ELECTROCEMICAL DEPOSITION OF GOLD NANORODS VIA AAO TEMPLATE FOR VOCS SENSING

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Abstract: The use of gold nanostructures for the creation of sensing devices for volatile organic compounds (VOCs) is particularly important because of their unique electronic, optical, and catalytic properties. In this paper, the synthesis of gold nanorods was described. The preparation of nanoporous alumina template was done via electrochemical anodization. The fabrication of gold nanorods was provided via electrochemical deposition into the nanoporous alumina template. Working conditions during the anodization had a significant influence on the pore diameter and thus on size of gold nanorods. The detailed topography of the nanostructured surfaces was characterized by scanning electron microscopy (SEM).

Keywords: Gold nanorods, electrochemical anodization, electrochemical deposition, anodization voltage, pore geometry, VOCs sensors

1. INTRODUCTION

Gold nanostructures have attracted great attention due to their potential application in chemical and biochemical sensing, medical diagnostics and therapeutics, and biological imaging because of their unique optical and electrical properties [1]. Gas sensors based on gold nanostructures have high sensitivity and selectivity, good reproducibility and long-term stability [2]. Geometrical parameters and size of nanostructures play an important role in performances of a gas sensor [3]. Among various shaped gold nanoparticles, nanorods and nanofibers have received the most attention, especially in the field of optical sensors. When gold nanorods are exposed to laser light resonant with their surface plasmon oscillation, they can strongly absorb the light and rapidly convert it into heat via a series of photophysical processes, what is suitable for practical application. The intensity and wavelength of these surface plasmon resonances is highly shape and size dependent [4].

Another important characteristic of gold is that it can bind thiols with high affinity and it does not undergo any unusual reactions with them, e.g., the formation of a substitutional sulphide interphase [5]. This characteristic of gold is important for gas sensing. Gold nanoparticles covered with thiols are used like sensitive layer in chemiresistive sensors for detection of VOCs. VOCs have been found as significant biomarkers in exhaled breath, which reflect the biochemical alterations related to metabolic changes. Therefore, they are extremely helpful in diagnosis and monitoring of various diseases [6]. Those kind of sensors have a very high sensitivity, they are able to give response with a wide range of concentrations from tens of ppb to hundreds of ppm, with a detection limit of 1–5 ppb. Thiols help making a surface of sensitive layer hydrophobic. The sensor shows a low sensitivity to water and it is particularly suitable for breath testing, which is an advantage since the exhaled breath contains ~ 80% relative humidity [7].

A combination of nanostructures with conducting polymers could improve characteristic of gas sensors, by giving them properties such as faster response, long-term stability and high sensitivity [8]. Lee et al. developed VOCs gas sensors based on metal-organic framework of gold–polypyrrole (Au–Ppy) nanorods, see Figure 1 [9]. This gas sensor operates on the principle of localized surface plasmon resonance. The authors used an electrochemical deposition method for fabrication of Au–

Ppy nanorods via anodic aluminum oxide template with 200 nm diameter of pores. This kind of sensor shows a good stability and high sensitivity up to 10 ppm of target VOCs gases [9].

