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# In situ patterning of hierarchical nanoporous gold structures by in-plane dealloying

ABSTRACT

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# 1. Introduction

Nanoporous gold (NPG) as a bulk nanostructured material not only has many advantages such as large specific surface area, crystalline alignment and clean surface for catalytic function [1,2], but also shows interesting optical properties such as mixed localized/propagating surface plasmons [3,4]. These properties make NPG an attractive material in many applications such as catalysis [5], sensor [6], actuator [7] and energy storage [8]. Selective dealloying of the less noble material in Au-Ag alloy by nitric acid is a simple method for fabricating semi-infinite NPG films. During dealloying, silver atoms are removed, providing mobility to gold atoms to reassemble into a nanoporous network with a typical pore size of 5–50 nm [9]. Fabricating semi-infinite NPG thin films through this approach has been the primary technique of choice in existing work. For example, using either commercially available "whitegold leaf" or custom-made alloy ingot, several groups have produced NPG thin films this way [10-12]. Beyond NPG thin films, a few recent studies have further employed post-dealloying modifications to generate hierarchical NPG structures with longer-range structural modulation. For example, Zhang et al. employed thermally induced wrinkling in NPG film for surface-enhanced Raman scattering (SERS) measurements [13]. Jiao et al. used mechanical stamping

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We report a novel in situ patterning method that generates hierarchical nanoporous gold (NPG) struc-

tures such as sub-micron NPG disks and microscale NPG patterns during dealloying for the first time. Our

patterning method also enables the quantification of dealloying rate by scanning electron microscopy

(SEM) without the need for depth-resolving imaging modalities. As potential applications, we demon-

strate that the hierarchical NPG dot arrays are effective for surface-enhanced Raman scattering (SERS) and metal-enhanced fluorescence (MEF), both are highly sensitive molecular sensing techniques.

to generate one- or two-dimensional grating-like structures with a characteristic pitch of a few hundreds of nanometers [14].

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Recently, our group developed a novel approach to fabricate sub-micron NPG disks by the combination of top-down lithography and bottom-up atomic dealloying [15]. The large surface area of NPG disks and hot-spots inside the nanoporous structures have contributed to an average SERS enhancement factor exceeding 10<sup>8</sup> and surprisingly high photothermal conversion efficiency (>50%) among metal nanoparticles of similar size with various shapes and compositions [16,17]. NPG disk substrates have also been employed for biomolecular sensing by a novel stamping approach without any wet sample preparation [18]. Our approach involved pre-patterning alloy thin films into individual alloy disks before dealloying, and thus can be classified as *pre-dealloying* modifications.

Although highly effective, the dealloying rate using concentrated nitric can be as high as hundreds of nanometers per second, thus making the precise control and observation of dealloying progress challenging. In most of the works mentioned above, unrestricted dealloying typically occurred from all fronts where Ag atoms were met with nitric acid and then dealloying propagated three-dimensionally throughout the alloy, producing the internal nanoporous network. To accurately determine dealloying rate Chen-Wiegart et *al.* reported the observation of dealloying front buried inside a partially dealloyed cylindrical rod of diameter 16 µm using transmission X-ray microscopy [19].

In this work, we report a novel in situ NPG patterning method that generates hierarchical NPG structures *during dealloying* for the first time. In situ patterning is achieved by limiting the initiation







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Fig. 1. Schematic diagram of the fabrication process: (a) sputter deposition of adhesion (optional), alloy and top Cr layers. (b) PMMA spin-coating, exposure and development. (c) Wet etching of top Cr layer and removing of PMMA with acetone. (d) Time-controlled dealloying in concentrated nitric acid.

point of dealloying to designated locations and restrict the reaction to only progress in-plane. The fabrication processes are shown schematically in Fig. 1 and briefly described here. After forming a film stack of an optional adhesion layer, an alloy film, and a Cr layer, vias were opened on the top Cr layer, followed by a timedimmersion in concentrated nitric acid for dealloying. Due to the protection provided by the Cr layer, nitric acid could only etch the alloy through the via openings, and then progressed in-plane or laterally. By controlling the dealloying time, NPG disks with various diameters were fabricated during dealloying.

