Two-Photon Fabrication of Three-Dimensional Metallic Nanostructures for Plasmonic Metamaterials

Atsushi ISHIKAWA and Takuo TANAKA

1- Metamaterials Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
2- Research Inst. for Electronic Science, Hokkaido University, Sapporo, Hokkaido 001-0020, Japan
E-mail: a-ishikawa@riken.jp and i-tanaka@riken.jp

We propose a novel laser fabrication technique based on two-photon-induced reduction of metal ions for 3D metallic micro/nanostructures. Electrically conductive silver nanostructures with arbitrary 3D shape are demonstrated. By introducing dopant surfactant molecules, which prohibit unwanted metal growth, we demonstrate considerable improvement of the reduction properties to achieve a spatial resolution down to 120 nm. Plasmonic metamaterials fabricated using this technique exhibit magnetic resonances with negative permeability at far-infrared frequencies.

Keywords: Laser fabrication, Two-photon absorption, Photoreduction of metal ions, 3D metallic nanostructures, Plasmonic metamaterials

1. Introduction

Plasmonic metamaterials have recently attracted much interest from researchers by introducing a new paradigm in electromagnetism. Metamaterial is a new class of artificial materials made of three-dimensional (3D) metallic nanostructures. Electromagnetic responses of the metamaterial are specified by its internal nanostructures, not by the composition. Therefore, by engineering the nanostructures, we are able to create unprecedented optical functionalities at will, even optical magnetism and negative index of refraction, which are never provided by natural materials [1-5].

There have recently been a number of reports on the realization of metamaterials by using lithography-based nanofabrication technologies, bringing various new optical phenomena into reality. However, such metamaterials demonstrated so far are mostly two-dimensional (2D) planar structures with strong anisotropy, thus their optical functionalities are extremely limited. This is due to lack of the ability to make arbitrary 3D metallic nanostructures in such conventional technologies, and the realization of 3D isotropic metamaterials remains a major challenge.

In this paper, we propose a novel laser fabrication technique based on two-photon-induced reduction of metal complex ions to realize 3D metallic micro/nanostructures. Electrically conductive silver nanostructures with arbitrary 3D shape are demonstrated. Using this technique, we fabricated plasmonic metamaterials that exhibit magnetic resonances with negative permeability at far-infrared frequencies.

2. Two-photon fabrication of 3D metallic nanostructures

To realize the fabrication resolution in three dimensions, we employed the process of two-photon absorption (TPA), which has recently been investigated and widely used in various applications, such as fluorescence microscopy, optical data storage, and photo-polymerization. Since light absorption in the TPA process is highly localized at the focal point, it is possible to confine successive chemical or physical reactions in a small volume with high spatial resolution in three dimensions. By utilizing this unique property of the TPA process, we have recently proposed a novel fabrication technique based on two-photon-induced reduction of metal complex ions to realize 3D metallic micro/nanostructures [6,7].

A schematic of the proposed technique is shown in Figure 1. A mode-locked Ti:Sapphire laser system (Spectra-Physics, Tunami) was used as a light source. The center wavelength, pulse width, and repetition rate are 800 nm, 80 fs, and 82 MHz, respectively. The beam from the laser system was introduced into an inverted microscope (Olympus, IX71) and tightly focused into a host material including metal complex ions on a glass cover slip with an oil-immersion objective lens (60×, NA = 1.42). In the fabrication process, a metal ion absorbs two photons simultaneously, being photo-reduced into metal nanoparticles. Since the TPA process occurs only at the focal point where the
The photon density is high enough, 3D fabrication below the diffraction limit can be achieved. The focused laser beam was then scanned two-dimensionally (x-y scanning) with two-axis galvanometer mirrors. The focused laser beam was also scanned in the longitudinal direction (z scanning) by translating the objective lens with a computer-controlled motor stage installed in the microscope (Chuo Precision Industrial, MSS-FU). Since the laser beam scanning area was limited by the field view of the objective lens, which is up to about 300 µm in diameter, the sample was also mounted on an x-y translation stage in order to extend the fabrication area.

As a photoreactive medium, we initially use silver-ion solution, which was prepared by mixing 0.2 mol/l silver nitrate (AgNO₃) aqueous solution with 0.01 wt.-% Coumarin 440 (Exciton Inc.) ethanol solution in a 1 : 1 volume ratio at room temperature. As shown in Figure 2, the solution had peak absorption and fluorescence wavelengths of 350 nm and 430 nm due to the Coumarin 440. Since the AgNO₃ aqueous solution without the dye is originally colorless, suggesting that its absorption cross-section is very small at visible wavelengths, incident light of 800 nm in wavelength is mainly absorbed by Coumarin 440 through the TPA process. At the same time, electron transfer from the excited dye to silver ions induces the reduction of the silver ions. This photosensitized reduction process allowed a low laser power to trigger the reduction of silver ions, and sub-diffraction-limit fabrication was realized while suppressing local heating [7].

