Two-photon-induced reduction of metal ions for fabricating three-dimensional electrically conductive metallic microstructure

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We developed techniques for fabricating three-dimensional metallic microstructures using two-photon-induced metal-ion reduction. In this process, ions in a metal-ion aqueous solution were directly reduced by a tightly focused femtosecond pulsed laser to fabricate arbitrary three-dimensional structures. A self-standing metallic microstructure with high electrical conductivity was demonstrated. © 2006 American Institute of Physics. [DOI: 10.1063/1.2177636]

In recent years, two-photon-induced microfabrication has been widely studied and developed for creating three-dimensional (3-D) microstructures. The main difference between this technique and photolithography is its ability to form arbitrary 3-D structures by scanning a tightly focused laser beam spot. Maruo first demonstrated two-photon photopolymerization to make 3-D spiral structures in 1997. In 1999, Kawata made a minute bull-shaped figure that was a self-standing, complete 3-D structure with a height of 7 μm and a length of 10 μm. While the majority of two-photon microfabrication techniques involve the use photopolymerizable resin as the fabrication material, studies using other materials have also been reported. For example, Kaneko reported the two-photon photoreduction of gold ions inside a polyvinyl alcohol (PVA) film, and he used this technique to form metallic nanoparticle gratings. Also, Baldacchini demonstrated multiphoton laser direct writing of 2-D silver structures inside 1 μm thick polyvinylpyrrolidone (PVP) films.

Wu fabricated three-dimensional spiral structures made of silver using two-photon-induced latent Ag-particle image formation followed by the development of the image by the reduction of aqueous AgClO₄ within a sol-gel matrix. Although these researchers succeeded in fabricating metal structures inside polymer or sol-gel host material, the fabricated structures were aggregations of isolated metal particles, and they were not electrically conductive. Perry and his colleagues demonstrated 2-D and 3-D patterning of electrically conductive silver and gold structures using laser- or electron-beam-induced growth of metal nanoparticles inside a polymer or on ITO substrates. Although the silver structures made by his group were electrically conductive, the resistivity was 10⁻² Ω m, which is 1000 times larger than that of bulk silver.

In this letter, we report a two-photon-induced metal-ion reduction technique in a metal-ion aqueous solution, and we demonstrate a self-standing three-dimensional microstructure with high electrical conductivity (low resistivity).

A Ti:Sapphire laser system (Spectra-Physics Tsunami) with an operating wavelength of 800 nm, a pulse width of 80 fs, and a repetition frequency of 80 MHz was used as a light source. The laser beam was introduced to an inverted microscope and tightly focused at the interface between an ion solution and a cover slip (glass substrate) using an oil-immersion objective lens (60×, NA=1.42). The focused laser beam was scanned two dimensionally (x-y scanning) using a pair of galvanometer mirrors. Z scanning was achieved by translating the objective lens using a computer-controlled motor stage. The intensity of the laser beam was modulated by an electro-optical modulator. By synchronizing the beam scanning with the intensity modulation, three-dimensional metal structures were fabricated directly in metal-ion solutions.

To fabricate silver structures, a 0.2 M aqueous solution of silver nitrate (AgNO₃) was used, and to fabricate gold structures, a 0.24 M aqueous solution of tetra chloroauric acid (H₄AuCl₄) was used. Prior to metal fabrication, the cover slips were sonicated in acetone and then in purified water for 5 min each. This was followed by cleaning in a piranha solution (H₂O₂:H₂SO₄=3:1 by volume) for 5 min and then by rinsing again with purified water. After cleaning, the surface of the cover slip was coated with a film of 3-aminopropyltrimethoxysilane to encourage fixing of the metal pattern onto the glass surface.

A drop of metal-ion solution was placed on the cover slip. Because the laser beam scanning area was limited by the field view of the objective lens, that is, up to about 300 μm in diameter, the sample glass substrate was mounted on a computer controlled x-y translation stage in order to extend the fabrication area. After drawing the three-dimensional structures, the remaining ion solution was washed off using ethanol and deionized water, and the structure was then dried with desiccated nitrogen.

Figure 1 shows two-dimensional metallic structures fabricated on the cover slip. Figure 1(a) shows a silver ring structure, and Fig. 1(b) shows a gold ring structure with the same pattern. These photographs were taken using a reflection optical microscope. Figure 1(c) is a scanning electron micrograph of a magnified portion of the gold ring structure, indicated by the rectangle in Fig. 1(b). The width of the gold line was about 0.7 μm; this value was almost the same as the...
diameter of the diffraction-limited focused laser beam spot. Note that no metal deposition was observed when mode locking of the Ti:sapphire laser was turned off, which substantiates the role of the multiphoton process.

