Two-step approach for the nanofabrication of highly ordered ultra-long porous gold nanowires with an adjustable porosity for SERS-based sensors

Adrien Chauvin,[†] Cyril Delacôte,[‡] Leopoldo Molina-Luna,[‖] Mohammed Boujtita,[‡] Damien Thiry,[†] Ke Du,[§] Junjun Ding,[§] Chang-Hwan Choi,[§] Bernard Humbert,[†] Jean-Yves Mevellec,[†] Pierre-Yves Tessier,[†] and Abdel-Aziz El Mel[†]

[†]Institut des Matériaux Jean Rouxel, IMN, Université de Nantes, CNRS, 2 rue de la Houssinière B.P. 32229, 44322 Nantes cedex 3, France
[‡]CEISAM, Université de Nantes, CNRS, 2 rue de la Houssinière, 44322 Nantes Cedex 3, France
[‖]Technische Universität Darmstadt, Department of Material- and Geosciences, Alarich-Weiss-Strasse 2, 64287 Darmstadt, Germany
[§]Department of Mechanical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030, USA

ABSTRACT

Recently, nanoporous gold has been pointed out as a promising candidate for the development of SERS-based sensors for the detection of environmental toxins and small molecules. One way to improve the detection ability of such sensors is by engineering the porosity and shape of nanoporous materials. In this work we report on a versatile two-step approach for the synthesis of porous nanowires involving plasma deposition of gold-copper alloy on a nanograted substrate followed by a selective electrochemical etching. The relevance of this approach is its ability to prepare highly ordered ultra-long porous gold nanowires with an adjustable porosity and a length up to the macroscale. The resulting gold porous nanowire exhibits a very high roughness and high specific surface area suitable for highly sensitive detection of small molecules by SERS.

Keywords: gold, nanoporous, sensors, dealloying, electrochemistry

1 INTRODUCTION

Nanoporous material attract a lot of interest due to their three dimensional open structure which increases remarkably the specific surface area of the material [1]. A promising issue for this porous structure is their use for the development of optical sensors based on the SERS (Surface Enhanced Raman Scattering) effect [2,3].

Nanoporous materials can be made in a three-dimensional structure such as bulk or thin films [4], in a one-dimensional structure like nanotubes or nanowires [5] and finally in zero-dimension like nanoparticules [6]. The advantage of the one-dimensional structure originates from the anisotropic shape and the high aspect ratio compared to porous thin films [7]. Compared to nanoparticles, the manipulation of one-dimensional nanostructures is also easier for the integration of such materials in nanodevices [8].

The most used technique to create porous nanowires is based on a two step approach consisting in the electrodeposition of alloys in a porous template followed by free corrosion in highly corrosive electrolyte which is a dealloying process [9]. Briefly, the dealloying process consists of removing the less noble metal from a binary alloy. The main drawback of this technique is i) the limitation in length of the prepared porous nanowires due to the low thickness of the host template and ii) the poor organization of the nanowires due to the removal of the host template. Moreover, the free corrosion technique does not allow an accurate control of the final porosity of the porous nanowires.

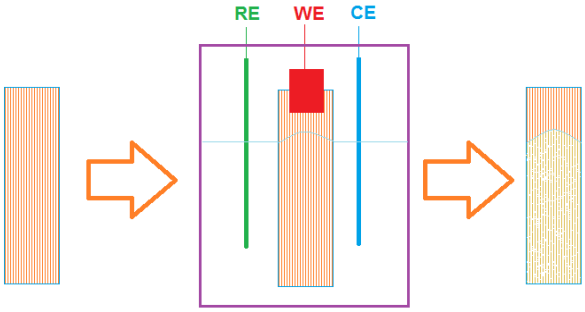

Figure 1: Scheme of the process used in this work to prepare ultra long porous gold nanowire. It consists in gold-copper deposition on nanograted substrate followed by electrochemical dealloying; RE, WE and CE correspond to reference electrode, working electrode and counter electrode respectively.

In this report, we have developed a two step approach for the creation of highly ordered and ultra-long porous gold nanowires. We performed a DC co-sputtering of gold-copper alloy on a nanograted substrate serving as physical template followed by a selective electrochemical dealloying (Figure 1).

2 METHODS

2.1 Nanopatterned substrates

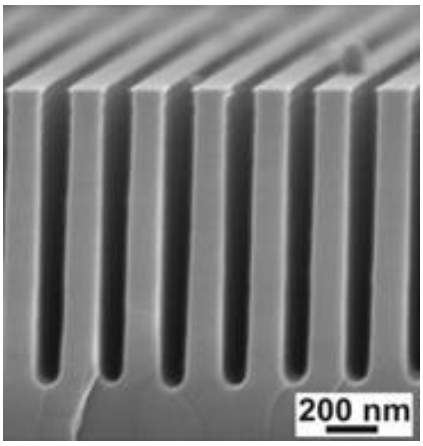

Figure 2: Typical SEM micrograph of the nanograted substrates used in this work to prepare the planar arrays of nanoporous gold nanowires.

