THERMAL STABILITY OF GOLD NANOSTRUCTURED ELECTRODES AND INFLUENCE OF ANNEALING ON ELECTROCHEMICAL IMPEDANCE MEASUREMENTS

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Abstract

Studying the influence of vacuum and atmospheric pressure annealing on the shape of gold nanostructures is crucial for detection purposes. The nanostructured surfaces on a tungsten substrate have been made by electrochemical anodic oxidation of the aluminium layer. The pulse deposition of gold has been consequently employed to fill the nanopores with the gold material. At first, the appropriate temperature for both types of annealing was experimentally determined. The fabricated surfaces were then annealed either in the air or in the vacuum. Characterization of differently treated surfaces (annealed in air, annealed in vacuum and non-annealed) was performed using electrochemical impedance spectroscopy with utilization of commercial conductivity solutions.

Keywords:

Gold nanocolumns, Electrochemical impedance spectroscopy, Tungsten oxide, Annealing, Nanoporous alumina

1. INTRODUCTION

Gold nanostructured electrodes made by anodic oxidation and electrochemical deposition have a wide utilization at electrochemical sensing of biological samples as cells, proteins, nucleic acids etc. [1]. Anodic oxidation is 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]. It is able to improve detection properties of electrode and to decrease a detection limit. Substrate, covered by a conductive layer and the 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 was obtained. In the next step, the tungsten oxide is selectively removed by etching in phosphate buffer. After this step, were obtained nanopores with wider dimples on the bottom. The gold material is then deposited into the pores. After alumina template is dissolved, the highly ordered gold nanostructured surface is obtained [3, 4]. Annealing in the atmospheric pressure is used for oxidation of bottom tungsten layer. After this annealing, tungsten layer does not participate in the processes at the interface between nanostructured electrode and bulk of solution. Only nanocolumns are participating in electron transfer at the interface. Vacuum annealing is suitable for better interconnection of materials at the tungsten interface with gold nanocolumns.

The influence of two types annealing is studied by electrochemical impedance spectroscopy. This method is a powerful tool for characterization of nanostructured surfaces. The aim of this study is comparison of influence of vacuum annealing and annealing in the air in relation to electrochemical impedance measurement. The thermal stability of manufactured nanostructures annealed in the vacuum and in the atmospheric pressure was also observed [5, 6].

