Applied Surface Science 302 (2014) 74–78

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Complex patterned gold structures fabricated via laser annealing and dealloying

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ARTICLE INFO

Article history:
Received 10 June 2013
Received in revised form
12 December 2013
Accepted 12 December 2013
Available online 19 December 2013

Keywords:
Laser annealing
Periodic structure
Nanoporous gold
Dealloying

ABSTRACT

Gold films with periodic stripes of nanoporous structure are realized by using pulsed laser annealing in a mask projection arrangement in combination with a dealloying process. An Ag–Au alloy is first formed in the exposed areas of Ag/Au bi-layers by annealing, and then the Ag is removed from Ag–Au alloy by submerging in HNO_3 solution and nanoporous gold is formed. The Ag top-layer in the unexposed areas of the Ag/Au bi-layers is also removed and the Au under-layer remains. Laser annealing is performed with 2 pulses and 10 pulses at different energy densities. Optimized laser annealing parameters for the 140 nm Ag/80 nm Au bi-layers is found with 10 pulses at fluences of 132 and 143 mJ/cm^2.

1. Introduction

Micro- and nano-structured metals have drawn increased attention due to the potential applications in catalysis [1], plasmonics [2], magnetic storage [3], DNA detection [4] and surface-enhanced Raman spectroscopy (SERS) [5]. Besides using photolithography and electron beam lithography, laser radiation based techniques are often used for fabrication of micro- and nanostructured metals. For example, structuring can be realized directly by laser ablation [6], and laser radiation induced dewetting is often used for forming metallic nanoparticles [7,8]. Both laser induced and thermal annealing induced dewetting of metal films on templated substrates can lead to formation of ordered arrays of metal nanoparticles with well-defined particle size and spacing [9–14]. In addition, thermodynamic metallurgic properties are also utilized for producing micro- and nano-scaled metal structures. For instance, different (bi-metallic and supersaturated) Ni–Au alloy nanoparticles can be fabricated via annealing of Ni/Au bi-layers by controlling the annealing temperature and cooling rate [15,16]. Nanoporous Au nanoparticles with ultrahigh surface-to-volume ratio are fabricated from Ag–Au alloy nanoparticles [17,18]. Periodic alloy patterns can be even fabricated by laser interference metallurgy [19], by which metallic multilayers are annealed for alloying in the periodic exposed areas. In this paper, complex patterned Au structure consisting of periodic stripes of nanoporous gold is fabricated via a combination of masked laser annealing and dealloying. Periodic stripes of Ag–Au alloy are fabricated by the laser annealing of Ag/Au bi-layers and then transformed into periodic stripes of nanoporous Au via selective removing of Ag with HNO_3 solution (dealloying). These complex structures possess two structural levels: periodic stripes with period in microns range and nanoporous gold with ligament/pore size around 10 nm.

2. Experimental

The fabrication of the complex patterned gold structures is schematically presented in Fig. 1. 140 nm Ag/80 nm Ag bi-layers were deposited on SiO_2/Si substrates using electron beam evaporation. Before the deposition of the bi-layers, 200 nm thick SiO_2 was thermally grown on the Si to avoid the reaction between the metallic films and Si substrate. The Ag/Au bi-layers were then annealed using pulsed excimer laser (ArF-excimer laser with wavelength of 193 nm, 20 ns pulse duration and pulse frequency of 5 Hz) irradiation in a mask projection arrangement. Periodic stripes with width of 5 μm and period of 10 μm can be projected by using the mask. 2 pulses and 10 pulses were applied at fluences of 80, 100, 116, 132, 143, 166, 189, and 216 mJ/cm^2. These fluence data were determined as follows: Total laser pulse energy arriving at the sample (with mask in place) divided by the whole irradiated field (570 μm × 570 μm). Thus, this fluence is an average over the

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http://dx.doi.org/10.1016/j.apsusc.2013.12.066

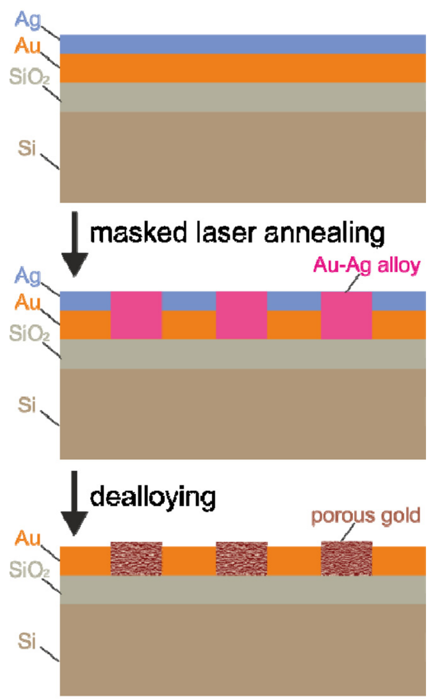

Fig. 1. Schematic of the fabrication of the complex patterned gold structures.

whole field of irradiated and non-irradiated zones. As the actual irradiation takes place on a stripe pattern accounting for half of this field (the other half is masked), the actual energy densities within the irradiated stripes are two times of these values. The annealed samples were then submerged in a 65 wt% HNO_3 solution for dealloying process. After about 30 s, Ag layer seems to be removed, however, the samples were submerged in HNO_3 solution for 5 min to assure the complete removing of Ag. HNO_3 can only selectively etch or remove the Ag from the Au–Ag alloy, so when the Ag was completely removed, the process stopped. (This selective etching can take place only for Ag-rich alloy [20].) The SiO_2 underlayer was not affected by HNO_3. The samples were investigated using an ultra-high resolution scanning electron microscope (SEM, Hitachi S-4800).