Figure 3 shows 2D/3D silver microstructures fabricated in the silver-ion solution using this technique. During the fabrication, quenching of the fluorescence of the dye was clearly observed, indicating the photosensitized reduction occurred. Fig. 3(a) is silver wires fabricated with a laser power of 4.32 mW and a scan speed of 50 µm/s. As seen in the inset of Fig. 3(a), the minimum wire width of 400 nm was achieved under this condition. In addition to the improved reduction properties and spatial resolution based on the photosensitized reduction process, the electrical properties of the wires were at least as good as those fabricated without using a dye [6]. The averaged resistivity of 5.30 x 10⁸ Ωm was obtained in these wires, and this value is only 3.3 times larger than that of bulk silver (1.62 x 10⁸ Ωm). The discrepancy is due to the roughness and oxidization or sulfurization of the silver wire surface. Since the solution with the dye was highly reactive, we could fabricate a large silver structure in short time periods. Fig. 3(b) is a silver mesh with a total size of 120 µm x 120 µm fabricated with a total exposure time of 12.15 s and a laser power of 13.66 mW. It should be possible to fabricate even larger structures in less time by combining our method with a laser beam interference or micro-lens array technique [8,9].

When building up an arbitrary 3D silver structure, the local heating is unavoidable because the laser beam must be focused at the surface of the existing silver structure to deposit more silver there. Therefore, addition of the dye is highly effective in improving the quality of the 3D silver structure. Fig. 3(c) is a silver tilted rod fabricated with a laser power of 18.85 mW and a total exposure time of 10.24 s. The length of the rod and the angle relative to the substrate were 34.64 µm and 60 degree, respectively. During the fabrication, we could deposit silver three-dimensionally while maintaining a constant angle because of the suppression of the local heating by the dye. As shown in Fig. 3(d), we also fabricated a top-heavy silver cup with a laser power of 18.85 mW and a total exposure time of 49.15 s. The height and the top and bottom diameter of the silver cup were 26 µm, 20 µm, and 5 µm, respectively. Since the photooxidative reaction above the substrate is susceptible to the conditions in the solution (convection, turbulence, and so on), its efficiency is somewhat low and variable as compared to that at the interface between the substrate and the solution. However, the high
reactivity of the solution enabled us to build up solid silver structures efficiently and repeatably. The strength of the structures produced was sufficient to fabricate a silver cup that could independently stand on the substrate, as seen in Figs. 3(c) and 3(d).

3. Improvement of the reduction properties using dopant surfactant molecules

Since the feature size of plasmonic metamaterials operating at optical frequencies is typically on the order of 100 nm or even smaller, further improvement of the reduction properties, especially in the resolution, is highly anticipated. In addition to the local heating, the major problem that inhibited the nanoscale resolution is the unwanted growth of the metal nanoparticles during laser irradiation. Therefore, the main issue to gain the nanometer scale depends on a way to avoid this unwanted metal particle growth and produce smaller nanoparticles to serve as building blocks.

To attack this problem, we introduced a dopant surfactant molecule, a nitrogen-atomcontaining alkyl carboxylate (n-decanoyl)sarcosine sodium, NDSS) as a metal growth inhibitor into silver-ion solution [10]. Figure 4 shows the absorption spectra of 0.05 mol/l diammine silver ions (DSI) aqueous solution mixed with 0.099 mol/l NDSS aqueous solution. For the reference in Fig. 4, we also show the absorption spectra of pure DSI and pure NDSS aqueous solutions. An absorption band with the peak at 302 nm is clearly visible in the spectra for both the pure DSI and the mixture of DSI and NDSS solutions, but not in that for pure NDSS. This absorption band originates from the DSI itself. In all spectra, the remarkable other absorption band is not observed at the laser wavelength of 800 nm. This implies that the photo-induced reduction of complex silver ions was associated with exciting the chemicals by the two-photon absorption process.

Figure 5 shows 2D/3D silver nanostructures fabricated in the silver-ion solution with NDSS. Fig. 5(a) is a silver wire fabricated with a laser power of 0.87 mW and a scan speed of 6 µm/s. During the fabrication, NDSS molecules immediately cover the surface of the silver particles after the nucleation process and then eliminate further metal growth and decreases the particle size down to around 20 nm. These growth-suppressed particles densely aggregate to compose silver patterns. The concentration of particles is higher at the center of the focused laser spot, since there is a higher nucleation probability associated with the higher laser power. At the same time, the higher laser power also helps to break the surfactant layer surrounding the particles, which in turn enhances the particle aggregation. These two conditions lead to the aggregation of silver particles directed to the center of the laser beam. As a result, we have successfully improved the spatial resolution down to 120 nm, as shown in Fig. 5(a).

Fig. 5(b) demonstrates free-standing 3D silver pyramids fabricated with a laser power of 1.3 mW and a scanning speed of 2.5 µm/s. These silver pyramids structures were strong enough to resist the surface tension in the washing process, which demonstrates that the silver particles were closely combined. The right inset in Fig. 5(b) reveals that the height was 5 µm and the angle for each leg relative to the substrate was 60°. Consequently, the direct photoreduction of complex metal ions with the help of surfactant molecules could lead to 3D metal nanostructures with the resolution exceeding the diffraction limit of light.

