Fabrication of porous nanostructures for Raman signal amplification

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Abstract. Pulsed-laser dry printing of noble-metal microrings with a tunable internal porous structure, which can be revealed via an ion-beam etching post-procedure, was demonstrated. Average size of the pores inside the microrings were shown to be tuned in a wide range by varying the incident pulse energy and a nitrogen doping level controlled in the process of magnetron deposition of the gold film in the appropriate gaseous environment. The fabricated porous microrings were shown to provide many-fold near-field enhancement of incident electromagnetic fields, which was confirmed by mapping of the characteristic Raman band of a nanometer-thick covering layer of Rhodamine 6G molecules and supporting calculations. The proposed laser-printing/ion-beam etching approach is demonstrated to be a unique tool aimed at designing and fabricating multifunctional plasmonic structures and metasurfaces for spectroscopic bioidentification based on surface-enhanced Raman scattering and photoluminescence detection schemes.

Surface-enhanced Raman scattering (SERS) is an ultrasensitive non-invasive spectroscopic technique based on a label-free identification of different molecules placed in the vicinity of plasmonic-active nanostructured metallic substrates. Intensity of the characteristic Raman signal defining the specific vibrational signatures of individual molecules is usually very weak, but it can be significantly increased near nanotextured surfaces or nanostructures generating localized, strongly enhanced plasmon-mediated electromagnetic fields. Multiple attempts were undertaken to increase the efficiency of SERS-active nanotextured substrates in terms of the achieved maximal enhancement factor inside a single “hot spot” as well as the number of “hot spots” per individual nanostructure.

A variety of nanotextured structures, predominantly having a large surface-to-volume ratio and generating dense hot spots were fabricated and tested as versatile SERS substrates. Specifically, porous materials, nanostructures, and nanoparticles, routinely reaching uniform SERS enhancement sufficient to overcome the single-molecule detection limit independently of excitation/detection conditions, are of growing interest. Meanwhile, to design sensitive elements for advanced biosensors, along with desirable porosity, it is also important to control the overall size and shape of such porous templates as well as to arrange them into ordered arrays at a specific point on a substrate with micrometer-scale lateral accuracy.

In this work, an ion-beam assisted, liquid-free nanosecond (ns) laser printing of isolated plasmonic ring-shaped nanostructures with pronounced porosity is demonstrated. The proposed procedure for fabricating the isolated porous rings includes two consecutive steps schematically illustrated in figure 1. First, a 50-nm thick glass- or Si-supported Au film is irradiated with single second-harmonic (532 nm), 7-ns pulses delivered by a Nd:YAG laser system (Brio, Quantel) focused with a dry objective lens of...
Figure 1. Schematic of the two-step fabrication procedure for printing of the isolated porous plasmonic rings.

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numerical aperture NA = 0.6. In all our experiments, we used the same focusing conditions, while the only incident pulse energy was varied by means of an adjustable attenuator. In a certain range of incident pulse energies [1], such single-pulse ns-laser ablation of the metal film leaves a through hole surrounded by a smooth resolidified rim typically 2.5–3 times thicker, compared to the initial thickness of the deposited Au film. The second step involves removal of the unprocessed parts of the film using a liquid-free etching with an accelerated argon-ion beam (IM4000, Hitachi) at fixed values of an acceleration voltage of 3 kV, a discharge current of 105 µA, and a gas flow of 0.1 cm³/min. This parameter set provides a relatively slow rate of 1 nm/s to avoid film melting. The removal of the residual, initially deposited 50-nm thick Au film leaves the isolated microrings on the substrate surface.

Main geometric parameters of the microrings produced with the developed two-step procedure were shown to be tuned by varying the thickness of the deposited film and the incident pulse energy [1, 2]. In the present study, we demonstrate that an additional degree of tunability of the internal structure of the produced microrings can be provided by a minor variation in the chemical composition of the sputtered metal film via its controlled magnetron deposition in appropriate gaseous environments. To deposit the Au film on a glass substrate, a commercial magnetron sputter was used (Quorum Technologies). Typically, argon is used as a discharge gas for such magnetron sputtering. Then, ns-laser printing followed by the subsequent ion-beam polishing usually results in formation of smooth microrings with a relatively small amount of defects.

Surprisingly, detailed imaging of the structures produced with the single-shot ns-pulse ablative patterning of an Au film sputtered in a mixture of the argon and nitrogen (50/50 wt. %) reveals dense pores inside the fabricated microrings. The nanosized (approx. 60-nm diameter) spherical-shape pores initially located inside the resolidified metal rim can be further visualized through the ion-polishing post-procedure. Moreover, even more pronounced porosity with a significantly larger averaged pore size was found for such structures produced on the surface of the Au film deposited in the nitrogen atmosphere [Figure 2(a)]. The statistical study of the distribution of the pore size inside the microrings produced at the same pulse energy indicates the clear correlation between the nitrogen concentration in the deposition chamber and the average nanopore diameter in the produced microrings [figure 2(a)].

