ELECTROCHEMICAL PROPERTIES AND THERMAL STABILITY OF CUP-LIKE SHAPE GOLD NANOSTRUCTURES

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Abstract: Nanostructured surfaces are useful in enlargement of electroactive area of sensing electrodes. The electrodes are very sensitive with maintaining small electrode geometry. In this study, surfaces modified by cup-like gold nanoparticles were fabricated by electrochemical methods. Subsequently, electrochemical properties and thermal stability of fabricated nanostructured electrodes were studied. Thereafter, the electrochemical results were compared with unmodified flat gold layer and contribution of nanostructuring was evaluated. Stability of nanoparticles after thermal vacuum and air pressure treatment was studied using scanning electron microscope. These results are useful for subsequent research of nanostructured sensors.

Keywords: gold nanoparticles, nanostructured electrode, electrochemical impedance spectroscopy, cyclic voltammetry

1. INTRODUCTION

Gold nanostructured electrodes have a wide utilization for electrochemical sensing of biological samples as cells, proteins, nucleic acids etc. [1]. Anodic oxidation of aluminium layer, utilized as a template for creating of nanostructured surfaces, is a low cost method with good reproducibility. For sensing applications, the nanostructures are useful considering the effective enlargement of the electroactive surface of the sensors [2]. Nanoparticles are able to improve detection properties of electrodes and to decrease a detection limit. Substrate, covered by a conductive layer and an aluminium layer, is necessary for the manufacturing of the nanostructured surfaces. The production of nanostructured surface begins with the anodization of the upper aluminium layer in acidic solution. Performing the anodic oxidation, a nanoporous alumina template with tungsten oxide nanoparticles beneath the alumina template is obtained. In the next step, the tungsten oxide is selectively removed by etching in phosphate buffer. After this step, nanopores with wider dimples on the bottom are obtained. The gold material is then electrochemically deposited into the pores. After alumina template is dissolved, the highly ordered gold nanostructured surface is obtained [3, 4].

Annealing in the air is used for oxidation of bottom tungsten layer. After this annealing, conductive tungsten layer does not participate in the processes at the interface between nanostructured electrode and bulk of solution. Only conductive nanocolumns are participating in electron transfer at the interface due to higher conductivity of gold. Vacuum annealing is suitable for better interconnection of materials at the tungsten interface with gold nanocolumns [5, 6]. These reasons have caused this study of thermal stability of manufactured nanostructures annealed in vacuum and in air. Studying the thermal stability of nanostructures is very important for future involvement of annealing techniques in order to improve electrochemical behaviour of nanostructured sensors.

2. EXPERIMENTAL

2.1. CHEMICALS

Titanium (99.99%, Porexi, CZ), tungsten (99.999%, Porexi, CZ), aluminium (99.999%, Goodfellow, UK), gold (99.999%, Goodfellow, UK), oxalic acid ($(COOH)_2$, Penta, CZ), potassium dicyanoaurate ($K[Au(CN)_2]$, 68%, Safina, CZ), boric acid (H_3BO_3, p., Penta, CZ), chromium trioxide (CrO_3, Penta, CZ), phosphoric acid (H_3PO_4, 98%, p.a., Penta, CZ), sulphuric acid (H_2SO_4, 96% pa, Penta), dihydrate sodium dihydrogen phosphate ($NaH_2PO_4.2H_2O$, 99%, Penta, CZ), dihydrate sodium hydrogen phosphate ($Na_2HPO_4.2H_2O$, 98%, Fluka, CZ), conductivity standards (100 µS cm^{-1}±1%, 706 µS cm^{-1}±1%, 1413 µS cm^{-1}±1%, Hamilton, Switzerland) were used as purchased without any purification. Deionised water (18.2 MΩ) was obtained from Millipore RG system MiliQ (Millipore Corp., USA).

2.2. ELECTRODES

Nanostructured electrodes (Figure **1**) were fabricated in several steps using electrochemical anodic oxidation, which transformed the aluminium layer to the porous alumina layer.