3. Results and discussion

Fig. 2 shows the SEM images of the morphology of the Ag/Au bi-layers after laser exposure with 2 pulses at different fluences. The width of stripes with modified morphology increases with increase of fluence. At low fluence, heat loss or heat flow out of the irradiated area leads to a narrower modified stripe; at high fluence this heat flow leads to modification even of non-irradiated regions. As fluence was increased to 216 mJ/cm^2, melting seems to occur and agglomeration and large substrate-exposing voids can be seen clearly. Grain growth within the exposed areas initiated after the exposure at 80 mJ/cm^2 (as seen in the inset SEM image), and clear grain growth can be observed after the exposure

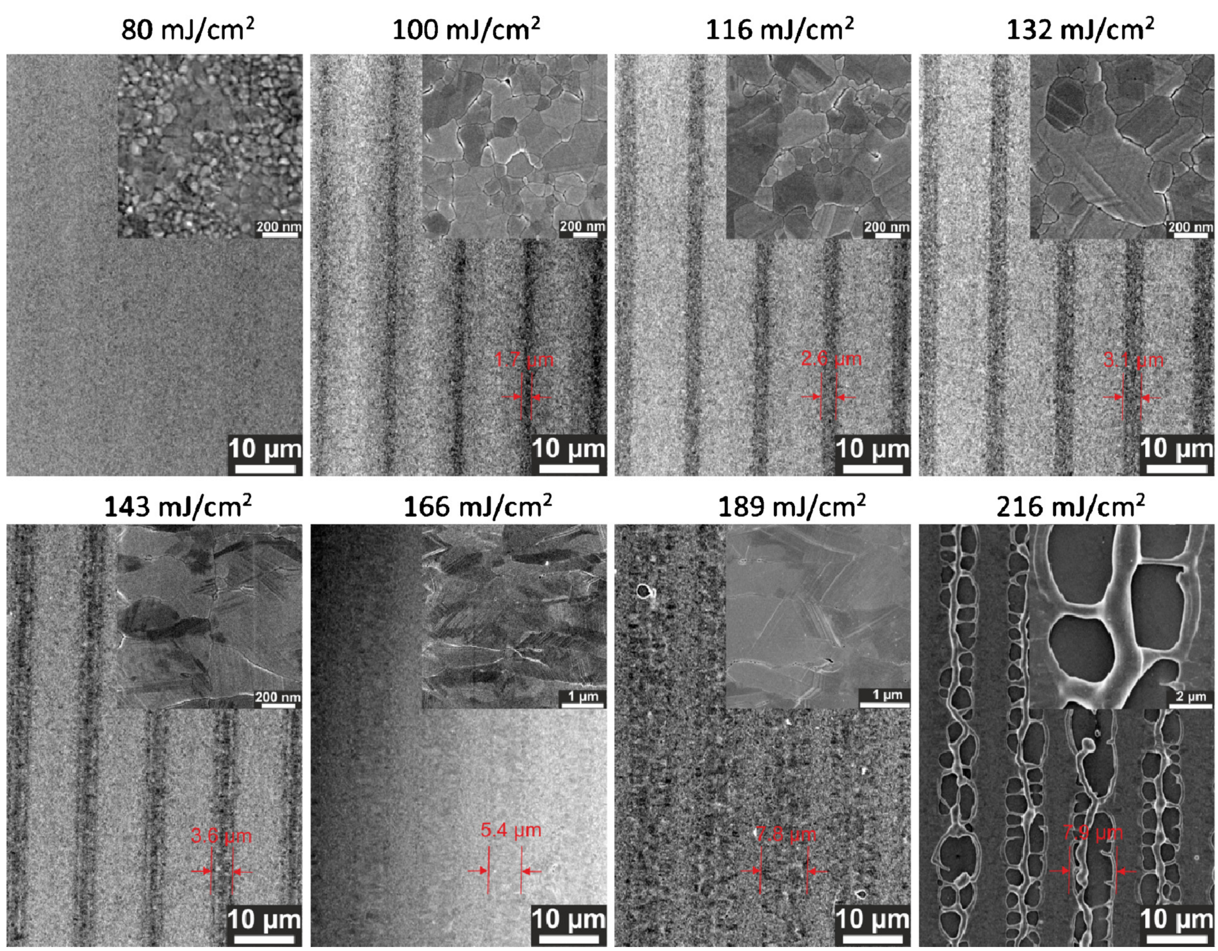

Fig. 2. SEM images of the morphology after masked laser annealing with 2 pulses at different fluences. The insets are magnified SEM images of the corresponding annealed areas.