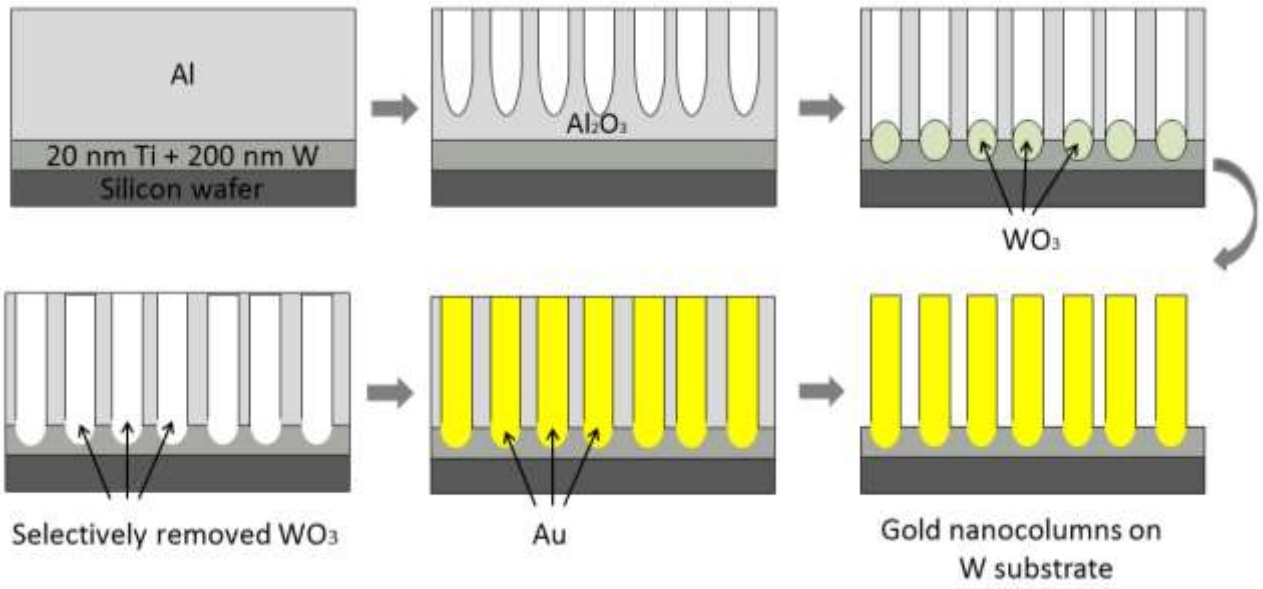

Figure 1 Scheme of production of gold nanostructured surfaces

2. EXPERIMENTAL

Chemicals

Titanium (99.99%, Porexi, CZ), tungsten (99.999%, Porexi, CZ), aluminium (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), 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 (1.3 $\mu S.cm^{-1}$±1%, 5 $\mu S.cm^{-1}$±1%, 15 $\mu S.cm^{-1}$±1%, 100 $\mu S.cm^{-1}$±1%, 706 $\mu S.cm^{-1}$±1%, 1413 $\mu S.cm^{-1}$±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).

Electrodes

Nanostructured electrodes were fabricated using electrochemical anodic oxidation which transformed the aluminium layer to the porous alumina layer. At first, titanium layer 20 nm and tungsten layer 200 nm were deposited on the silicon wafer using the ion sputtering. The aluminium layer with thickness 100 nm was then deposited by thermal evaporation on the wafer with titanium and tungsten. Titanium layer also serves as the adhesive layer. In the second step, the aluminium layer was transformed to hexagonally ordered 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 0.3M oxalic acid at 10°C temperature. As soon as the aluminium oxidation was finished, the bottom tungsten layer was transformed by oxidation to tungsten oxide nanoparticles. 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. Subsequently, templates were etched in phosphate buffer pH 7.0 at the temperature of 25 °C to dissolve tungsten oxide. After these steps, nanopores with

dimples at the bottom were obtained. The dimples served as 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. Produced nanopores had a shape reminding wine glass. 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 with amplitude 5 V. Temperature of solution was 50°C. Finally, aluminium template was dissolved in 100 ml of mixture solution containing 3 g of chromium trioxide and 5 ml of phosphorous acid. Surface modified by gold nanocolumns on the tungsten substrate layer was obtained and then characterised on the SEM (Tescan Mira II, Tescan, CZ). Fabricated nanocolumns were approximately 130 nm high and 40 nm wide.

Electrochemical methods

The measurements were performed using μAUTOLAB III/FRA2 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 nanoparticles was placed into electrochemical measurement cell which define the working electrode area on 3 mm in diameter. The impedance spectroscopy was measured at zero potential in a frequency range from 500 kHz to 0.1 Hz and amplitude of 20 mV. Electrochemical characterization of electrodes was done in standard conductivity solutions of various conductivities from 1.3 $\mu S.cm^{-1}$ to 1413 $\mu S.cm^{-1}$.

3. RESULTS AND DISCUSSION

Tungsten electrodes modified by gold nanocolumns were successfully fabricated, and consequently characterized by SEM and electrochemical impedance spectroscopy. In the Figure 2, there are SEM images of nanoporous alumina template (left), and fabricated nanostructures on the tungsten layer in the template (right), which was created by electrochemical growth of gold through highly ordered nanoporous template. The images of produced nanostructures from top view (left) and cross section image (right) are shown in the Figure 3 . It can be observed that the overall homogeneity of distribution is good and nanocolumns look very stable. The cross section image shows interesting wine glass shape of fabricated gold nanostructures as a result of etching in 5% phosphorous acid.