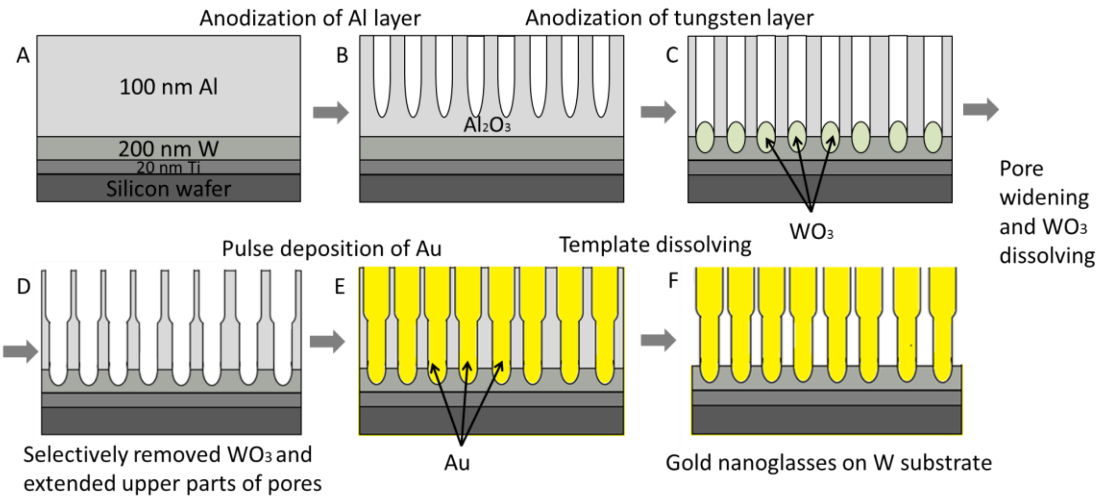

Figure 1: Scheme of production of gold nanostructured surfaces.

At first, titanium layer 20 nm and tungsten layer 200 nm were deposited on a silicon wafer using ion sputtering machine. The aluminium layer with thickness of 100 nm was then deposited by thermal evaporation on the wafer with titanium and tungsten. Titanium layer also serves as an adhesive layer and does not change during the process (A). In the second step, the aluminium layer was transformed to porous alumina template (Al_2O_3) by anodization. The thin porous anodic alumina template was obtained by anodization process under constant voltage (50 V) in 0.3 M oxalic acid at 10°C temperature (B). As soon as the aluminium oxidation was finished, the bottom tungsten layer was partly transformed by oxidation to tungsten oxide nanoparticles (C). The alumina template was then treated by etching in 5% phosphorous acid heated up to temperature of 50°C for 3 minutes to open the pores. The pore widening is controlled by time of etching, temperature and concentration of acid. Subsequently, templates were etched in phosphate buffer pH 7.0 at the temperature of 25 °C to selectively dissolve tungsten oxide. After these steps, nanopores with dimples at the bottom were obtained. The dimples served as a base for future gold nanocolumns and ensured better stability of gold nanoparticles. Upper part of nanopores was wider than middle part due to pore opening by phosphorous acid while bottom part was protected by tungsten oxide nanostructures. Produced nanopores had a shape resembling wine glass (D). Thereafter, the gold material was deposited by pulse deposition method into the pores by electrochemical reduction of gold ions from potassium dicyanoaurate solution. The time length of pulses was 400 ms with period 2 seconds at constant current of 1 mA, area 19 mm^2 and amplitude 5 V. Temperature of solution was 50°C (E). Finally, aluminium template was dissolved in 100 ml of mixture solution containing 3 g of chromium trioxide and 5 ml of phosphorous acid (84%) at 50°C for 10 minutes. Surface modified by gold nanocolumns on the tungsten substrate layer was obtained (F) and then characterized by scanning electron microscope (SEM, Tescan Mira II, Tescan, CZ). Flat gold electrodes were made by ion sputtering of 250 nm thick gold layer on silicon substrate.

2.3. ELECTROCHEMICAL METHODS

Electrochemical measurements were performed using Autolab PGSTAT204/FRA32M in connection with NOVA 1.10 software (Metrohm Autolab, NL). Three-electrode cell with Pt auxiliary electrode and Ag/AgCl/3M KCl reference electrode (both Metrohm AG, CH) were used for all experiments. The sample with gold nanostructures was placed into an electrochemical measurement cell, which defines the working electrode area as a circle with 3 mm diameter. All measured samples were electrochemically cleaned in 0.1 M H_2SO_4 by CV method in range from -0.7 V to 0.7 V. The impedance spectroscopy was measured at zero potential vs. reference electrode in a frequency range from 500 kHz to 100 mHz and amplitude of 20 mV in standard conductivity solutions of various conductivities (100 µS cm^{-1}, 706 µS cm^{-1}, 1413 µS cm^{-1}). Cyclic voltammetry curves were measured in a range from -0.7 V to 0.7 V with a scan rate of 50 mV.s^{-1}. The measurements were performed in 0.1 M potassium chloride with additions of potassium ferricyanide and ferrocyanide of three various concentrations (2.5 mM, 5 mM and 7.5 mM).

3. RESULTS AND DISCUSSION

Tungsten electrodes modified by gold nanocolumns were successfully fabricated, and consequently characterized by SEM and electrochemically studied by impedance spectroscopy and cyclic voltammetry. According SEM images, nanocolumns were approximately 130 nm high and 40 nm wide. In the Figure **2**, there are SEM images of nanoporous alumina template (left), fabricated nanostructures on the tungsten layer in the template (middle) and cross section of fabricated nanostructures after template removal. It can be observed that the overall homogeneity of distribution is good and nanocolumns look mechanically stable. The cross section image shows interesting wine glass shape of fabricated gold nanostructures as a result of etching in 5% phosphorous acid.