Next, we demonstrate that this fabrication technique permits the dealloying front of as-produced NPG structures to be directly observed by scanning electron microscopy (SEM), a commonly available imaging tool. Using SEM, we have investigated the influence of the starting alloy composition, as well as the effect of an underlying adhesion layer. Since only lateral dealloying is allowed, this technique requires longer dealloying time to complete compared to non-restricted dealloying such as in Ref. [16]. Finally, we show that various hierarchical NPG structures can be fabricated, including highly regular arrays for SERS and metal-enhanced fluorescence (MEF).

#### 2. Methods

The fabrication processes are shown schematically in Fig. 1. The first step produces the original film stack, in which DC sputtering deposition was applied for each layer (see Fig. 1a). An optional adhesion layer consisting of 5 nm of Cr and 100 nm of Au was first deposited onto a clean silicon surface, followed by depositing a 90 nm alloy layer and a 20 nm of Cr top layer. The underlying adhesion layer is a necessary component for most experiments involving thin film NPG. However, in our experiment, the alloy film only partially dealloyed into NPG, together with the existence of top cover layer, the adhesion layer becomes optional. Two alloy compositions were used in different experiments: Ag<sub>82.5</sub>Au<sub>17.5</sub> and Ag<sub>72</sub>Au<sub>28</sub> in atomic ratio (ACI Alloy).

The next step was to generate desired initiation points in poly(methyl methacrylate) (PMMA) photoresist (see Fig. 1b). PMMA (PMMA 495 A4, MicroChem Crop.) was spun onto the Cr film by a two-step coating process (500 rpm for 5 s and 4000 rpm for 45 s), producing a 200 nm thick film. After a soft-bake at 180 °C for 90 s, the photoresist was exposed by SEM equipped with nanopattern generation system (FEI XL-30FEG) with 15 keV and 400  $\mu$ C/cm<sup>2</sup> for electron energy and exposure dosage, respectively. The sample was then gently vibrated in 1:3 Methyl Isobutyl Ketone (MIBK) to isopropyl alcohol (IPA) solution for 45 s to dissolve the exposed area, leaving PMMA film containing the via patterns for the top Cr layer. The sample was rinsed thoroughly with de-ionized (DI) water and blow-dried by nitrogen gas.

Next, the pattern was transferred from PMMA to the top Cr layer by wet etching (see Fig. 1c). Commercially available Cr etchant generally etches Ag as well, thus not suitable for our experiment. Hydrochloric acid (HCl) diluted from a commercial 37% solution by DI water with volume ratio of 1:3 was used in this work. In order to remove the thin native oxide layer which always covers the Cr film with diluted HCl solution, an Al sheet was placed in the solution at a uniform distance from the sample and electrical contact was made between the sample and Al sheet outside the solution. This resulted in a battery that generated a small current capable of removing the oxide layer in 5 s. The sample remained in the solution for another 15 s followed by thorough cleaning in DI water and blow-dried with nitrogen gas. Then the PMMA layer was removed by rinsing the sample in acetone for 1 min.

The final step of the process was to submerge the sample into concentrated nitric acid (see Fig. 1d). In this step, Cr was quickly oxidized and become impermeable to nitric acid, and dealloying initiated at the via locations and progressed laterally. After time-controlled dealloying, the sample was rapidly transferred into DI water, gently vibrated for 2 min allowing residual nitric acid underneath the top Cr layer to be thoroughly removed. The sample was then blow-dried with nitrogen gas and imaged with SEM.

