

Research Article

Grafting of Gold Nanoparticles on Glass Using Sputtered Gold Interlayers

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Three-step preparation of nanostructured Au layer on glass substrate is described. The procedure starts with sputtered gold interlayer, followed by grafting with dithiols and final coverage with gold nanoparticles (AuNPs). Successful binding of dithiols on the sputtered Au film was confirmed by X-ray photoelectron spectroscopy measurement. AuNPs bound to the surface were observed using atomic force microscopy. Both single nanoparticles and their aggregates were observed. UV-Vis spectra show broadening of surface plasmon resonance peak after AuNPs binding caused by aggregation of AuNPs on the sample surface. Zeta potential measurements suggest that a large part of the dithiol molecules are preferentially bound to the gold interlayer via both –SH groups.

1. Introduction

Controlled formation of metal nanostructures on solid surfaces is being very extensively studied. Isolated nanoparticles bound to flat surfaces show properties that are very different from bulk material. The specific properties make nanoparticles promising for applications in many different areas such as microelectronics, optoelectronics [1], preparation of biosensor devices, or medicine [2–4]. In modern analytical methods, surface-enhanced Raman scattering and surface plasmon resonance (SPR) sensing (both using nanostructured metal surfaces) draw great attention. Various methods were employed to prepare suitable nanostructures. Treatment of the substrate surface with different agents with the aim of improving its reactivity for subsequent modification by various organic compounds followed by coating with gold nanoparticles (AuNPs) has been investigated [5, 6]. Another approach is to modify the surface of the particles themselves to facilitate their interaction with substrates [7]. Sputtering, thermal, and e-beam evaporation methods of thin film preparation combined with postdeposition thermal treatment have been used to fabricate nanoisland-like structure of Au on

substrates [8, 9]. Other methods comprise forming of self-assembled monolayers [10] or laser ablation/gas deposition [11].

This work focuses on binding of AuNPs on smooth Au layer rather than structuring the thin gold layer itself (Figure 1). For potential applications, uniformity of AuNPs coverage over the substrate surface is very important. According to some previous studies smooth Au surfaces can be covered with highly organized structures of reactive organic compounds like dithiols. The surface treated in this way may facilitate subsequent grafting with AuNPs. In this study octane-1,8-dithiol with two –SH groups in molecule is used to mediate binding of AuNPs to underlying gold layer deposited on glass substrate. The resulting surface structure and its properties were characterized by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), electrokinetic analysis, and UV-Vis spectroscopy.

2. Materials and Methods

Borosilicate microscopic cover glass $15 \times 15 \text{ mm}^2$ supplied by Menzel-Gläser was used as a substrate for deposition. Glass

was cleaned with methanol (p.a.) and dried in a stream of N_2 . The quality of the glass surface was controlled by AFM (see AFM scan of clean pristine glass slide in Figure 1). Au layer was deposited by sputtering from Au target of 99.95% purity (supplied by SAFINA a. s.) on Balzers sputter-coater SCD 050 device. Chamber was evacuated to a pressure lower than 1 Pa; then sputtering was accomplished at Ar work gas pressure of 6 Pa. Electric current between electrodes during deposition was 20 mA. The deposition times 20 and 200 s were chosen. According to our previous study [8] at shorter deposition time, a gold layer comprising isolated gold islands is produced. For longer deposition time the islands become interconnected and homogenous gold coverage is formed. Gold layers prepared by this method were proven by X-ray diffraction to have high ratio of (111) orientation on substrate [12]. This is supposed to support formation of organized regions of bound dithiols [10].

Samples with Au films were immersed in 10^{-3} mol·dm $^{-3}$ methanol solution of octane-1,8-dithiol (ODT) for 24 hours. After ODT treatment the samples were cleaned with methanol to wash off excessive dithiol molecules that did not form covalent bond with the surface. To graft samples with AuNPs the samples were immersed for 24 hours into freshly prepared gold colloid solution (concentration of 0.05 g·dm $^{-3}$, citrate reduction [13, 14]). Control measurements show that the AuNPs are about 20 nm in diameter (Figure 1). Finally, samples were cleaned with methanol again to wash off excessive AuNPs.