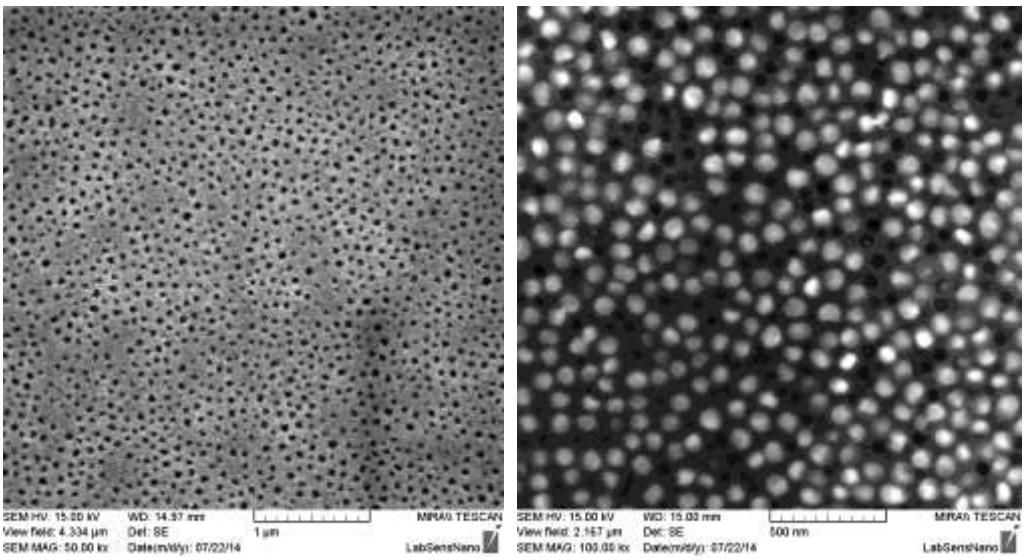

Figure 2 SEM images of alumina template (magnification 50 kx, left) and deposited gold into the nanoporous template (magnification 100 kx, right)

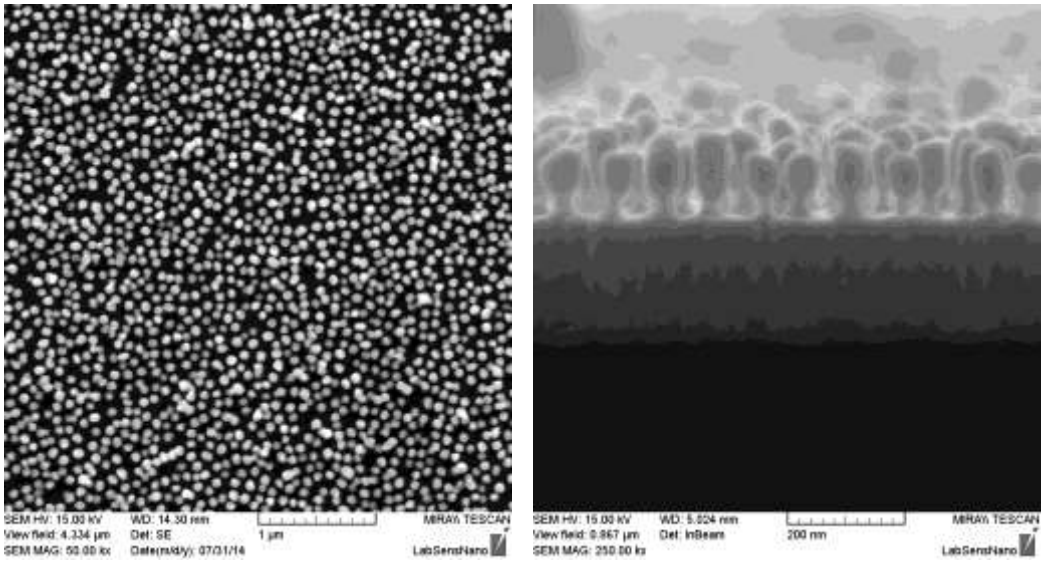

Figure 3 Gold nanostructures from top view (magnification 50 kx, left) and cross section of gold nanostructured surface (magnification 250 kx, right)

Annealing

Firstly, the appropriate temperatures for both types of annealing were determined. The nanostructured surfaces were annealed in the air employing the muffle furnace at the temperature range from 100°C to 800°C for 1 hour. All samples were investigated on the SEM after each annealing and possible structural changes of nanoparticles were observed. In the Figure 4, there is shown the progress of annealing in the air with particular temperature increase. The maximal annealing temperature for gold nanoparticle, when there was no structural change observed, was appeared to be 400°C for 1 hour. Higher temperatures caused changes in the shape of nanocolumns. Nanostructures look smoother with shorter length. Therefore, the temperature of 400°C was chosen for annealing on the atmospheric pressure.

