Chemical surface growth and physical properties of the Au nanoparticles array on glass slides

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Gold nanoparticle array on pretreated glass substrates was fabricated by chemical surface growth from the $AuCl_3$, CH_2O and Na_2CO_3 components in aqueous solutions mixture. Transmission, absorption and reflectivity spectra were measured with an UV-Vis spectrophotometer. A change in plasmon maximum absorption position depending on the growth conditions was investigated. The surface morphology was studied by atomic force microscopy. The statistical analysis of the heights, particles diameter and image cross-sections was carried out by scanning probe microscopy methods and the Au NPs size dependence on the growth time was experimentally determined. The results of this paper will contribute to the optimization of plasmonic CdS/CdTe solar cell.

Keywords: *Au NPs; chemical growth; surface morphology; optical properties*

1. Introduction

Nowadays, numerous methods of Au nanoparticles (NPs) fabrication are known. Some of them are recognized since ancient times but most of them were developed in the past two decades [1, 2]. The top-down nanotechnology approach of the Au NPs fabrication is represented by well controlled expensive methods like lithography [3] and less controlled inexpensive thermal annealing of thin films [4]. The bottom-up approach is represented by quite well controlled inexpensive wet-chemical methods [5].

Growing interest in NPs is caused by a number of potential applications and photovoltaics [6, 7] is one of most important among them. The NPs utilization in solar cells (SC) has several technological requirements: it must be easily added to one of the solar cell layers and should not initiate its composition changes. It should not also introduce

additional organic layers that could negatively affect the electric performance of SC.

The purpose of our study was to chemically grow the Au NPs array without any organic compounds, directly on the top of an optically transparent dielectric substrate in order to apply this method for the CdS semiconductor thin film. Cadmium sulfide thin films ($\leqslant$100 nm) are recognized as the best buffer layer for the commercial thin film SC based on the CdTe and the $CuIn_xGa_{(1-x)}Se_2$ absorbing layer.

2. Experimental

The Au NPs array was chemically deposited from a mixture of $AuCl_3$, CH_2O and Na_2CO_3 aqueous solutions on the pretreated 22 mm × 26 nm × 2.2 mm glass slides. The substrate was covered by 300 μL of working solution for 0.5 min to 2 min and rinsed in distilled water to prevent precipitation of NPs in the solution volume. Post deposition (400 °C, 1 h) annealing was performed to evaporate water residuals and improve NPs adhesion.

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The surface morphology was investigated by atomic force microscope XE-70 Park System (Park, South Korea). The measurements were carried out in a semi-contact mode of operation at a scanning frequency of 1 GHz using a silicon NSG 10 A probe with the curvature radius of 10 nm. All experiments were performed in the air ambient. Experimental data processing and calculation of surface morphology parameters were performed by Gwyddion 2.45, free data analysis software.

Transmission R(λ) and reflectivity R(λ) spectra of the samples in the wavelength range from 300 nm to 1100 nm with a 5 nm step were measured by the spectrophotometer Bentham PVE 300 (Bentham, UK). Absorption spectra were calculated using the equation $-\log(T(\lambda)/100)$. Reference spectra were measured for the glass plates identical to the substrates.

3. Results and discussion

The optical absorption and reflectivity spectra of the deposited Au NPs array on glass (Fig. 1) clearly show the presence of the surface plasmon absorption peak localized in the 500 nm to 800 nm wavelength range which confirms the growth of the gold NPs. Plasmon absorption maximum of Au NPs array with 40 s deposition time is observed at 610 nm. The absorption curve 1 shown in Fig. 1a is typical of ~20 nm ultrathin continuous gold films and densely packed NPs array [4]. The absorption maxima of the Au NPs array with longer deposition times (60 s to 120 s) are down-shifted to the narrow region of wavelengths 530 nm to 555 nm. Nonlinear time dependence of peak positions and changes in the curves shape can be explained by considering time evolution of the sample surface morphology parameters, NPs average diameter and height, presented underneath. For curves 2 to 4 shown in Fig. 1a one can notice the deposition time dependent increase of both the plasmon absorption intensity and the half-width of the plasmon absorption peak. The experimental spectrum broadening might be caused by the particle dimension distribution changes.

Reflectivity spectra were acquired with the integration sphere. The plasmon reflectivity maxima of the Au NPs array are up-shifted by 19 nm to 32 nm in comparison to corresponding absorption maxima.