AFM measurements were carried out to examine surface morphology and roughness of ODT treated and AuNPs grafted samples. Digital instrument CP II Veeco was used in noncontact mode with silicon P-doped probes RTESPA-CP with a spring constant of 20–80 N·m $^{-1}$. Images of $1 \times 1 \mu\text{m}^2$ area of surface were taken. Surface roughness was calculated using data obtained from three $10 \mu\text{m}$ area scans on random position on the sample. Both arithmetic average (R_a) and root mean square (RMS) values of the surface roughness were calculated.

Electrical sheet resistance (R_s) of the samples was determined by a two-point method using KEITHLEY 487 picoammeter. For this measurement, additional Au contacts, about 50 nm thick, were created by sputtering. The electrical measurements were performed at a pressure of about 10 Pa to eliminate the influence of humidity. The typical error of the sheet resistance measurement did not exceed $\pm 5\%$.

Elemental composition of the modified surface layer was measured by XPS 24 hours after the grafting with AuNPs. Omicron Nanotechnology ESCAProbeP spectrometer was used to measure photoelectron spectra (error of 10%). Exposed and analyzed area had dimension of $2 \times 3 \text{ mm}^2$. Spectra were measured in two sample regions to check for the sample homogeneity. X-ray source was monochromated at 1486.7 eV and the incidence angles were 0° and 81° with respect to the sample surface normal. The spectra were collected using step size of 0.05 eV. The O (1s), C (1s), S (2p), and Au (4f) peaks were evaluated using CasaXPS program [14]; elemental surface composition was calculated on the base of peak area of respective elements.

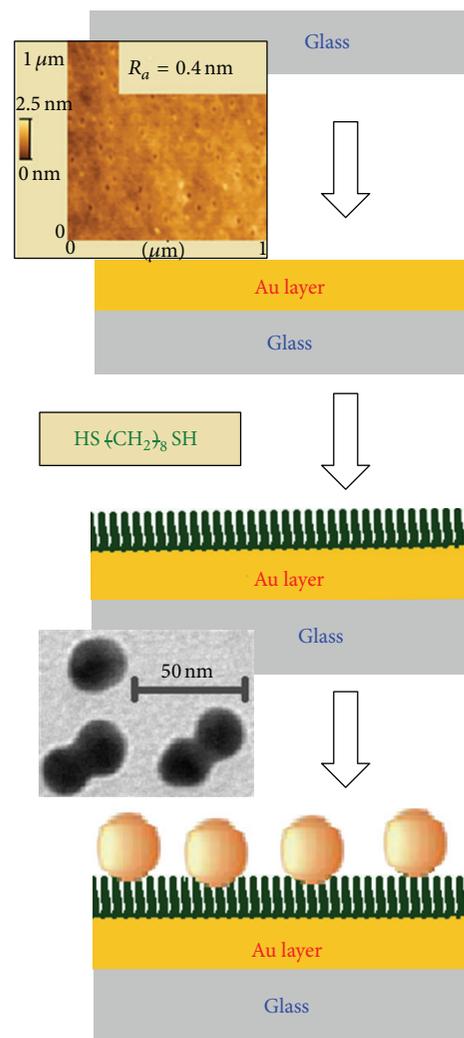


FIGURE 1: Schematic of the sample preparation process. AFM scan of pristine glass substrate (with values of surface roughness) is shown in the top left cut. Chemical formula of the octane-1,8-dithiol is shown in the middle left cut. In the bottom left cut a TEM (JEOL-JEM 1010, Japan) image of freshly prepared AuNPs is shown.

