

Metal Deposition Deep into Microstructure by Electroless Plating

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It is generally difficult to deposit metal on an occluded part of a structure or inside a long tubular structure. In this paper, we report an electroless plating method that is useful for metal deposition onto internal obscured regions of a complex structure, and we show that the technique can deposit metal over a wide area. We demonstrate gold deposition inside a capillary tube and a complex concave structure of micrometer scale consisting of polystyrene microbeads sandwiched between glass plates. [DOI: 10.1143/JJAP.44.L1134]

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Metal microfabrication has been actively studied and used in various fields because of the unique optical, electrical, and catalytic properties of the fine structures that it can produce.^{1–6)} The ability to simultaneously and precisely fabricate a number of micro-objects over a wide region is essential to the practical application of nanotechnology. In these processes, plating methods are occasionally used for metal deposition. Plating is a conventional method of depositing metal onto substrates,⁷⁾ and can be used not only with conductors, but also with insulators such as plastics and ceramics. Among known plating techniques, electroless plating is commonly used for metal deposition on insulators because it does not require any external electric field. Electroless plating is chemically performed with a solution, and it results in a uniform metal deposition over the entire surface area of micro-objects.^{8–10)} With this method, it is possible to deposit metal effectively even though the area is limited to less than a micrometer in width.^{11,12)} Moreover, a number of micrometer-scale metal patterns can be fabricated simultaneously over a very wide area much more easily than with sputtering or vacuum evaporation, which require large, complex equipment. These techniques have been long studied, and are used widely for metal fabrication processes. However, it is generally very difficult, using these methods, to deposit metal on a deep or normally occluded part of a structure, such as the inner wall of a long tubular structure.

In this letter, we demonstrate electroless plating on three types of structure. First, gold was deposited on the inner wall of a fused-silica capillary, which is difficult to achieve by other methods. Second, silver was deposited onto glass beads. Third, gold was deposited inside a complex concave structure formed by polystyrene microbeads sandwiched between glass plates.

As mentioned above, although it is generally difficult to coat metals onto the inside of a concave structure using other methods (such as vacuum evaporation and sputtering), with electroless plating the plating solution containing metal ions naturally goes into the inside of even a fine, complex structure, and therefore all surfaces contacting the plating solution are uniformly coated with metal.

To determine the main features of our process and to verify its effectiveness, we first investigated the relationship between the amount of gold deposited onto the surface of a polystyrene substrate at room temperature (295 K) by

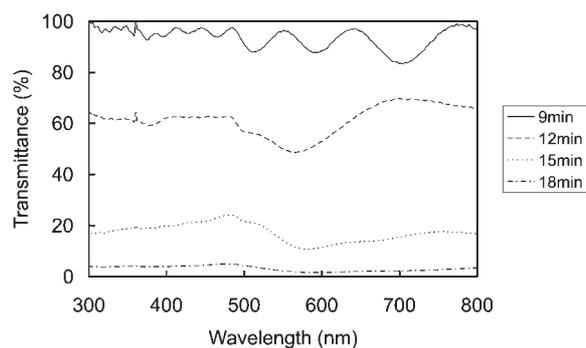


Fig. 1. Transmission spectra of gold-deposited polystyrene plate from 300 to 800 nm at different reaction times.

measuring the transmission spectrum. We prepared 0.024 M tetra-chloro auric acid (HAuCl_4), 0.75 M sodium hydroxide (NaOH), and 0.086 M sodium chloride (NaCl) in water as a gold ion solution, and 0.5 vol % glycerol ($\text{C}_3\text{H}_8\text{O}_3$) in water as a reduction agent. Samples were obtained by terminating the reaction at 9, 12, 15, and 18 min from mixing the plating solution and the reduction agent. The transmission spectra were measured from 300 to 800 nm for these samples by an absorptiometer (Shimadzu, UV-2500PC), and are shown in Fig. 1. For reaction times of less than 9 min, no noticeable deposition of gold was observed. A region with a lower transmittance compared to the others was found from 500 to 600 nm; this was due to the local plasmon-mode resonance absorption of gold particles.¹³⁾ The resonance absorption became more noticeable at 12 min. The total transmittance decreased as the reaction time increased, and a red shift of the absorption peak was observed as the reaction time increased. This implies that the gold particle size also increased with reaction time. A suitably reflective gold mirror was formed on the polystyrene substrate after 18 min, as indicated by the fact that incident light was almost completely reflected by the deposited gold film. Moreover, the deposited gold was strongly fixed to the polystyrene substrate.