Subsurface boiling around nitrogen-doped cracks and N₂-reach areas of the film appears to be the key mechanism responsible for the formation of the densely packed nanopores inside the molten rim [3]. As known, gold can interact with nitrogen, producing gold-nitride phase Au₅N, upon Au target bombardment with accelerated nitrogen ions [4, 5]. Also, Au₅N films were fabricated, using ablative pulsed laser deposition in a N₂ containing atmosphere. Mass and X-ray inspections show that increased amount of nitrogen corresponds to case of film deposition in nitrogen ambient.

The printed microrings, with their well-controlled micrometer-scale diameter and pronounced nanotexture governed by the unveiled multiple circumferentially spaced pores, are expected to provide strong near-field enhancement of incident electromagnetic waves in visible and IR spectra ranges, making them promising for chemo- and biosensing applications. In this respect, the porous rings arranged into the ordered array can be considered as multifunctional substrates, providing enhancement of both photoluminescence and SERS signals from adsorbed analyte molecules commonly pumped in
Figure 2. (a) Series of normal-view false-color SEM images of microrings produced on the 100-nm thick Au films deposited in the argon (top), argon-nitrogen (50/50 wt. %) gas mixture (middle), and nitrogen gas atmospheres (bottom) via magnetron sputtering. All three microrings were produced at the same pulse energy $E = 17$ nJ. (b) 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.

the optical range, while giving also possibility to utilize near-to-mid infrared wavelengths to excite main dipolar localized plasmon resonances of the microrings.

We restrict our studies of biosensing performance for the laser-printed porous microrings by measuring their Raman response from a self-organized monolayer of Rhodamine 6G (R6G) molecules and mapping surface intensity distribution of their specific main bands. A commercial Raman microscope (Alpha, WiTec) was used to determine the SERS performance of the fabricated microrings. An ethanol solution of R6G with a concentration of $10^{-5}$ M was drop-cast on the sample surface, and after complete drying, it was rinsed with distilled water producing a monolayer. All Raman spectra were measured at the 1-mW excitation laser power and the accumulation time of 0.5 s per point. Similar parameters were used for mapping of the surface intensity distribution of the main R6G Raman bands near the several smooth and porous microrings within the 2x2 µm² square sample area with 0.2-µm sampling step. The build-in software (WiTec Project) was used to obtain the 2D maps related to each spectrally narrow Raman band.

Typical Raman spectra acquired from the R6G layer on both smooth and porous microrings, having almost the same outer diameter and the wall thickness, reveal all main Raman bands characteristic for R6G molecules, while these “fingerprints” cannot be identified on the glass substrate even under 10 times increased accumulation time [figure 3(a)]. This measurement indicates strong SERS performance of the fabricated structures. It points out a clear plasmonic contribution to the SERS enhancement, rather than the concentration effect. Mapping the surface distribution of the Raman intensity at the 1361-cm⁻¹ band of the R6G molecules, covering the smooth microring, reveals the position of the local electromagnetic “hot spots”, which were found to depend on the polarization direction of the exciting laser source [orange arrows in figures 3(b)-3(e)].

According to our supporting FDTD calculations [1] such 532-nm, normal-incident linearly polarized laser irradiation provides low-efficiency excitation of the smooth microring walls with quite moderate 5-fold enhancement of the squared electric field amplitude [figure 3(d)], while the corresponding hot spots, following the linear polarization direction, are distributed non-uniformly along the ring circumference, yielding similar distribution of the SERS signal [figure 3(b)]. On the contrary, according to our FDTD calculation performed for the porous microring, nanosized surface features produce
Figure 3. Biosensing performance of smooth and porous microrings presented as R6G Raman spectra measured on the smooth (brown curve) and porous microrings (purple curve) as well as on the glass substrate after complete removal of the Au film via the ion polishing post-procedure. (b) and (c) SERS maps measured for the 1361-cm\(^{-1}\) Raman band of the R6G molecules nanolayer covering the smooth (b) and porous microrings (c). These maps were found to provide SERS enhancement according to the characteristic E-field amplitude distribution near the smooth (d) and porous microrings (e) calculated for the normally incident, linearly polarized 532-nm laser radiation. The orange arrows indicate the polarization direction. The white circles show the actual dimensions of the microrings.

Multiple strongly enhanced E-fields, homogeneously distributed along the microring surface independently of the polarization direction [figure 3(e)] and generally correlating with the acquired SERS map [figure 3(c)].

In conclusion, in this work, we have fabricated porous microrings from thin gold films deposited in nitrogen and nitrogen-argon mixed atmospheres, by their ns-laser ablation and the following ion-beam etching post-procedure, and studied their SERS performance. The proposed approach allows us to fabricate both smooth and porous microrings with variable geometric parameters as well as tunable inner structure. The developed laser-printing/ion-beam etching procedure is demonstrated to be a versatile tool for fabricating multifunctional plasmonic structures and metasurfaces for spectroscopic bioidentification based on the combination of SERS and photoluminescence detection schemes on a single sensing substrate.

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