UV-Vis absorption spectra were measured by Perkin-Elmer Lambda 25 spectrophotometer. Absorbance values were obtained in wavelength range of 300–800 nm with a step of 1 nm. Halogen lamp was used as radiation source. Absorption spectrum of clean, pristine glass slide was used as a background standard for all measured spectra.

Electrokinetic potential (zeta potential) of all samples was determined by SurPASS Instrument (Anton Paar, Austria). Samples were studied inside the adjustable gap cell in contact with the electrolyte (0.001 mol·dm $^{-3}$ KCl). For each measurement a pair of samples was fixed on two sample holders (with an area of $20 \times 10 \text{ mm}^2$ and gap of $100 \mu\text{m}$). Zeta potential of all samples was measured four times repeatedly at room temperature and constant pH value 5.9 with the relative error of 10%. Two methods of calculation were applied for zeta potential determination. Helmholtz-Smoluchowski (HS)

TABLE 1: Element concentration in near surface layers measured by XPS method. Spectra were obtained for samples of gold sputtered for 20 and 200 s after dithiol treatment and AuNPs grafting. The measurements were performed at analytical beam incidence angles of 0° and 81° with respect to the sample surface normal.

Sample	Deposition time	Element concentration (at. %)							
		C (1s)		O (1s)		Au (4f)		S (2p)	
		0	81	0	81	0	81	0	81
Dithiol treated	20 s	57.9	68.8	14.3	1.2	23.2	18.4	4.6	11.6
	200 s	55.5	62.5	3.5	3.7	37.2	23.0	3.8	10.8
AuNPs grafted	20 s	48.6	67.3	18.4	1.2	28.9	25.2	4.1	6.3
	200 s	69.3	71.9	5.0	2.1	23.0	18.6	2.7	7.4

equation was used to calculate potential from streaming current; Fairbrother-Mastin (FM) equation was used to determine zeta potential from streaming potential [15].

3. Results and Discussion

AFM images of the samples with Au layers sputtered for 20 and 200 s are shown in Figure 2 together with values of surface roughness (R_a and RMS). The image of the sample sputtered for 20 s shows a noncontinuous structure typical for early phase of layer growth. Isolated Au grains are seen on the glass surface. Larger isolated Au islands occur on the surface since grains with certain lattice orientation are favoured. After the grafting with AuNPs the surface is covered with round shape structures and the structure of underlying gold layer is not seen so clearly. From the scale attached to the image and the shape of these structures we can estimate the mean diameter of the attached AuNPs to be 20–25 nm. The change in the surface is manifested by a decrease of R_a to RMS ratio. Although the density of grafted AuNPs is quite low and they are randomly scattered over the surface, aggregates of 2–3 AuNPs are often formed. Structure of the sample of Au, as sputtered for 200 s, shows larger islands of Au interconnected by areas filled with smaller grains. After AuNPs grafting, this structure becomes covered by inhomogeneously distributed aggregates of AuNPs. The scale suggests that several layers of AuNPs are attached.

Changes in optical parameters during the sample preparation are documented in Figure 3. UV-Vis spectra were measured after each step of sample preparation. The absorption increases after AuNPs grafting since more gold is present on the surface. For the samples sputtered for 20 s the UV-Vis spectra from as-sputtered and dithiol treated samples differ only slightly. The dithiol treatment should not have any significant influence on the absorption, because 1,8-octanedithiol does not significantly absorb light in the UV-Vis region of the spectra. The small difference between the spectra may be caused by the uncertainty in deposition times. In the case of 200 s deposition time, the well-defined SPR peak broadens after the dithiol treatment. This could be caused by ablation of loosely bound parts of Au layer

during the preparation. Further change in the spectrum form after the AuNPs grafting suggests preferential binding of nanoparticles into valleys occurring in the sputtered Au leading to further broadening of the SPR peak. This effect may also be intensified by aggregation of grafted AuNPs, because the large aggregates do not produce sharp SPR peak.