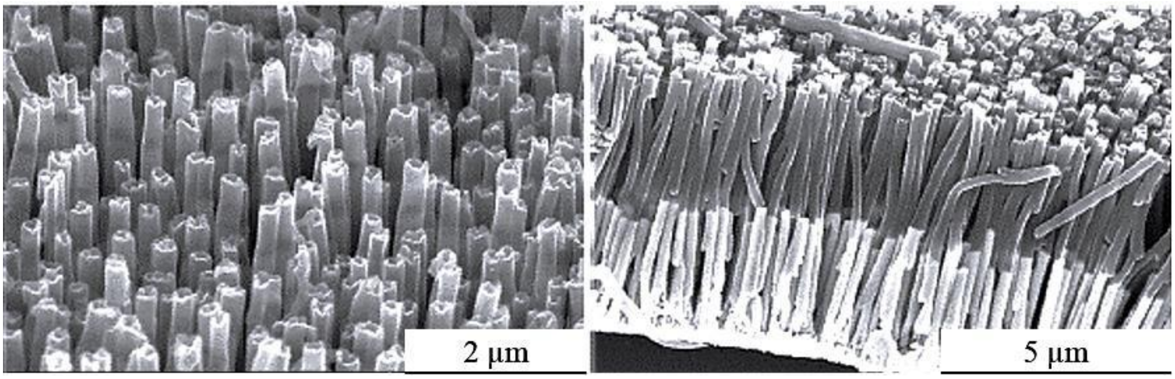

Figure 1: SEM images of the Au-Ppy nanorods [9]

Nanostructures can be synthesized by wet-chemical synthesis or fabricated by templates such as nanoporous alumina template. It can be prepared by electrochemical anodization of aluminum, which allows to produce uniform pores with the diameter as small as 5 nm [10]. An acidic solution is usually used as an electrolyte. A length of nanopores is dependent on the anodization time. An electrochemical deposition of metal into pores leads to the growth of metal nanorods and nanowires [11]. The fabrication using anodic alumina oxide is less complicated, less expensive, and less time–consuming when compared to traditional lithographic approach or epitaxial growth of highly ordered arrays of nanostructures [12].

This work describes a developing of gold nanorods by electrochemical anodization and electrochemical deposition. It shows a different working conditions during the anodization, which have significant role for the size of the gold nanorods. The anodization voltage together with the current density and the electrolyte type are recognized as the most critical parameters to control the pore geometry [13].

2. EXPERIMENTAL

2.1. MATERIALS

Titanium (99.99%), tungsten (99.999%), purchased from Porexi, Czech Republic, and aluminium (99.999%), purchased from Goodfellow, United Kingdom, were used for the PVD deposition of metallic layers. For electrochemical fabrication of gold nanostructures were used: oxalic acid, sulphuric acid (96%), boric acid, chromium trioxide, phosphoric acid (98%), sodium dihydrogen phosphate dihydrate (99%), obtained from Penta, Czech Republic, potassium dicyanoaurate (gold 68.3%, purity 99.9%), obtained from Safina, Czech Republic, and disodium hydrogen phosphate dihydrate (98%), obtained from Fluka, Czech Republic. Deionized water (18.2 MΩ) was bought from Millipore RG system MilliQ (Millipore Corp., USA).

2.2. PREPARATION OF THIN LAYERS FOR FABRICATION OF NANORODS

The silicon wafer was covered by SiO_2 layer with thickness of 1 μm to isolate the nanostructures from n–doped silicon and thus to minimize junction effects at the interface between Si and other metal layers [12]. Titanium layer with a thickness of 20 nm was sputtered on a silicon wafer. Titanium layer serves as an adhesive layer and does not change during the electrochemical fabrication of gold nanorods. The 150 nm tungsten layer was deposited by the ion beam sputtering method. The aluminium layer with a thickness of 300 nm was obtained by thermal evaporation.

2.3. CHARACTERISTIC OF PREPARED GOLD NANORODS

The morphology of nanostructures, homogeneity of surface coverage, and the nanostructures size were studied by SEM (Tescan Mira II, Tescan, Czech Republic).

2.4. ELECTROCHEMICAL FABRICATION OF NANOSTRUCTURED SURFACES

In the first step, the aluminium layer was transformed by anodic oxidation to nanoporous alumina template (Al_2O_3). The anodization process was done as described in the following paper[14], under constant voltage, either at 53 V in 0.3 M oxalic acid or at 20 V in 2 M sulphuric acid. In both cases, the temperature of acid electrolyte was kept at 10 °C. In the second step, when the anodization of aluminium was finished, the bottom tungsten layer was oxidized into the tungsten trioxide nanostructures. In the third step, the WO_3 nanostructures were selectively etched in the phosphate buffer solution at pH= 7. The temperatures of the etching solution were: 25 °C, 40 °C and 60 °C. After etching of WO_3, tungsten nano-dimpled structure was created on the surface. Those nanodimples are a base for gold nanorods and they help to improve their stability. In the fourth step, the gold was electrodeposited from potassium dicyanoaurate solution into the alumina oxide template with the nanodimpled bottom. The conditions were set up during this process as follows: the constant current of 1 mA, the pulse length of 400 ms, the period between pulses of 2 s, the amplitude of 5 V, and the number of pulses 45. In the fifth step, the alumina template was selectively etched in the mixture of chromium trioxide and phosphoric acid at 60 °C for 10 min. All those steps are schematically shown in Figure 2 [12].