The nanopatterned silicon substrates used to grow the Au-Cu nanowire arrays were prepared by laser interference lithography followed by deep reactive ion etching [10]. Such substrates consist of silicon nanograted structures (120 nm in width and 1000 nm in height) of 220 nm in pitch and an aspect ratio of ~6 (Figure 2).

2.2 Growth of Au-Cu alloy nanowires

The Au-Cu nanowires, used to prepare the porous Au nanowires, were synthesized by DC co-sputtering in pure argon plasma of an Au (diameter: 76.2 mm; purity: 99.99%) and a Cu (diameter: 76.2 mm; purity: 99.99%) targets in a co-focal geometry. The distance between the targets and the substrate was 130 mm. Rotation of substrate was performed at a speed rate of 5 rpm to provide a homogenous deposition over a large surface area. The deposition of the Au-Cu nanowire was then carried out at a pressure of 0.5 Pa without applying any intentional heating to the substrate. For all the depositions, the base pressure was less than $4 \cdot 10^{-5}$ Pa.

In order to control the composition of the nanowires, the electrical power applied to the Cu target was fixed to 300 W whereas the one applied to the Au target was tuned. Two electrical powers applied to the Au target were selected (30 and 50 W) allowing growing nanowires with 11 and 23 at. % of Au, respectively. Moreover, two deposition times were selected to tune the initial diameter of the as-grown nanowires (60 and 140 s) allowing growing wires with 135 and 200 nm +/- 3 nm, respectively.

2.3 Electrochemical dealloying process

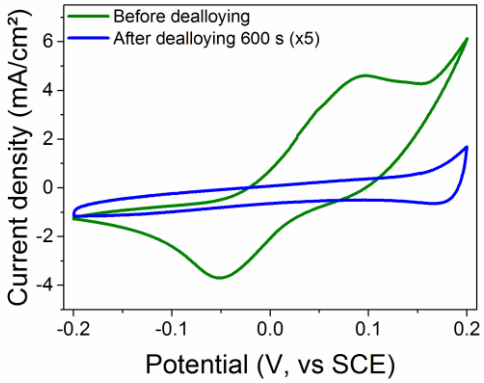

Figure 3: Cyclic voltammograms recorded on nanowire arrays before (in green) and after (in blue) dealloying. The dealloying of this sample was performed at 0.2 V vs SCE for 600 s.

The porous gold nanowires were prepared by electrochemical dealloying of Au-Cu alloy nanowires. These experiments consist in the selective dissolution of Cu by an anodic process. Platinum wire and saturated calomel electrode (SCE) served as the counter and the reference electrode, respectively. All working electrode potentials are provided with respect to the SCE reference electrode. Electrochemical treatments were performed in diluted H_2SO_4 at 0.1 M (pH less than 1) as supporting electrolyte. An analysis by cyclic voltametry (between -0.2 V and the dealloying potential at 50 $mV.s^{-1}$) was made before and after the dealloying process to check the current injection in the nanowires and the Cu removal (Figure 3). The dealloying was proceeded by applying an anodic potential (typically from +0.2 V to 0.5 V) for a given duration (from 150 s to 600 s). During the dealloying process, a magnetic stirring (650 rpm) was applied to ensure a better diffusion of the Cu^{2+} leached during the process.

At the end of each treatment, the samples were removed from the electrolytic solution and dipped in distilled water and then rinsed with methanol.

3 RESULTS AND DISCUSSION

3.1 Tuning final porosity

The aim of this study was to tune the final porosity of the nanowires. For this purpose, dealloying time and dealloying voltage was the two key parameters. In this part, gold composition of the initial nanowires was fixed to 11 at. % (as determined by energy dispersive X-ray spectroscopy) and the initial diameter to 200 nm.

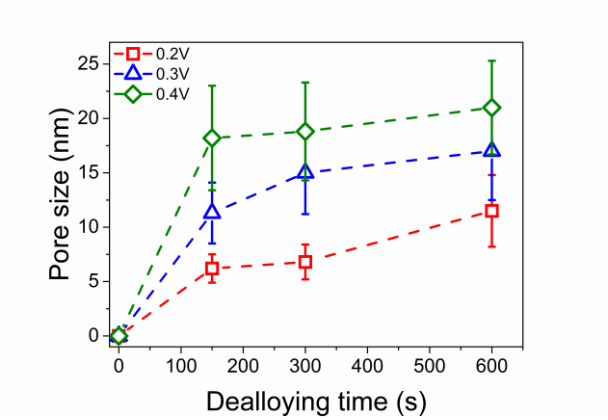

Figure 4: Evolution of the nanowires porosity at different dealloying voltages as a function of the dealloying time. The pore size was determined based on a statistical study performed on several SEM images recorded on each sample.