It should be noted that the peaks positions, shape of absorption and reflectivity curves 2 to 4, Fig. 1a and Fig. 1b, are in accord with the data characteristic of Au NPs fabricated by more sophisticated methods [3–5, 8].
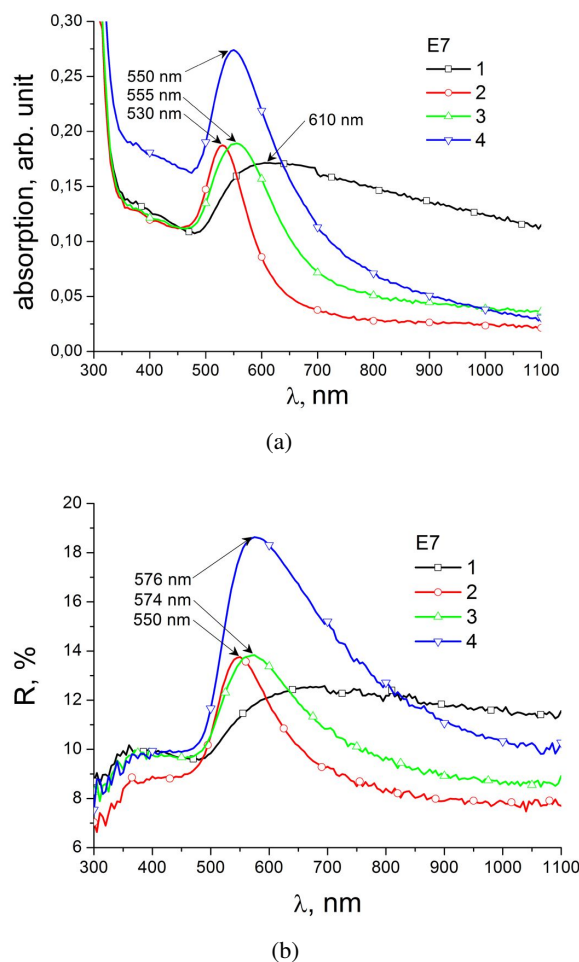

(a)

(b)

Fig. 1. Absorption (a) and reflectivity (b) spectra of the Au NPs arrays with 40 s (1), 60 s (2), 90 s (3) and 120 s (4) deposition time.

The AFM images of the samples are shown in Fig. 2. Pretreated glass slide surface was smooth without big grains or grain aggregates of microdefects. The images confirm formation of the Au NPs
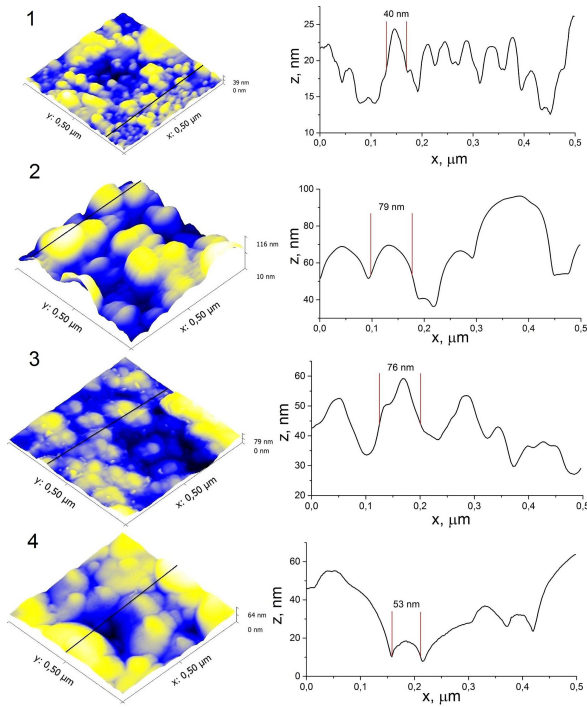
Fig. 2. Three-dimensional AFM-images and the surface cross-sections of the Au NPs arrays with 40 s (1), 60 s (2), 90 s (3) and 120 s (4) deposition time.

array which consists of NPs with various shapes and sizes. The statistical analysis of the heights, particles diameter and image cross-sections was carried out by the scanning probe microscopy methods.

The parameters of the film surface morphology, such as the average height above the zero point of the surface Z_{ave} and the root mean square roughness R_{ms} were determined and collected in Table 1. Additionally, the statistical analysis of the images was performed. The height and diameter distributions (Fig. 3) as well as the average diameter (D_{ave}) and height (H_{ave}) of the NPs were determined and are given in Table 1. NPs centre positions in the longitudinal and transverse directions were determined and were found to be linear. It means that the NPs distribution in the plane is uniform.

The 40 s deposition time resulted in the array of the NPs with a broad distribution of heights from 50 nm to 200 nm with the average height of 120 nm

Table 1. Optical and morfolgical parameters of the Au NPs arrays.