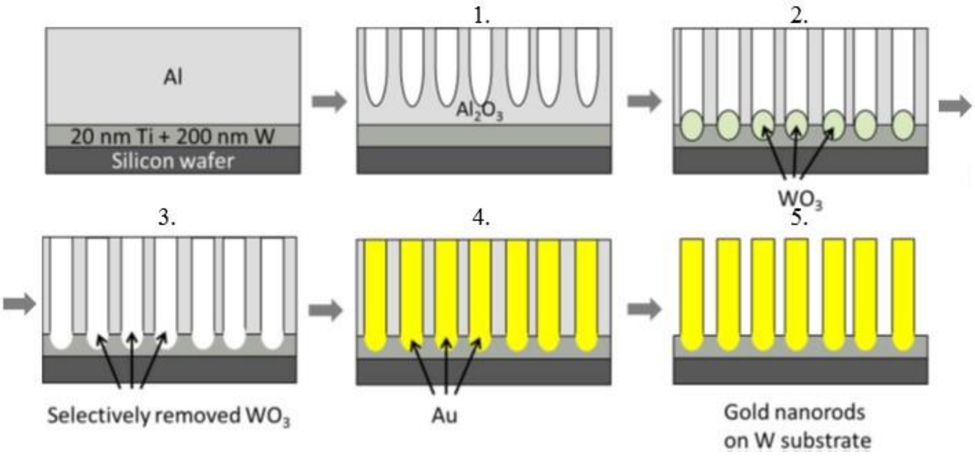

Figure 2: The fabrication process of gold nanorods [10]

3. RESULTS AND DISCUSSION

The analysis confirmed that the anodization of aluminium layer in different acid electrolytes gives the different pore geometry of the alumina template. In 0.3 M oxalic acid and at applied voltage of 53 V was obtained the nanopores with the pore diameter of about 50–60 nm. The pore length depends on the thickness of the alumina layer, it was ~ 300 nm. The interpore distance is similar to the pore diameter, i.e. ~ 50–60 nm. In 2 M sulphuric acid and at applied voltage of 20 V, the nanopores have the size of pores of around 25 nm and similar interpore distance, which is two times smaller than in the previous case. These results confirmed the very well–known theory, the anodization voltage and the electrolyte type are the most important parameters to control the pore geometry of the alumina nanoporous template. The Figure 3 shows SEM images of template after etching of Al_2O_3 and WO_3 nanostructures, anodized in oxalic acid (left) and sulphuric acid (right). On the left, half of WO_3 nanostuctures was not etched, because the phosphate buffer solution did not reach that part. The influence of etching is clearly seen.

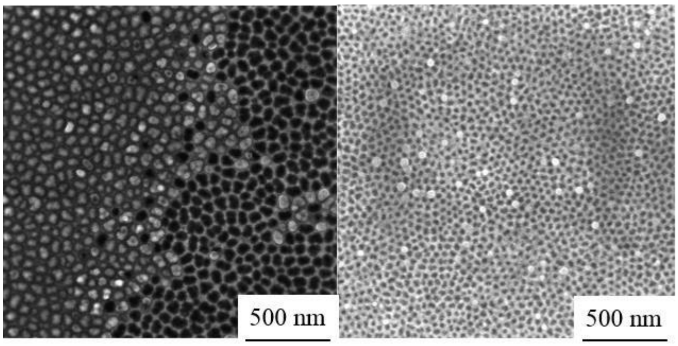

Figure 3: SEM images of template after etching of WO_3 and Al_2O_3 nanostructures, anodized in: 3 M oxalic acid at applied voltage of 53 V (left) and 2 M sulphuric acid at applied voltage of 20 V (right);

The results of selective etching of tungsten oxide nanostructures can be seen in Figure 4. The time of etching process was 60 min when temperature of etching solution was 25 °C (left) and 40 °C (middle), and 45 min when temperature was 60 °C (right). The electrochemical anodization of those samples was done in the sulphuric acid.