Results of XPS measurements are summarized in Table 1. While the measurements made at the take-off angle of 81° give information on the composition of thin, near surface layer, the measurements at 0° angle cover about six times thicker surface layer of the sample. The results of sulfur measurements suggest that the observed sulfur is present on the very surface of the samples. Significant decrease in sulfur concentration after the AuNPs grafting confirms successful coverage of the surface with AuNPs. The concentration of O decreases with increasing incidence angle since the main part of oxygen is located in the deeper layers of the sample and it is a major part of the glass substrate. It may be concluded that oxidation of the sputtered gold film is negligible. High measured concentrations of C come from both the dithiol and the glass substrate, which may contain a certain amount of carbon, as was proven in our previous work [5]. In the case of the sample of Au sputtered for 200 s, the decrease in gold concentration observed after the grafting with AuNPs may be caused by formation of thicker dithiol coverage which could prevent the analytical beam from detecting the gold in underlying sputtered layer.

Electrical sheet resistance measurements prove that different structures of the gold layers sputtered for 20 and 200 s are formed. While the layers sputtered for a longer time exhibit good conductivity (measured resistance $R_s = 60 \Omega$) typical for continuous surface coverage, the layers deposited for 20 s are not continuous and exhibit sheet resistance $R_s > 10^9 \Omega$. Significant deformation of the XPS gold peaks, observed on the sample sputtered for 200 s with Au and with grafted AuNPs in comparison with sample with Au deposited for 20 s (see Figure 4), cannot be caused by sample charging during the XPS measurement and rather indicates the presence of two forms of Au in the samples.

Results of zeta potential measurement are shown in Figure 5. Zeta potential of the samples increases after the Au sputtering. The big difference between the values determined

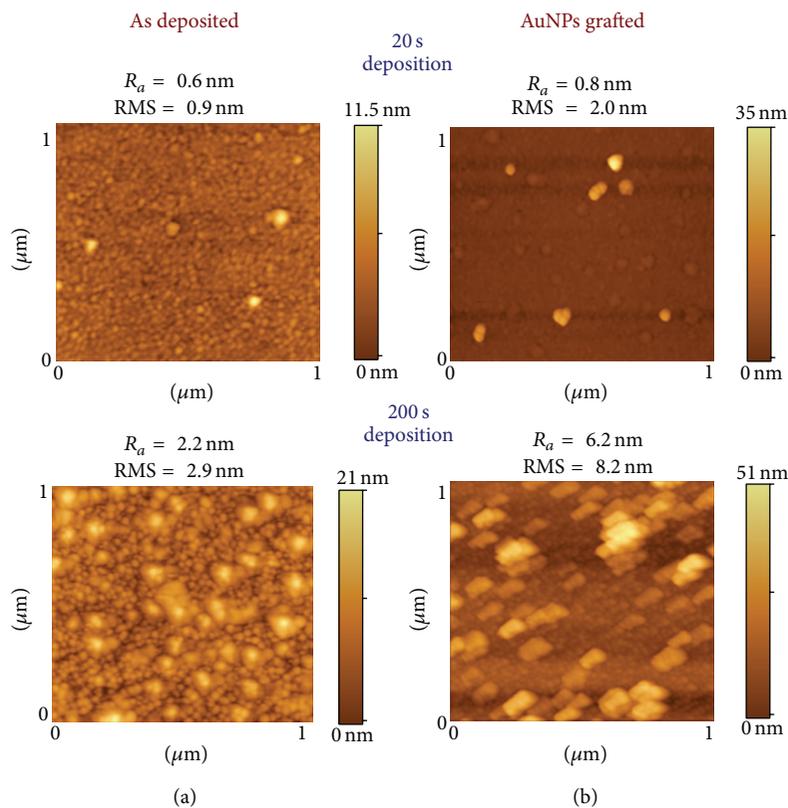


FIGURE 2: AFM images of the samples Au sputtered for 20 and 200 s (a) and after dithiol treatment and AuNPs grafting (b).