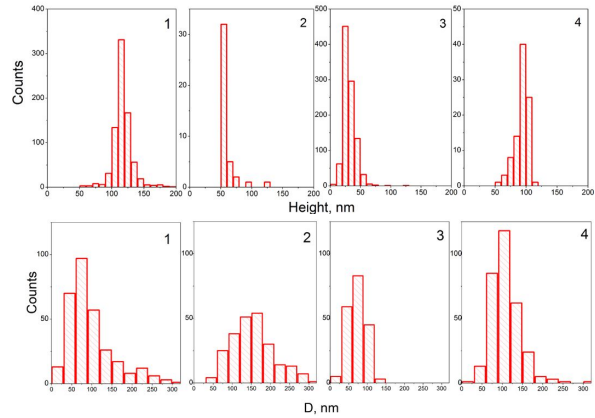| Sample	λ^{abs}_{max} [nm]	λ^{R}_{max} [nm]	Z_{ave} [nm]	R_{ms} [nm]	D_{ave} [nm]	H_{ave} [nm]
0*			25±3	8±1	−	25
1	610	642	112±3	19±1	75	120
2	530	550	67±3	18±1	150	50
3	555	574	128±4	33±2	80	30
4	550	576	104±3	30±2	120	100

*glass substrate

Fig. 3. Bar charts of height (H) and diameter (D) distribution of the Au NPs arrays with 40 s (1), 60 s (2), 90 s (3) and 120 s (4) deposition time.

and broad distribution of diameters from 10 nm to 350 nm with the average diameter of 75 nm (Fig. 3(1)). The AFM-image of the sample and its cross-section (Fig. 2(1)) reveal that the surface is decorated with several large area particles and multiple small coalesced particles with D = 10 nm to 80 nm. Broad size distributions and possible interaction between small NPs are the reasons of the broad plasmon absorption and reflectivity peaks.

The deposition time increase to 60 s results in narrowing of the height distributions, doubling of the average diameter and smaller average height as well as the narrow plasmon absorption and reflection peaks. The decrease of the NPs height is rather due to the AFM tip limiting factor because the value of Z_{ave} also decreases (Fig. 4) instead of anticipated obvious increase. Formation of densely packed array of separated NPs,
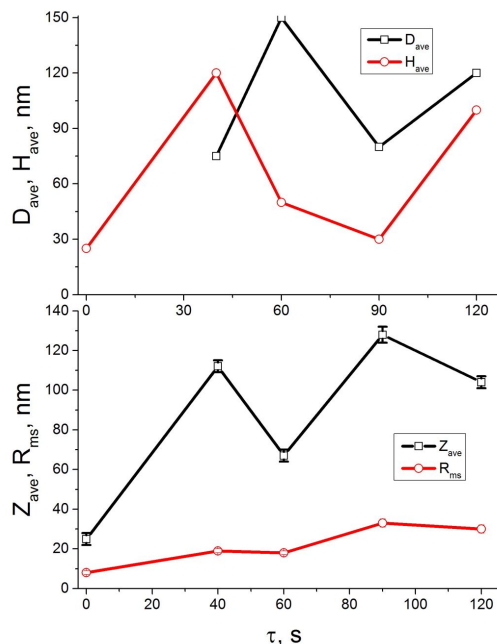
Fig. 4. Time evolution of the Au NPs average diameter (D_{ave}) and average height (H_{ave}), Au NPs decorated surface average height (Z_{ave}) and the root mean square roughness (R_{ms}).

broadening of the plasmon absorption peak and red-shift of its maximum is observed for the 90 s deposited sample (Fig. 2(3)). The 120 s deposition time results in the array of the NPs with narrow distribution of heights 50 nm to 120 nm and diameters 10 nm to 220 nm with the average $H_{ave} = 100$ nm and $D_{ave} = 120$ nm values, similar to that for the sample with 40 s deposition time. The AFM-image of the sample and the cross-section (Fig. 2(4)) reveal that the rough surface is decorated with small particles with D = 50 nm to 80 nm. The plasmon absorption and reflectivity peaks broadening and intensity increase (Fig. 1(4)) can be explained by the effective thickness increase of the NPs array.

By taking into consideration optical properties and results of surface morphology analysis we can assume the following sequences of the NPs growth (with increasing deposition time): (1) the NPs growth on a glass substrate at the chemically active places and creation of a densely packed NPs array; (2) NPs sizes enlarging and developing;

(3) further NPs sizes enlarging and coalescence; (4) growth of the next NPs on the top of already settled deposit.

4. Conclusions

In this paper, we have shown the possibility of formation of gold NPs array on glass substrates by the method of chemical surface growth. According to the AFM data, Au NPs array consists of spheroids with a mean diameter of 75 nm to 150 nm and a mean height of 30 nm to 120 nm, depending on the growth time.

The conditions of chemical deposition of the Au NPs array with 150 nm and 50 nm average diameter and height, respectively, and plasmon absorption and reflectivity maximum at 530 nm and 550 nm correspondingly were identified.

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