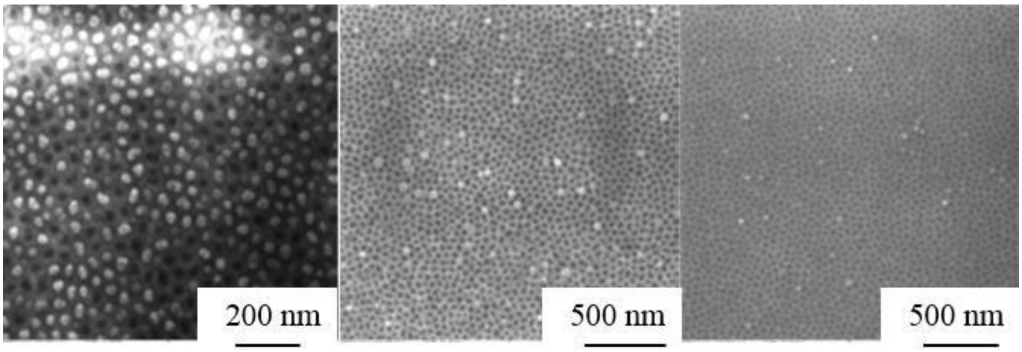

Figure 4: SEM images of etched WO_3 nanostructures in the phosphate buffer solution, pH= 7; A) etching temperature (T_e)= 25 °C, etching time (t_e)= 60 min; B) (T_e)= 40 °C, te= 60 min; C) (T_e)= 60°C, t_e= 45 min;

The SEM characterization shows that the increasing temperature strongly affected the dissolution of WO3 nanostructures. The best dissolution of tungsten oxide nanostructures was reached when temperature was 60 °C. The increase in temperature successfully decreased the etching time to 45 min at 60 °C. The final dimpled surface was nicely homogenous and can serve for electrochemical deposition of gold nanorods. The electrochemical deposition of gold into nanoporous alumina template was successfully done under above mentioned conditions. It was possible to obtain gold nanorods with the uniform size, the diameter of ~ 50–60 nm. The homogeneous surface of gold nanorods is illustrated in Figure 5.

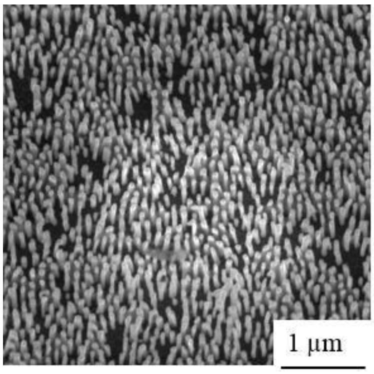

Figure 5: SEM image of gold nanorods prepared via electrochemical deposition

4. CONCLUSIONS

In summary, this work has demonstrated the preparation of nanoporous alumina template via electrochemical anodization of aluminum, and successfully synthesized gold nanorods via gold pulse deposition into the template. Sulphuric acid comparing to oxalic acid greatly decreased the pore diameter of nanoporous alumina template. In future work, gold nanorods will be obtained in the nanoporous alumina template created by sulphuric acid. Higher temperature of etching solution for WO_3 nanostructures perfectly improves the dissolving of WO_3 structures. This helps to create the nanodimpled surface and enables to successfully deposit gold into dimples via alumina template. With the rapid developments in nanorods preparation, surface modification, and assembly, the emergence of novel applications of gold nanorods are likely to impact the areas of VOCs sensing.

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