Figure 2 shows the relationship between the size of silver voxels and both the laser power and the exposure time. Figure 2(a) is a scanning electron micrograph of the silver voxels, and Fig. 2(b) shows the dependence of the voxel diameter on the exposure time and laser power. From Fig. 2(b), we found that as the exposure time increases, the diameter of the reduced metal voxel also increases. We also found that there are two trends in the dependences of the voxel diameter on the laser power. If the laser beam power is lower than 6 mW, the increase in diameter is almost linearly proportional to the exposure power for each exposure time. However, if the exposure power exceeds 6 mW, the degree of an increase in diameter declines, and in the 50 ms exposure time case (E), the voxel size is 1.02 μm and is almost saturated. This is explained as follows. For the metal dots to grow, in addition to the photon energy, a sufficient number of metal ions must exist at the laser beam spot. High-intensity laser irradiation expends the ions quickly in the vicinity of laser beam spot, and the resulting lack of metal ions stops further growth of the metal particles. The limited mobility of the ions restricts the supply of ions diffused from the region around the laser spot, thus determining the size of the metal particles. This explanation is supported by the analysis using the diffusion theory and the mobility of Ag ions in an aqueous solution. According to Fick’s first law, the volume of the reduced metal voxel can be expressed as

$$\frac{1}{2} \frac{4\pi(d/2)^3}{3} = \frac{S}{D} \frac{dc}{dx},$$

where $d$ is diameter of the voxel, $D$ is the diffusion coefficient, $dc/dx$ is the gradient of the concentration of ions, $t$ is the exposure time, and $S$ is the surface area of the laser beam spot. To estimate the gradient of the concentration, we assumed that at the center of the laser spot, all metal ions were spent out and at the outside of the Airy disk, whose radius is given by

$$r = \frac{0.61 \lambda}{NA};$$

no ions were reduced, and then we approximated that the gradient of the concentration was given by $C/r$, where $C$ is the concentration of silver aqueous solution. Using $D = 1.648 \times 10^{-9} \text{m}^2/\text{s}$, $\lambda = 800 \text{nm}$, $NA = 1.42$, $t = 50 \text{ms}$, $S = 4 \pi r^2$, $C = 0.2 \text{mol/l}$, we finally obtained that the diameter of the reduced metal voxel is 1.12 μm.

To verify the electrical continuity of the metal structure, we measured the resistivity of the fabricated metal wires. Two electrode pads made of silver were fabricated on the glass substrate by electroless plating. A silver wire was then fabricated between these electrodes to connect them. Figure 3(a) is a scanning electron micrograph of the fabricated silver wire and the two electrodes. Figure 3(b) shows a magnified image of the silver wire. As shown in this figure, the fabricated line consisted of silver particles or crystals. The length ($l$), the width ($w$), and the height ($h$) of the wire were estimated from this image. The shape of the cross section of the line was assumed to be semil elliptical, and its area was calculated using $w$ and $h$, as shown in Fig. 3(c). Figure 3(d) shows the relationship between current and applied voltage for five silver wire samples. The gradient of the line corresponds to the resistance. Using the measured resistance, length, width, and height for each wire, we have determined that the average of resistivity was 5.30 x 10^{-8} Ω m. This value is only 3.3 times larger than that of bulk silver (1.62 x 10^{-5} Ω m), and this indicates the high conductivity of the fabricated silver wires. The discrepancy is due to the roughness and oxidation or sulfurization of the silver wire surface.
During laser irradiation, just after metal particle formation, sudden growth of the metal particle was observed. This is because of heating of the laser spot area due to the high light absorption of the metal. This phenomenon degrades the controllability of the fabrication parameters, such as the linewidth, the shape, and the resolution of the pattern. We also sometimes observed the creation of bubbles at the laser spot, which destroyed the metal structure and blocked the diffusion of ions, resulting in discontinuities in the metal structure. This is also caused by thermal effects due to light absorption. To avoid the creation of bubbles or to remove the bubbles immediately, the solvent should have large heat capacity and low viscosity. From this point of view, water is currently the most suitable solvent.

In conclusion, we demonstrated two-photon-induced direct metal-ion reduction for fabricating three-dimensional electrically conductive metallic microstructures. The fabricated metal structures have low resistivity, only a few times larger than that of bulk metal. To fabricate more complicated structures with a uniform linewidth, the precise control of the laser power is essential because the materials tend to respond differently when they are heated for different exposure times; the relationship between the laser power and the linewidth produced is not necessarily linear. The quantum yield of the photoreduction of silver ions in an aqueous solution have already studied by Hada, and the improvement of ultrafine metal particle generation by using a photoinitiator has been investigated by Itakura. These results give us the guideline to optimize the exposure procedures, and technically the laser power control techniques used in recordable optical disks, which is often called the "write strategy," can be adopted.