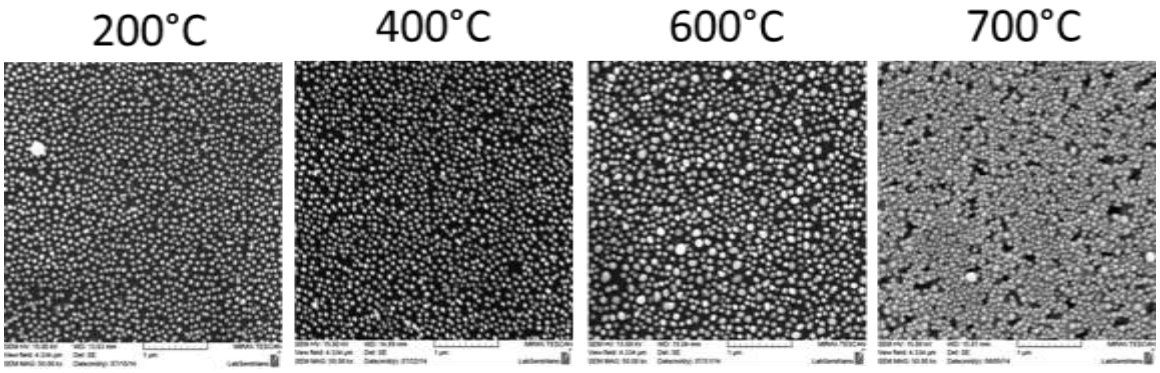

Figure 4 SEM microimages of atmospheric pressure annealing at various temperatures

Low pressure annealing was performed in 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 5). The samples for electrochemical measurement were stable in whole range of studied temperatures. The measured samples were also annealed at the temperature 400°C and pressure 4.10^{-4} Pa.

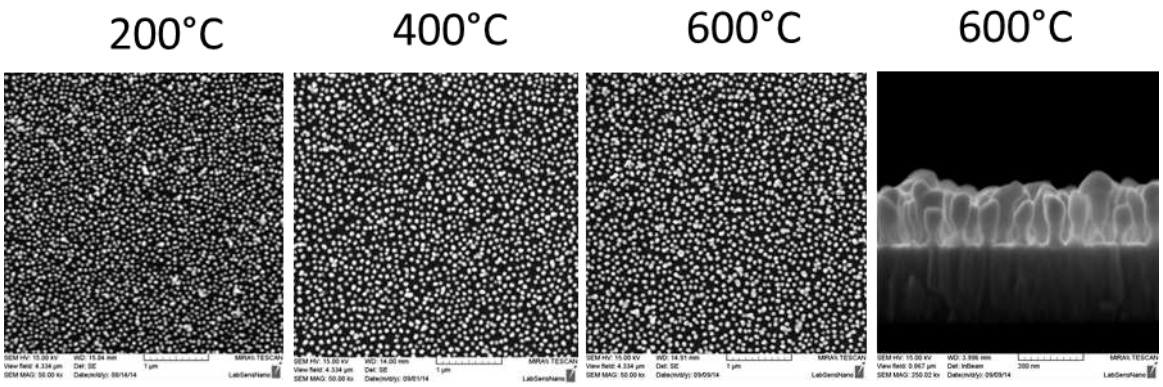

Figure 5 SEM microimages of vacuum annealing at various temperatures and cross section image for structures after vacuum annealing at 600°C

Characterization of differently treated surfaces (annealed in the air, annealed in the vacuum and non-annealed) was performed by electrochemical impedance spectroscopy using commercial conductivity solutions. Measurements were performed for three samples of each type of treatment, and were measured in six various solution concentrations. The results of all measurements were compared. In Figure 6, there are shown impedance spectra for differently treated surfaces using the same concentrations of solutions (100 $\mu S.cm^{-1}$ on the left, and 706 $\mu S.cm^{-1}$ on the right). The Figure 7 presents dependencies of real value of maximum part of impedance spectra on concentration. The important requirements for sensors are high electroactive surface and good conductivity indicating low value of impedance. According to the impedance results, it can be considered that during atmosphere annealing the bottom tungsten was oxidized. Therefore, the electroactive area is lower and the impedance value is higher. This result also means tungsten substrate is participating in the electrochemical measurements. Namely, the electrolytic solution penetrates deep among nanostructures and involves the electrodes processes. The results for non-annealed samples and vacuum annealed samples are similar, non-annealed samples show slightly lower values. It can mean that there is an excellent connection between tungsten substrate and gold nanostructures for non-annealed samples.