# 3. Results

#### 3.1. Characterization of dealloying area and dealloying rate

Experiments were conducted under 4 different conditions, two types of alloys were used with Ag/Au atomic ratio of 82.5:17.5 and 72:28, as well as the option of an adhesion layer underneath the alloy film.

The 20 nm top Cr layer is semi-transparent in SEM, allowing the dealloying front and dealloyed area to be directly observed. The SEM images at three typical dealloying time points for each condition are shown in Fig. 2. In each image, we observe a central bright spot corresponding to the Cr via openings. The dealloying front can be identified and are marked by four arrows. The intervals between the dealloying time points were chosen such that the dealloyed distance between adjacent time points was larger than 500 nm to reduce measurement errors. Due to the isotropic nature of the laterally progressed dealloying, the results were NPG disks. In Fig. 2a, apparent cracks are observed in the NPG within the via opening area from the Ag<sub>82.5</sub>Au<sub>17.5</sub> alloy without an adhesion layer. Comparing Fig. 2a and c with Fig. 2b and d, although all four experiments produced disk shaped NPG region, the edge roughness varied. Smoother disk edges are observed from samples without adhesion layers (Fig. 2a and c), whereas rougher edges from samples with adhesion layers (Fig. 2b and d). The results suggest that the adhesion layer caused larger variability in the dealloying rate for different directions, or anisotropic in-plane dealloying. The roughness of the edges is approximately 2-3 hundred nanometers.

Fig. 3 shows zoomed-in SEM images near the Cr via openings. Because of the lower free electron density in chromium oxide compared to gold, in SEM images the exposed NPG at the via has much higher brightness than the top Cr layer. The distinct brightness



**Fig. 2.** SEM images corresponding *to each condition* at typical dealloying time: (a) Ag<sub>82.5</sub>Au<sub>17.5</sub> alloy without adhesion layer. The bright strip inside the red box shows a crack in top Cr layer at a very early stage. (b) Ag<sub>82.5</sub>Au<sub>17.5</sub> alloy with adhesion layer. (c) Ag<sub>72</sub>Au<sub>28</sub> alloy without adhesion layer. (d) Ag<sub>72</sub>Au<sub>28</sub> alloy with adhesion layer. The red arrows in each image indicate the dealloying front.

change at the Cr via could be used to identify the Cr boundary, which is marked with red circle in the figures.

The dealloying front or the boundary between NPG and alloy could be identified either from structural or brightness change. In our previous work, volume shrinkage induced tensile stress during dealloying led to micro-cracking in the NPG structures. The shrinkage and micro-cracking are more pronounced with higher Ag content in the starting alloy. In the case of Ag<sub>82.5</sub>Au<sub>17.5</sub> alloy, large cracks on the order of a few hundred nanometers are observed in the NPG structures without the adhesion layer (see Fig. 3a and d). In contrast, in the case with adhesion layer, the adhesion layer plays an important role by providing "anchors" for the mobile Au atoms during dealloy, resulting in nano-cracking of tens of nanometers in width (see Fig. 3b and e)

The Ag<sub>72</sub>Au<sub>28</sub> alloy experienced less volume shrinkage during dealloying, and thus smaller tensile stress in the NPG structures, from which only sparse and nanopore-sized cracks are observed either with or without the adhesion layer (see Fig. 3c and f). The nanoporous structure is too small to be directly observed through the top Cr layer, therefore there is no visible structural change in

the SEM image. However, NPG does exhibit different brightness in the SEM image compared to alloy due to the electron scattering caused by the nanoporous structure (see supporting information), so the boundary between them could still be easily identified. The dealloying front is depicted by the blue circle in Fig. 3, outside of which is undealloyed.

Supplementary Fig. I related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mseb.2014.12.016.