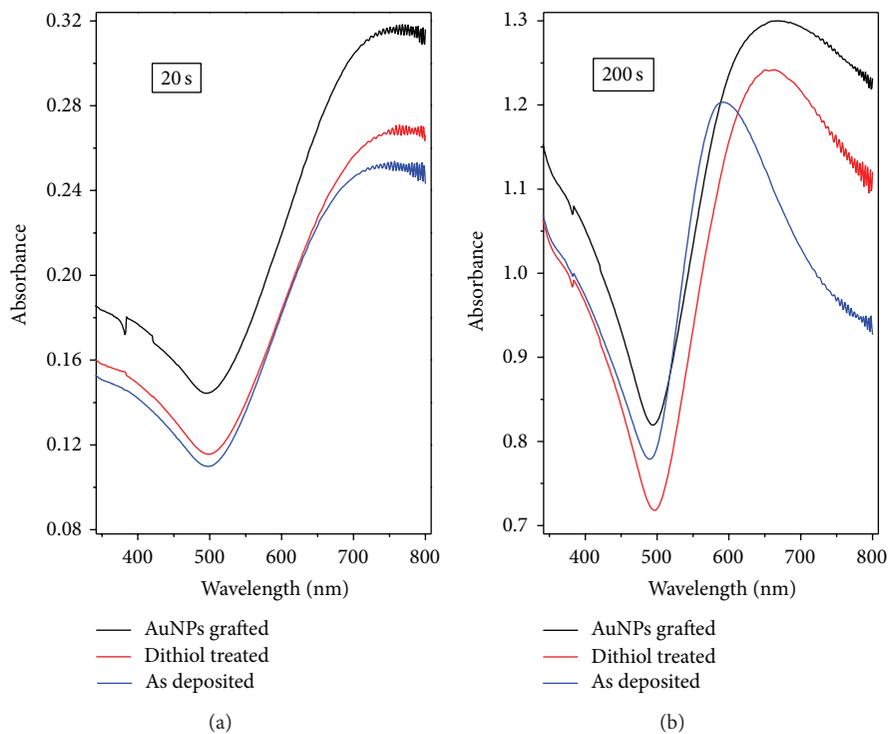


FIGURE 3: UV-Vis spectra of the samples after each step of preparation (as sputtered with gold, after dithiol treatment and subsequent AuNPs grafting). Samples were sputtered with Au for 20 s (a) and 200 s (b).

