Laser-printed plasmonic nanotextures with controlled porosity

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Abstract. We propose efficient approach for fabrication of various plasmonic nanostructures in the shape of the sub-micro rings and nanohillocks having tailored inner porosity. The fabrication approach combines the direct nanosecond-pulse ablation of the nitrogen-rich Au films covering glass or silicon substrates followed by a large-area etching with an Ar-ion beam. The average size of the nanopores inside the produced structures can be controlled via nitrogen doping level in the target metal films through tailoring the nitrogen gas concentration in the process of the film magnetron deposition, while the overall geometric shape of the produced plasmonic structures can be controlled by optimizing the thickness of the irradiated film as well as the laser irradiation parameters. Spherical-shape nanopores of variable size which depends on the initial nitrogen concentration in the irradiated film were directly revealed by preparing the cross-sectional cuts of the fabricated nanorings using focused ion beam milling. The proposed approach holds promise for easy-to-implement fast laser printing of the various nanostructures with the tailored porosity for chemo- and biosensing applications.

1. Introduction

Plasmonic nanostructures with pronounced porosity are of great interest for various applications ranging from the bio- and chemosensing to the photocatalysis and hydrogen storage [1]. In particular, the nanotextured surface of such porous structures produces the strongly localized and enhanced electromagnetic near-fields (hot spots) which density can be controlled by tailoring the geometric dimensions and density of the nanopores. Fabrication of such porous plasmonic nanostructures is rather challenging procedure typically requiring implementation of several consecutive time-consuming and expensive fabrication processes. For example, nanostructures consisting of a two-component metal alloy (say, Au and Ag) were fabricated using the electron-beam lithography, while the subsequent chemical dealloying in the acid provides the way to remove one of the material from the alloyed nanotextures to produce nanopores [2].

Here, we demonstrate facile laser-based approach allowing fabrication of various porous nanotextures on the glass/silicon substrates. The proposed approach combines the direct single-pulse ablation of the nitrogen-doped gold/silver film followed by the large-scale soft etching with the argon-ion beam. The average size of the nanopores was found to correlate with the nitrogen doping layer of the deposited metal films controlled via mixing the nitrogen and argon discharge gases in the process of the magnetron deposition. The formation of the nanopores results from the boiling of the nitrogen-
reach areas of the metal film irradiated with the laser pulse. Depending on the initial thickness of the irradiated film, the laser pulse can produce either a nanohillock or the nanoring allowing to tune the general geometry of the fabricated structures as well.

2. Results and Discussions

![Figure 1](image_url)

**Figure 1.** (a,b) Two-step fabrication of the porous nanorings and nanohillocks. Single nanosecond laser pulses first irradiate the surface of either “thin” (a) or “thick” Au film on a glass substrate. Depending on the Au film thickness, laser irradiation produces the through holes or the surface hillocks. The nanopores are mainly appear inside laser-modified areas. (c,d) Subsequent etching of the textured Au films with an accelerated defocused argon-ion beam results in removal of the surrounding unmodified metal film leaving the isolated plasmonic nanorings or nanohillocks on the substrate surface. Note that the etching process also reveals the initially hidden nanopores. (e,f) Normal-view SEM images showing arrays of porous nanorings and nanohillocks. Scale bar corresponds to 500 nm.

The proposed approach was adopted from [3,4] and contains two main fabrication steps. On the first step, we used the tightly focused ($D_{opt}=1 \mu m$) second-harmonic (532-nm) laser pulses generated by the Nd:YAG system (pulse duration of 7 ns, pulse repetition rate is 20 Hz) to locally ablate the Au film on a glass/silicon substrate (Fig.1(a,b)). We utilized the Au films with the thicknesses of 120 and 250 nm. Irradiation of the thinner film at the pulse above the ablation threshold [3] results in formation of the circular through holes with the rather thick resolidified rim. On the contrary, at similar applied energy the laser radiation is not able to melt the 250-nm thick Au film through all its thickness resulting in formation of parabola-shaped nanohillocks on the surface of the irradiated Au film. Subsequent etching of the textured Au films with an accelerated defocused argon-ion beam at etching rate of 1 nm/min results in removal of the surrounding unmodified metal film leaving the isolated plasmonic nanorings or nanohillocks on the substrate surface. Noteworthy, by shaping the focal-plane intensity
distribution of the laser pulse, one could also expect to produce other nanostructures having various geometric shapes and sizes.

The argon is a common discharge gas used for magnetron deposition of the Au films. The ablation of the Au films evaporated in the Ar atmosphere and subsequent Ar-beam etching results in formation of smooth structures without any surface or subsurface pores inside as it was previously reported in [4]. In a short contrast, the similar surface structures, nanorings and nanohillocks, produced from the Au film deposited in the nitrogen atmosphere demonstrate pronounced porosity (see Fig.1(e,f)). To study this feature in more details, using magnetron deposition we prepared a series of Au film evaporated at various mixing ratios of nitrogen and argon [5]. In all cases, the films have identical thickness of 120 nm. Our studies clearly shows the correlation between the initial concentration of the nitrogen in the evaporation chamber and the average size of the nanopores appeared in the fabricated microrings as it is illustrated by the series or SEM images (Fig.2(a-e)).

![Figure 2.](image)

**Figure 2.** (a-e) Normal-view SEM images of the isolated 900-nm diameter nanorings and corresponding cross-sectional FIB cuts of the nanoring wall showing the position and the average size of the nanopores. (f-j) Corresponding cross-sectional FIB cuts (k) Averaged distribution of nanopore diameters inside the fabricated microrings. The statistics for each film type was accumulated over 50 microrings of the same size produced under similar experimental conditions.

To reveal the location of the nanopores inside the fabricated nanorings we have prepared the cross-sectional cuts made across the ring wall using the focused ion-beam milling technique. For the nitrogen-doped Au films the formation of the spherical-shape nanopores can be identified in all the presented SEM images (Fig. 2(f-j)). The analysis of the SEM images indicates that the average diameter of the nanopores increases versus the concentration of the nitrogen in the Au film (Fig. 2(k)). Noteworthy, for weakly doped Au films (Fig.2(b,c)), the diameter distribution demonstrates the only size maxima, while for highly doped ones – several maxima in the diameter distribution can be
identified (Fig. 2(k)). We believe this feature can be explained by merging the smaller nanopores into the bigger ones for nitrogen-rich Au films.

3. Conclusions

Here, we propose efficient two-step approach for rapid laser printing of the sub-micro rings and nanohillocks having tailored inner porosity. The presented approach combines the direct single-pulse ablation of the nitrogen-doped Au film followed by the large-scale soft etching with the argon-ion beam. The average size of the nanopores was found to correlate with the nitrogen doping layer of the deposited metal films controlled via mixing the nitrogen and argon discharge gases in the process of the magnetron deposition. This tendency was directly revealed using SEM inspection of the FIB cuts produced along the fabricated nanoring walls. The proposed facile laser-based approach with its potential to tune also the general shape of the printed nanotextures via optimization of the laser intensity distribution as well as target characteristics holds promise for easy-to-implement fast laser printing of the various nanostructures with the tailored porosity for chemo- and biosensing applications.

Acknowledgments

Authors acknowledge support from Russian Science Foundation 17-19-01325.

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