The average distance between the Cr edge (red circle) and the dealloying front (blue circle) is defined as dealloying distance. Dealloying distance versus time for the four conditions discussed previously were plotted in Fig. 4 along with their linear fits. The slope of each linear fit represents the dealloying rate. The highest rate 266 nm/s was observed with the Ag<sub>82.5</sub>Au<sub>17.5</sub> alloy without the adhesion layer, and was reduced to 218 with the adhesion layer. In contrast, 43 nm/s and 58 nm/s dealloying rates were observed from the Ag<sub>72</sub>Au<sub>28</sub> alloy with and without adhesion layer, respectively. The different dealloying rates can be understood using the heuristic explanation below. For the Ag<sub>82.5</sub>Au<sub>17.5</sub> alloy without the adhesion layer, the cracks accelerated the flow of nitric acid



**Fig. 3.** SEM images showing structural change in dealloyed samples. (a) Ag<sub>82.5</sub>Au<sub>17.5</sub> alloy without adhesion layer. (b) Ag<sub>82.5</sub>Au<sub>17.5</sub> alloy with adhesion layer. (c) Ag<sub>72</sub>Au<sub>28</sub> alloy with/without adhesion layer. (d)–(f) are the zoomed-in images corresponding to (a)–(c), respectively.

through dealloyed area and resulted in the highest dealloying rate, whereas, a lower rate was obtained when the adhesion layer was present. The decrease in dealloying rate is attributed to an "anchoring" effect from the adhesion layer which reduced the size of the cracking size. In contrast, significantly lower dealloying rates were obtained from the Ag<sub>72</sub>Au<sub>28</sub> alloy because of the lower Ag atomic ratio, and thus the higher critical potential for dealloying. As the Ag<sub>72</sub>Au<sub>28</sub> samples only resulted in nanoporous-sized sparse cracks even without adhesion layer, the difference in dealloying rate caused by adhesion layer is hydrophobic which retards the nitric acid flow, whereas the hydrophilic oxide layer generated on silicon surface by nitric acid might promote the motion of nitric acid in the absence of the adhesion layer.

All four experiments show that the dealloying distance is linearly proportional to dealloying time, therefore the dealloying rate was nearly constant within our observation time. This indicates that the system has reached a steady-state, which further indicates that the free corrosion of both alloy with concentrated nitric acid is well above the bonding energy between silver and gold atom, as discussed in the literature [20] as an essential requirement for forming NPG structures. A 79 nm/s dealloying rate for Ag<sub>70</sub>Au<sub>30</sub> alloy in concentrated nitric acid was reported in Ref. 19 with free dealloying of



Fig. 4. Dealloying distance versus dealloying time.

an alloy rod. The same paper also concluded that lower gold ratio results in higher dealloying rate, hence for Ag<sub>72</sub>Au<sub>28</sub> alloy, the free dealloying rate should be higher than 79 nm/s. The dealloying rate measured in our work is slightly lower than that reported in the literature. This result could be explained by the fact that, in our work, the nitric acid can only reach the dealloying front through the vias in the top Cr layer, which could have limiting effect for the dealloying rate.

The dealloying rate difference caused by alloy composition is essentially due to the critical potential of the alloy [20]. Erlebacher proposed a model to describe steady-state dissolution [21], where the dealloying rate is predicted to have exponential relationship with the Ag/Au atomic ratio:

#### $v_d = a \exp(bR_{Ag-Au})$

where  $v_d$  is the dealloying rate and  $R_{Ag-Au}$  is the Ag/Au atomic ratio. By fitting the dealloying rates into the exponential equation we have obtained (*a*, *b*) equal to (9.3, 0.71) and (6.1, 0.76) for samples with and without the adhesion layer.

In addition to the crack formation, volume shrinkage during dealloying also caused the top Cr layer to be under tensile stress. With increased dealloying time, the accumulated stress would cause the top Cr layer to break, after which nitric acid would invade through the cracks and affect the NPG disk shape and the controllability of the dealloying. The bright strip inside the red box in the third SEM image of Fig. 2a shows this process at a very early stage. In this work, all the data were collected without Cr top layer breaking.