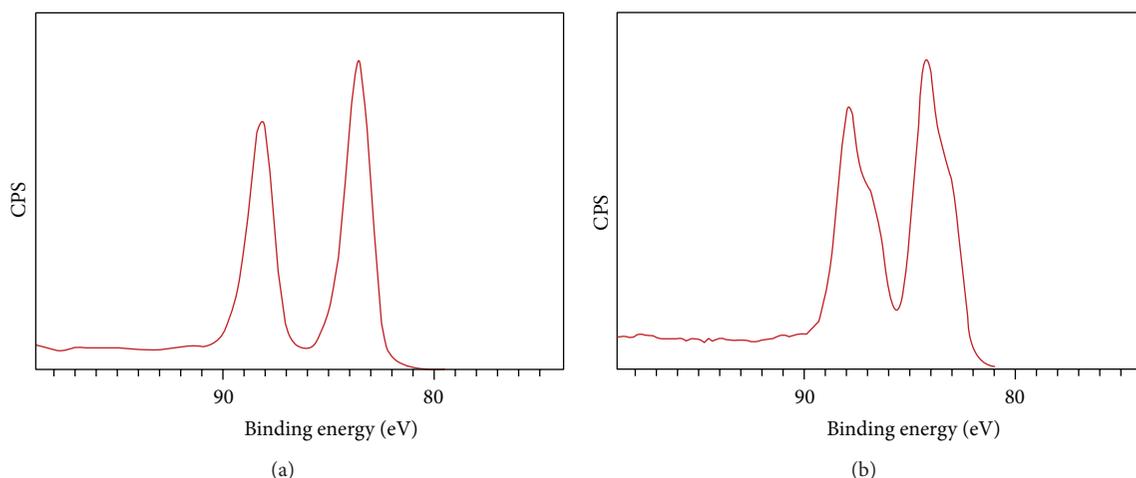


FIGURE 4: Comparison of XPS Au double peaks from the samples sputtered with Au for 20 s (a) and 200 s (b) and then treated with dithiol and grafted with AuNPs.

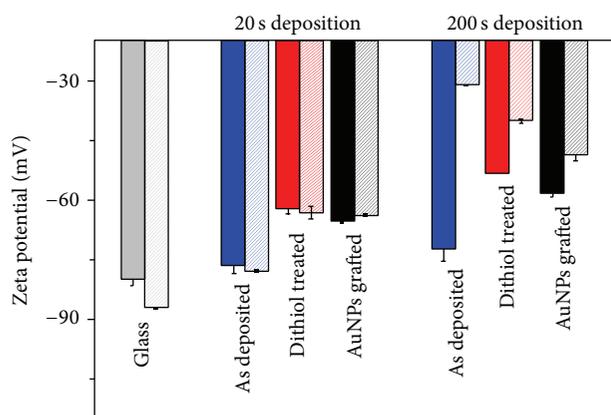


FIGURE 5: Dependence of zeta potential of the samples with Au layers deposited for 20 and 200 s. The values obtained after each step of the preparation process are compared. Values calculated from HS equation (streaming current method) are represented by the full columns; the striped columns correspond to values obtained from FM equation (streaming potential method).

by HS and FM equations (see above) in the case of the sample sputtered for 200 s documents the evolution of the surface structure into a continuous film, which is electrically conductive [15]. The increase of the zeta potential measured after the ODT binding shows that the presence of hydrocarbon chains limits the influence of $-SH$ groups significantly. In the case of full surface coverage with free $-SH$ groups, zeta potential should decrease due to the presence of negative surface charge caused by dissociation in the electrolyte. Observed increase of the zeta potential therefore suggests preferential binding of both $-SH$ groups to the underlying gold layer, while the structures with free $-SH$ groups capable of binding to AuNPs form only small fraction of bound ODT. This is also

confirmed by the mild decrease of the zeta potential after AuNPs grafting by which the former structures are covered by attached AuNPs.

4. Conclusions

Binding of gold nanoparticles (AuNPs) onto glass surface with sputtered thin Au underlayer, mediated by dithiol, was investigated. In accordance with previous studies the sputtering for 20 and 200 s leads to creation of island-like and continuous gold coverage of the glass substrate, respectively. The continuity of the gold coating was also controlled by measurement of the sheet resistance. After the treatment with dithiol and grafting with gold nanoparticles the surface roughness increases (R_a and RMS), the increase being more pronounced for samples sputtered for 200 s. The XPS measurement proves successful coverage of sputtered gold underlayer with dithiol molecules. Grafting with AuNPs does not change the gold concentration significantly with the only exception of the samples sputtered for 200 s, where the grafting results in a decrease of the observed gold concentration. Deformation of Au double peak in XPS spectrum suggests presence of two gold modifications. Optical properties of the created structures were characterized by UV-Vis spectra measurements. The treatment with dithiol and grafting with AuNPs lead to increase in UV-Vis absorbance and to significant change in the spectra shape in the case of the samples sputtered for 200 s. XPS and zeta potential measurements show that the majority of the adsorbed dithiol molecules are bound to underlying gold layer via both $-SH$ groups and only a small part of dithiol molecules have free $-SH$ groups available for AuNPs binding.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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