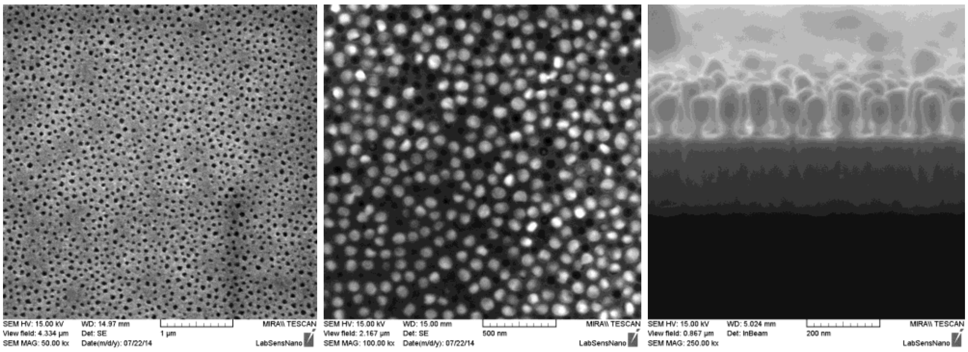

Figure 2: SEM images of alumina template (left), deposited gold into the nanoporous template (middle) and cross section of gold nanostructured surface (right).

The nanostructured surfaces were annealed in the air employing a muffle furnace at the temperature range from 100°C to 800°C for 1 hour with heating rate 10°C.min^{-1}. All samples were investigated by SEM after each annealing and possible morphological changes of nanostructures were observed. In

Figure **3**, the progress of annealing in air with particular temperature increase is shown. The maximal annealing temperature having no influence on morphology of the gold nanostructures was estimated to be 400°C. Higher temperatures caused changes in the shape and length of nanocolumns leading to smoother and shorter nanostructures.

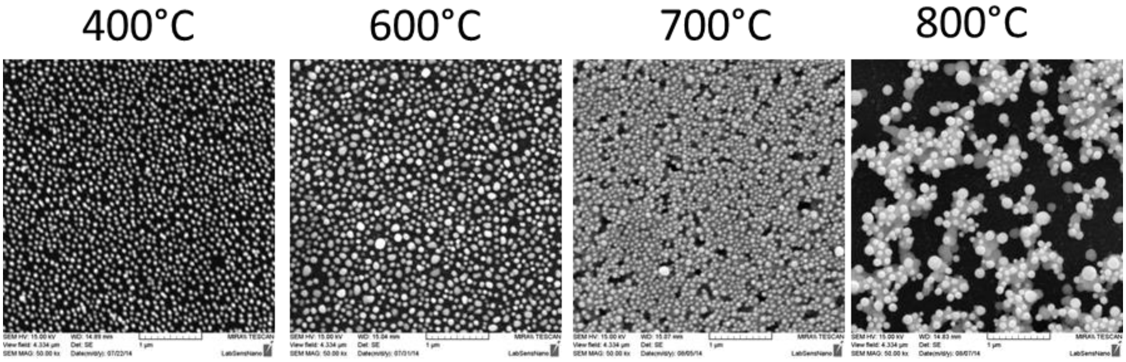

Figure 3: SEM images of samples annealed at various temperatures in air (scale 1 μm).

Low pressure annealing was performed in a vacuum furnace (Vacuum Prague). The temperature range for low pressure annealing was from 100°C to 600°C for 1 hour with heating rate 10°C.min^{-1} (Figure 4). The morphology of nanostructures samples was stable in whole studied temperature range.

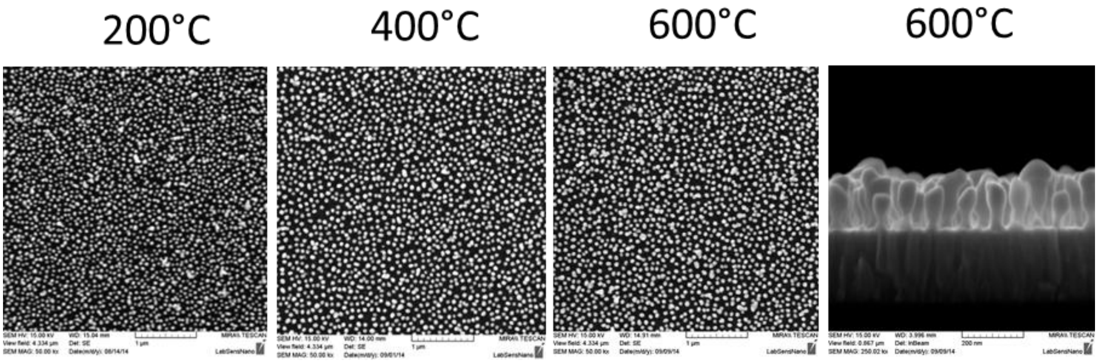

Figure 4: SEM images of samples annealed at various temperatures in vacuum (scale 1 μm) and cross section after 600°C vacuum annealing.

