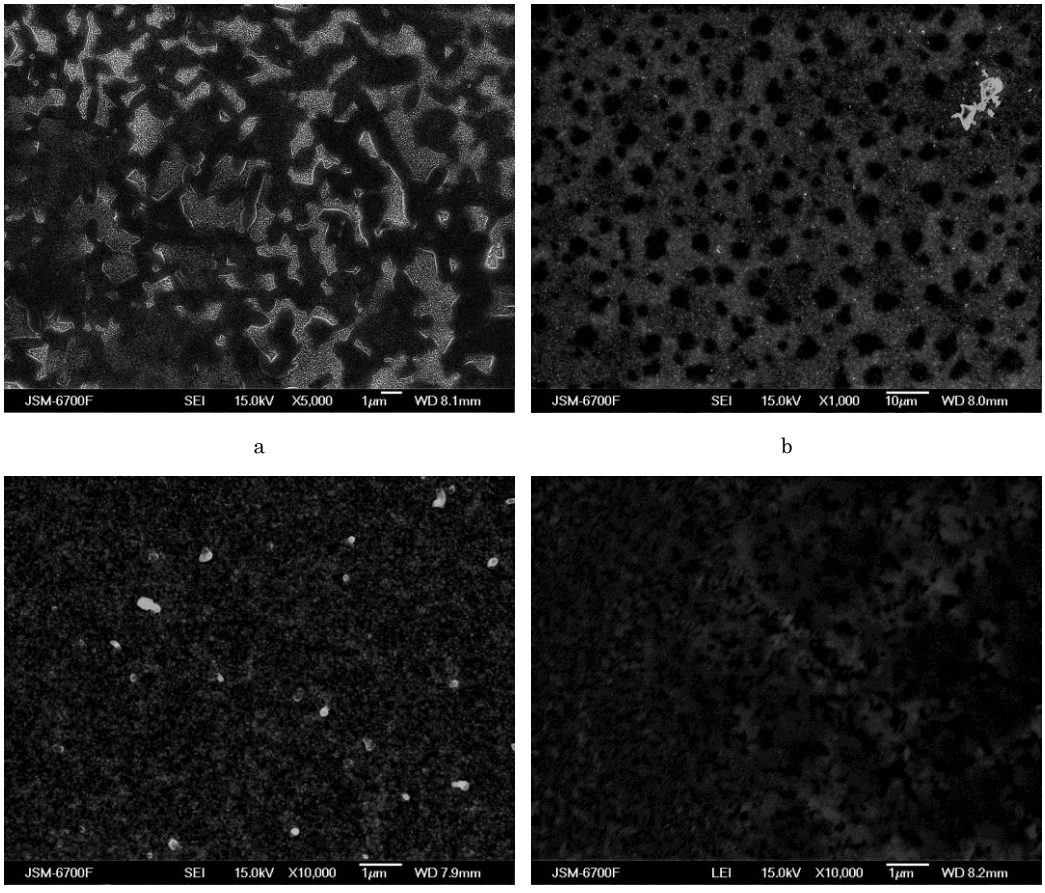

Fig. 4 – SEM images of gold films on the CdS surface for samples with initial thickness of deposited gold film (a) 0.5 nm, (b) 1 nm, (c) 2 nm, and (d) 3 nm.

To clarify such different behavior of the gold film on the CdS surface, we carried out the elemental analysis for different areas of the annealed samples with an initial film thickness of 0.5 nm. The analysis was carried out in the region of the island gold film (region 1 in Fig. 5), and outside, where the texture of the CdS film (region 2) is visible.

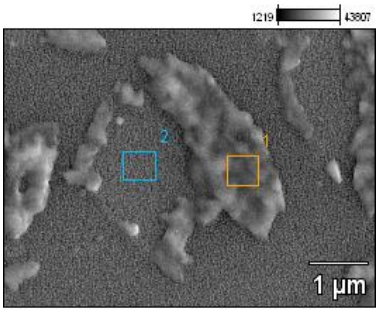

Fig. 5 – The regions of elemental analysis

Microanalysis by elements showed that a significant difference in the chemical composition of the two different regions consists in excess of cadmium in the region with island film. Since microanalysis is carried out at depths up to several microns, even if there was an excess of cadmium in the film, this would have a negligible effect on the total percentage content of the whole region volume. However, taking into account that Cd is a more volatile component of the compound, and the gold film prevents its escape during the annealing, the differences in the content of Cd become clear. Situation with content of sulfur is something different. The differences in composition of sulfur for the two regions give the result that exceeds the measurement error, and therefore in the first region, in fact, there is more sulfur. This excess of sulfur can form complexes with gold, greatly improving adhesion properties for structure of gold film at CdS substrate due to the affinity of sulfur ions with gold. As a result, the film adheres sufficiently to the surface of the CdS substrate and the energy supplied to the film by annealing is not enough to overcome the adhesion forces.

Table 2 – Mass content of elements in the investigated regions (%)

	O-K	S-K	Cd-L	Au-M
1	29.6	3.5	16.3	1.9
2	31.5	2.5	8.6	2.0

Table 3 – Atomic content of elements in the investigated regions (%)

	O-K	S-K	Cd-L	Au-M
1	48.3	2.9	3.8	0.3
2	47.1	1.8	1.8	0.2

Surprisingly, for thicker gold films and more gentle annealing regimes [10, 11] we have obtained the arrays of nanoparticles, presumably of gold, that can be reasoned by shorter time of thermal treatment.

4. CONCLUSIONS

The method of high-frequency magnetron sputtering with further film annealing is an effective way of formation of gold nanoparticle arrays on the glass surface using a "top-down" method. In this case, the array of nanoparticles, which have the form of oblate spheroids, is characterized by sufficiently narrow size distribution. Changing the initial thickness of the deposited film, it is possible to obtain the required average sizes of gold nanoparticles in a sufficiently wide radius range from several to several dozen nanometers. The obtained results can be directly used in devices operating on the phenomenon of plasmon resonance. Annealing of ultrathin gold films on the surface of CdS leads only to a partial exfoliation of the thinnest gold films, and for films of thickness 2 nm or more only small changes in the morphology of their surface are observed. In our view, this behavior of the film during annealing is due to the formation of gold and sulfur complexes, which will probably allow this approach to be used when creating organic solar cells with the inclusion of a CdS layer with gold to enhance the structure photocatalytic properties.

Вплив відпалювання на структуру ультратонких плівок золота на поверхні підкладок із скла та CdS

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Досліджено вплив відпалювання на структуру ультратонких плівок золота на поверхнях скляних підкладок і підкладок з CdS. Виявлено утворення масивів наночастинок при відпалі плівок на поверхні скла, проведено аналіз залежності середніх радіусів утворених частинок від початкової товщини плівки та проаналізовано форму частинок. Для відпалених плівок на поверхні CdS зауважено руйнування плівки для її початкової товщини 0.5 та 1 нанометрів, та зафіксовано малі зміни морфології поверхні для товщих плівок. На базі елементного аналізу зроблено припущення про причини такої температурної поведінки плівок.

Ключевые слова: Тонкі плівки, Відпалювання, Au, CdS, Сканувальна електронна мікроскопія, Наночастинки, Розподіл за розмірами.

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