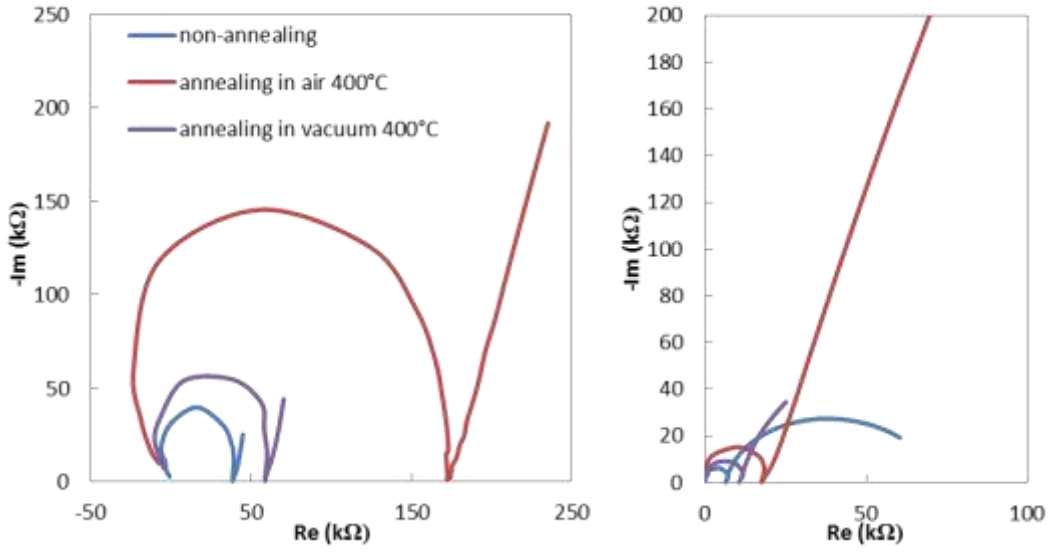

Figure 6 Impedance spectra for all types of treated surfaces measured in two concentrations of conductivity solutions: 100 $\mu S.cm^{-1}$ (left) and 706 $\mu S.cm^{-1}$(right)

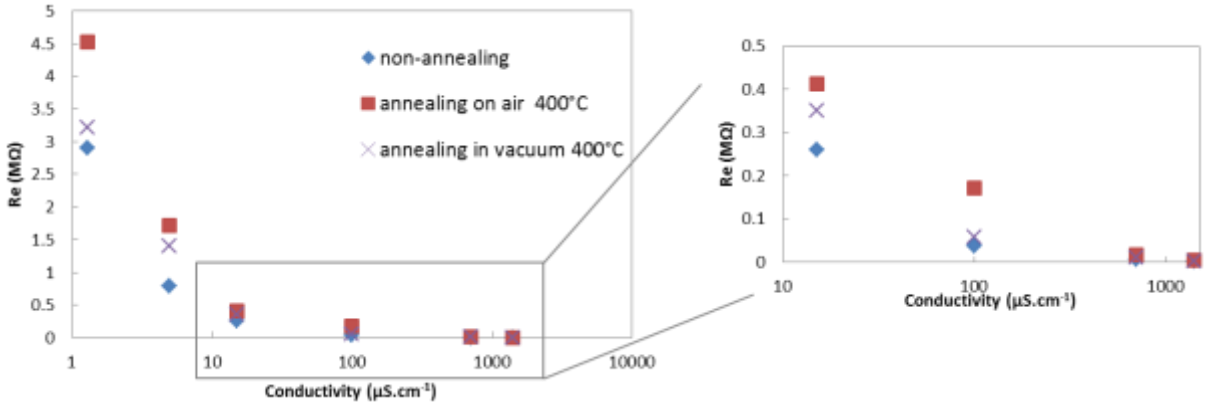

Figure 7 Dependencies of impedance minima on the concentration of solution for all types of treated surfaces

4. CONCLUSION

The electrodes modified by gold nanocolumns were fabricated by electrochemical method like anodic oxidation and pulse electrodeposition. The produced samples were annealed in vacuum and at atmospheric pressure. The electrochemical properties of treated surfaces were studied by impedance spectroscopy method. The non-annealed samples were also measured to compare to the annealed samples. The results indicate that manufactured electrodes have good properties without annealing treatment.

5. ACKNOWLEDGEMENT

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