The last step of cup-like nanostructure characterization was electrochemical measurement. The results are shown in Figure 5 and Figure 6.

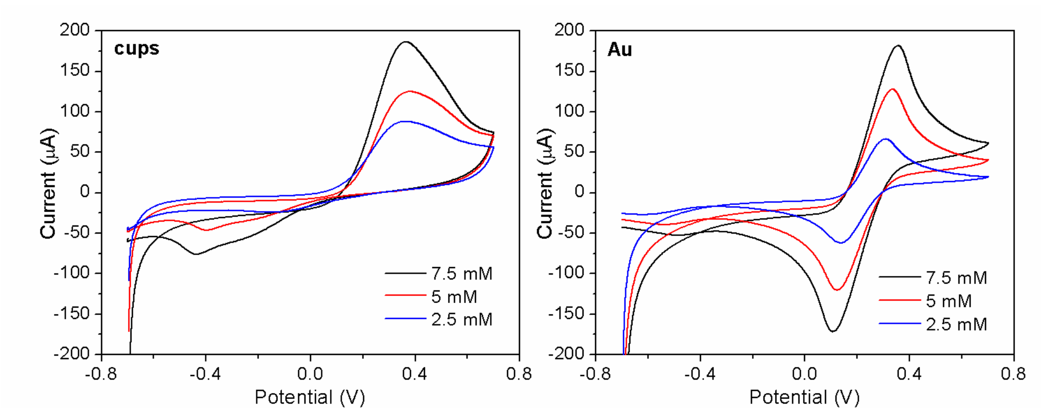

Figure 5: Cyclic voltammograms for various concentrations of potassium ferro-fericyanide.

The cyclic voltammetry curves for flat gold electrode without nanoparticles demonstrate excellent reversible behaviour. The results for cup-like nanostructures do not provide sufficient reversible behaviour. The voltammogram for nanostructured surface shows typical anodic peak and deformed cathodic peak with very low height. Nevertheless, the heights of anodic peaks measured for nanostructured electrode and flat gold electrode are approximately equivalent. Impedance results confirm the presence of nanostructures due to curved shape of diffusion part of impedance spectra whereas the impedance spectra for flat gold electrodes exhibit straight diffusion line.

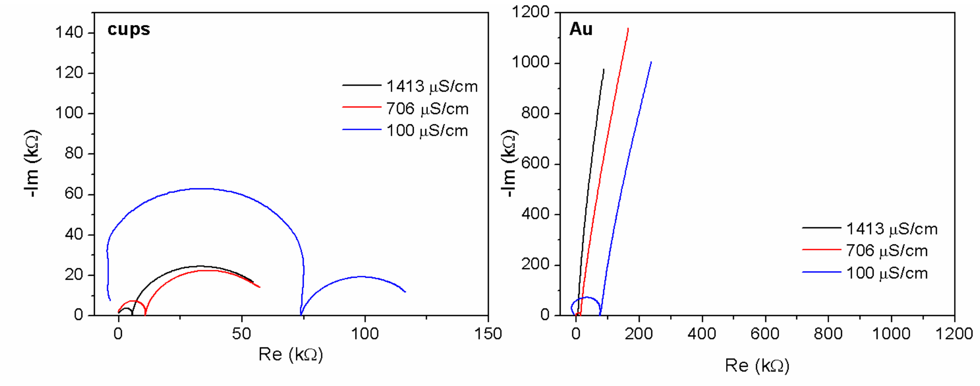

Figure 6: Nyquist plots of impedance spectra measured for nanostructured surface with cups and flat gold electrodes.

4. CONCLUSION

The cup-like nanostructured surfaces were successfully made by electrochemical anodic oxidation and consequent galvanic deposition. The resulted nanostructures have interesting wine glass shape as etching result of upper part of nanopores in template before gold deposition. The temperature stability was then examined by annealing at the atmospheric pressure and annealing in the vacuum. In the air, nanostructures are morphologically stable until annealing at temperature of 400°C whereas the vacuum annealing maintains stable nanostructures up to 600°C. Studying of the thermal stability of nanostructures is very important for the future involvement of annealing techniques into improving electrochemical nanostructured sensors. The last step was electrochemical characterization and comparing the results with measurement for flat gold layer without nanostructures. It is observed non-reversible behaviour for nanostructured electrodes is observed the anodic peak heights are approximately the same. According to the impedance results the presence of nanostructures is manifested in curvatures of the diffusion parts.

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