4. Magnetic metamaterials at far-infrared frequencies

Using the fabrication technique presented here, we have fabricated plasmonic metamaterials operating at far-infrared frequencies [11]. Figures 6(a) and 6(b) show SEM images of a metamaterial composed of a 2D array of silver rod pairs and its magnified image. The unit-cell dimensions,
of $a_x$ and $a_y$, were 15 $\mu$m, the rod length, $l$, was 10 $\mu$m, the rod width, $w$, was 1.5 $\mu$m, and the distance between two rods, $g$, was 4 $\mu$m; the total size of the sample was $3 \times 3$ mm$^2$. All silver structures were fabricated on a z-cut quartz substrate with a thickness of 150 $\mu$m. As shown in Figs. 6(c), the rod pair structure has the geometrical inductance ($L$) and capacitance ($C$), which respectively come from the rectangular area sandwiched between two rods and the gap between two rods; it acts as an LC-resonant circuit coupled with the magnetic field. When the incident angle $\theta$ (TE)-polarized light light passes through the sample at the incident angle of $\theta$, as shown in Fig. 6(d), the magnetic field perpendicular to the plane including two rods is $H \sin \theta$, where $H$ is the magnetic field of the incident light. Therefore, by increasing the incident angle at which the larger magnetic field is introduced, strong magnetic excitation of the magnetic resonances can be obtained. In addition to the rod pair array, we also fabricated a single (unpaired) rod array, which doesn’t form an LC-resonant circuit, to confirm that the magnetic responses were observed only in the rod pair array. The single rod array had the same rod-filling factor as that of the rod pair array; therefore, we could compensate for the influence of the electric interactions between the structures and light by comparing the transmission spectra of the two structures.

Figure 7(a) shows the incident angle dependencies of the transmittances of the rod pair array and the single rod array measured at 18 THz. All transmission spectra were measured by using a Fourier-transform infrared spectrometer (FT-IR; JASCO, FT/IR-6300FV). The measurement spectral range was from 0.9 to 20.4 THz, with a resolution of 0.1 THz. An aluminum aperture with a diameter of 3 mm was installed between the sample and the photodetector to improve the signal-to-noise ratio of the detected signal. When the incident angle increased, the transmittance of the single rod array did not change and remained almost constant at 65%, indicating that the single rod array did not interact with the magnetic field. On the other hand, the transmittance of the rod pair array uniformly decreased from 70% to 20% as the incident angle increased. Since the increase of the incident angle leads to an increase of the magnetic field that interacts with the rod pair structure, this result directly proves that magnetically excited magnetic resonances occurred in the rod pair array.

To investigate this experimental result further, we also performed a corresponding numerical simulation of the magnetic responses of the rod pair array [1-3]. Fig. 7(b) shows the numerically simulated real and imaginary parts of the effective permeability ($\mu_{re}$ and $\mu_{im}$) of the silver rod pair array. In the calculation, we used the damping constant $\gamma = 1.06 \times 10^{14}$ s$^{-1}$, which is 3.3 times larger than that of bulk silver ($\gamma = 3.23 \times 10^{13}$ s$^{-1}$) to consider the optical quality of the fabricated silver structure by using our technique. In Fig. 7(b), the magnetic resonance response in $\mu$ is clearly observed around the resonant frequency of 16.77 THz, which was in good agreement with the experimental results.

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**Fig. 6** SEM image of (a) silver rod pair array fabricated on a quartz substrate and (b) its magnified image. The unit-cell dimensions, $a_x$ and $a_y$, were 15 $\mu$m, the rod length, $l$, was 10 $\mu$m, the rod width, $w$, was 1.5 $\mu$m, and the distance between two rods, $g$, was 4 $\mu$m. (c) Optical setup for measuring the magnetically excited magnetic responses of the rod pair array by changing the incident angle ($\theta$) of $s$-polarized light. (d) The rod pair structure acts as an LC-resonant circuit, and the induced current $i$ is generated by the magnetic field perpendicular to the plane including two rods ($H \sin \theta$).
is in good agreement with the experimental results and the above discussion.

The proposed laser fabrication technique, in principle, can be applied to 3D plasmonic metamaterials by replacing aqueous solution by an appropriate host material to support and stack metallic nanostructures three-dimensionally. At the same time, such a medium has to be transparent both at 800 nm and at their operating wavelength. Mass production would be another issue, but may be solved by combining other promising techniques, such as a laser beam interference or micro-lens array [8,9].

5. Conclusions

We have proposed a novel laser fabrication technique based on two-photon-induced reduction of metal ions to realize 3D metallic micro/nanostructures. Electrically conductive silver nanostructures with arbitrary 3D shape are demonstrated. By introducing dopant surfactant molecules, which prohibit unwanted metal growth, we demonstrate considerable improvement of the reduction properties to achieve a spatial resolution down to 120 nm. Using the proposed technique, we have fabricated plasmonic metamaterials that exhibit magnetic resonances with negative permeability at far-infrared frequencies.

Acknowledgments

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