The smallest NPG disk that can be fabricated with in-plane dealloying is limited by the smallest via diameter and the precise dealloying time control. Since 20 nm via diameter can be routinely achieved by commercial e-beam writer, together with the wet etching undercut, 30 nm diameter via is achievable. NPG resulted from 5 s dealloying has been reported to have high SERS enhancement factor [16], hence decent nanoporous structures have been formed. Combining with the slowest dealloying rate 43 nm/s measured in the experiment with condition estimated above, the minimum diameter is 460 nm. With an even shorter dealloying time or diluted nitric acid, the diameter could be further decreased. Since the size of the NPG structure and the size of the pores are both controlled by



Fig. 5. "UH" pattern made from in-plane dealloying. The openings are 400 nm in diameter and 5 µm apart. (a) Overall image of the "UH" pattern. (b)-(f) Zoomed-in images at different dealloying time. As dealloying time increased, the initially separated NPG disks merged into one connected NPG pattern.



Fig. 6. "UH" pattern made from in-plane dealloying. The openings are 400 nm in diameter and 2 µm apart. (a) Overall image of the "UH" pattern. (b) Zoomed-in image of a convex corner. (c) Zoomed-in image of a concave corner. The convex corner is rounded and the concave corner is right angle.

the dealloying time, with our current method, the size of the pores induced by dealloying cannot be tuned independently. However, the pore size could be controlled by other methods such as thermal annealing [22,23], laser annealing [24] or surface modification [25], and the pore size could be controlled from a few to few hundreds of nanometers. In this work, the typical pore size is around 5–20 nm.

# 3.2. Patterning microscale hierarchical NPG structures

As timed-dealloying produces diameter-controlled NPG disks, our in-plane dealloying method can be readily used as a novel in situ method of patterning hierarchical NPG microstructures and NPG disk arrays. In this part of the experiment, Ag<sub>72</sub>Au<sub>28</sub> alloy with adhesion layer was used. Fig. 5a shows a pattern of "UH"



Fig. 7. SERS measurements: (a) Raman signal of benzenethiol and (b) SERS map of the sample shown in Fig. 7 obtained by line-scan Raman microscopy.



Fig. 8. MEF measurements: (a) fluorescence image of the UH pattern, (b) normalized fluorescence intensities across the red line shown in (a).

consisting of 400 nm diameter vias with 5  $\mu$ m center-to-center distance. Fig. 5b–f shows the NPG structure formation for four adjacent vias at different dealloying time. With the increase of dealloying time, eventually all separated NPG disks merged into one continuous NPG pattern (see Fig. 5f).

The in-plane dealloying approach is scalable to generate finer patterns. By decreasing the distance between the vias, the feature size of this approach could be easily decreased. The "UH" pattern was fabricated with the same numbers of vias with the center-to-center distance reduced to 2  $\mu$ m. The SEM images in Fig. 6 were taken after the NPG areas merged together by dealloying. In comparison to Fig. 4, the NPG pattern was reduced by 84%, thus a much smaller spacing was achieved.

The in-plane dealloying patterning method could be considered as a dot-based patterning technique, as each NPG area that constitutes a large pattern is disk shaped. This is further evidenced by the fact that convex corners of the pattern are rounded (see Fig. 6b), whereas the concave corners are right angles (see Fig. 6c).

The major advantage of this method is that only a small fraction of PMMA corresponding to the vias needs to be exposed, which is less than 5% of the total patterned area. This method saves exposure time and allows for bigger patterns to be generated with directwrite techniques such as e-beam lithography. The total time for the e-beam exposure was 10 s as compared to several minutes for exposing the entire "UH" area under the same condition. In addition, since the NPG disk diameter is controlled by dealloying time, the same via opening size can be employed.