To analyze the size, statistical study was performed on the dealloyed nanowires for different dealloying voltages and durations (Figure 4). It can be seen that for a constant dealloying voltage, the porosity increases slightly with the dealloying time. For a dealloying voltage fixed at 0.2 V, the pore size increases from 6 to 11 nm for a dealloying time of 150 and 600 s, respectively. Contrary to the dealloying time, the dealloying voltage has a significant influence on the pore size. For a dealloying time fixed at 150 s, the pore size increases from 6 to 18 nm for a dealloying voltage from 0.2 V to 0.4 V.

These two parameters allow adjusting the final porosity of the nanowires in a precise manner; the dealloying time allows a fine control but within a narrow range whereas the dealloying voltage allows a more significant control within a broader range of pore size. By playing on these two parameters we demonstrate that we are able to tune the final porosity precisely between 6 to 21 nm.

3.2 Organization of the nanowires

An important part of this study was the organization of the dealloyed nanowires over the substrate surface which is essential for the development of sensors and actuators. Indeed, for nanowire dealloyed with the previous experiments, the nanowires were found to partially delaminate from the substrate. One of the main objectives of our work was to obtain a good mechanical stability of the nanowires on the substrate in order to integrate them in practical devices. For this purpose, the deposition parameters were tuned to overcome the delamination issue. We have modified the: i) deposition time to tune the diameter of the Au-Cu nanowires and or ii) the electrical power applied to the gold target to adjust the gold content within the as-grown Au-Cu nanowires [11]. Figure 5 and 6 show the influence of these two parameters on the final morphology and adhesion of nanowires on the nanograted substrate.

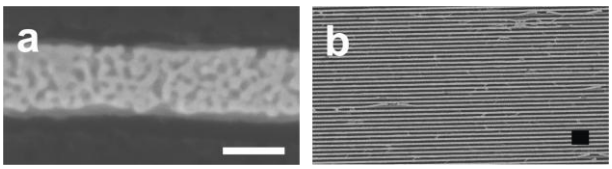

Figure 5: Plan view SEM micrographs of nanowire dealloyed at 0.3 V vs SCE during 300 s with an initial diameter of 135 nm and 11 at. % of initial gold content. White scale bar: 100 nm and black scale bar: 1 µm.

Figure 5a and b show nanowire dealloyed at 0.3 V during 300 s for a sample with an initial diameter of 135 nm and 11 at. % of initial gold content. This nanowire has a good adhesion to the substrate with the same pore size compared to the largest nanowires dealloyed under the same condition. We assume that decreasing the diameter of the nanowires allows decreasing the internal stress within the dealloyed porous nanowires which allows in turn overcoming the delamination issue encountered in the previous conditions [12].

Another way to overcome the delamination issue is by increasing the initial gold content of within the as-grown Au-Cu nanowires.

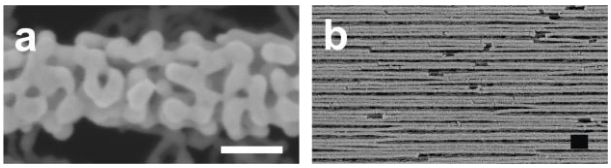

Figure 6: Plan view SEM micrographs of nanowire dealloyed at 0.5 V vs SCE during 300 s with an initial diameter of 200 nm and 23 at. % of initial gold content. White scale bar: 100 nm and black scale bar: 1 µm

Figure 6a and b show nanowires dealloyed at 0.5 V during 300 s with an initial gold content of 23 at. % and an initial diameter of 200 nm. At low dealloying voltage, a surface passivation by gold appears and prevents the formation and development of nanopores within the material during the dealloying process [13]. For this purpose, higher voltage was used due to the surface passivation of the nanowires by gold when working at low

leaching voltages. In such a way, one can obtain highly porous (a pore size up to 23 nm) nanowires while keeping a perfect organization over the nanograted substrate surface.

4 CONCLUSION

To conclude, a new two step approach for preparing planar arrays of nanoporous gold nanowires suitable for the development of sensors based on the SERS effect was developed. The ability of tuning the pore size (between 6 to 24 nm) and to obtain excellent organization of the nanowires over the substrate surface was also demonstrated. Our approach would be of great interest for the development of SERS based sensor for the detection of small molecules.

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