The leftover Cr layer has a thick oxide layer due to long time nitric acid treatment, causing the removal without damaging the NPG structures rather challenging. However, the Cr layer provides a "rooftop" which confine liquid movement inside the NPG structures. By replacing Cr with silicon oxide, optical techniques can be applied to directly observe fluidic behavior inside the tortuous NPG structures. Alternatively, the oxide can be easily removed after the dealloying is finished. The sample will then become an alloy film with imbedded NPG patterns, providing possible applications in sensing and other fields.

#### 3.3. SERS measurement

Plasmonic substrates are commonly characterized by localized surface plasmon resonance (LSPR). However, our current samples are fabricated on opaque silicon substrate, which prevents extinction measurements by standard transmission UV/vis spectrometer. An alternative way to characterize plasmonic substrate is SERS, which is compatible with our samples. SERS measurements were performed on the NPG dot arrays shown in Fig. 6, in which the bi-continuous NPG structure has been formed by dealloying. We have selected 785 nm as the laser excitation wavelength and benzenethiol (BT) molecules as the SERS marker since the absence of a BT absorption peak near 785 nm minimizes the ambiguity due to resonant Raman scattering, while the ability of BT to form selfassembled monolayers (SAMs) enables uniform coverage of tested substance. BT SAM was deposited on the substrates following the procedure of Ref. 16. SERS measurements were carried out using a home-built line-scan Raman microscopy system [26] to map a  $55 \,\mu\text{m} \times 75 \,\mu\text{m}$  regions with  $\sim 1 \,\mu\text{m}^2$  resolution (full width at half maximum, FWHM) at spectral resolution  $\sim 8 \,\text{cm}^{-1}$ .

A typical BT SERS spectrum is shown in Fig. 7a. The SERS map was generated using the peak at  $\sim 1076 \text{ cm}^{-1}$  (CCC stretch, CS bending). Clearly, SERS signal is maximum at the vias, and the diameter of the vias appears larger than 400 nm in the SERS map due to the resolution limit of the line-scan Raman system. The NPG formed under Cr top layer is assumed to be covered with Benzenethiol SAMs as well, however there were little SERS signal coming from such part. Thus 20 nm of Cr layer is enough to reduce the SERS signal to be under the detection limit of our system. Combined with multi-point Raman microscope based on active illumination [27], the NPG dot arrays can be a powerful analytical platform.

#### 3.4. MEF measurement

The measurements of another surface enhanced phenomenon MEF were also performed on the patterned NPG structures. The NPG dot arrays were incubated in 1 micromolar aqueous solution of Rhodamine 6G (R6G) for 24 h. The sample was then washed with in DI water and allowed to dry in ambient room conditions. Fluorescence images were collected using an epifluorescence microscope (Olympus BX61TRF) as shown in Fig. 8a. The filter set included an excitation bandpass filter centered at 531 nm and a 562 nm emission longpass filter. Excellent fluorescence was observed from the NPG dot arrays compared to the Cr regions where little fluorescence was observed.

# 4. Conclusions

In this paper we reported a novel in situ patterning method that generates hierarchical NPG structures *during in-plane dealloying*. Through our fabrication technique, the dealloying front of the NPG film structures were observed directly by SEM, allowing in-plane dealloying distance and rate to be determined without depthresolving imaging. Experiment results showed that the dealloying distance is linearly proportional to dealloying time, hence a fixed dealloying rate. Two different alloy compositions both with and without adhesion layer were tested to characterize compositionand adhesion-dependent dealloying rate. Experiment results also showed that lower gold ratio results in cracks in dealloyed film, causing a higher dealloying rate, while the presence of adhesion layer restricts the formation of cracks and reduces the dealloying rate. Besides NPG disks, microscale patterns were also generated from simple via arrangement with our approach. SERS and MEF measurements were demonstrated on NPG dot arrays as potential applications. The sensitivity of SERS and MEF of NPG materials was shown to be largely affected by its pore size. Thus, The SERS and MEF properties of NPG film can be tuned accordingly based on its physical dimensions.

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