As a first demonstration, gold was deposited onto the inner wall of a fused-silica capillary tube (Agilent Technologies, outer diameter = 0.150 mm). The tubes were coated with polyimide, and then the polyimide was removed from the middle of the tubes with a flame to form plating areas for observation with the optical microscope.

We prepared a 100-mm-long capillary with an inner

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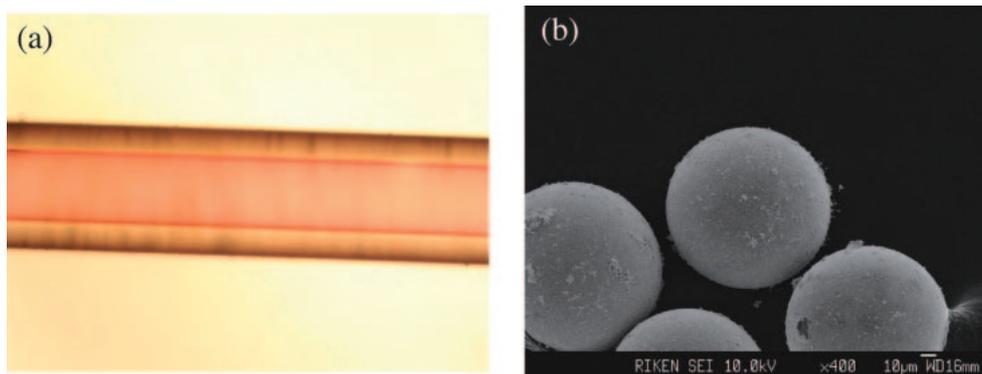


Fig. 2. (a) Inner wall of fused-silica capillary was coated by gold. The reddish area is the gold-coated part. The inner diameter of the capillary tube is 50 μm . (b) Silver-coated glass beads observed by SEM. The diameter of the beads is about 100 μm .

diameter of 50 μm . In the case of glass surface, gold adhesion was much worse compared to the polymer case. Therefore, the glass surface for gold deposition was pretreated by a mixed solution of 26 mM SnCl_2 and 70 mM trifluoroacetic acid in water.¹⁴⁾ One end of the capillary was dipped in a mixed solution of the gold plating solution and the reduction agent. The inner space of the capillary tube was naturally filled with the solution due to, and gold was uniformly deposited on the inner surface. The capillary tube was removed from the solution after 30 min, rinsed, and observed with an optical microscope (Nikon OPTIPHOTO).

Figure 2(a) shows a photomicrograph of a gold-coated capillary tube obtained with the optical microscope. The inside of the capillary tube became red in color, which was obviously different from the color of the outer tube. This indicates that gold particles were deposited inside the capillary tube. The gold coating was found over a length of several tens of millimeters.

Although a 50- μm capillary tube was used here, this electroless plating method may also be useful for metal coating on the interior of concave fine structures, even though their scale is typically less than a micrometer. Additionally, this method is also useful for metal coating over areas that are more than a millimeter wide. Since metal deposition occurs in places where the plating solution is in contact with the substrate, a relatively large area can be deposited with metal simultaneously, which is crucial for nanoengineering applications.

As a second demonstration, we showed that silver could be successfully deposited onto glass beads with a diameter of 100 μm . For silver deposition, we prepared 0.2 M silver nitrate (AgNO_3) in water, and 1.9 M glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in a solution of 30 vol % methanol (CH_4O) and 70 vol % water as a reduction agent.⁹⁾ It is relatively difficult to deposit metal uniformly onto a round shape; however, a uniform silver coating was readily obtained using our method. Glass microbeads were mixed in a silver plating solution and were gently agitated during the reaction. The beads were surrounded by the solution and silver was then uniformly deposited onto the beads. A scanning electron micrograph (SEM) of the silver-coated glass beads is shown in Fig. 2(b).

As a third demonstration, gold was deposited onto a finer, more complex structure containing polystyrene beads (Duke Scientific, $D = 49.8 \pm 0.8 \mu\text{m}$, 4250A). The polystyrene beads were first dispersed in water (1.0 vol %). The water

containing the beads was then dripped onto a glass slide. The beads were naturally arranged in a hexagonal pattern after drying. Subsequently, the beads were sandwiched by another glass slide, placed in a furnace for 10 min at 388 K, which exceeds the glass transfer temperature of polystyrene (378 K), and pressed. The resulting structure is shown in Fig. 3(a).

Deformation of the polystyrene beads resulted in disk shapes, and the flat surfaces at the top and bottom were completely attached to the slide glasses on both sides. Because of this phenomenon, it is usually impossible to obtain gold deposition at regions where the beads adhere to the slide glass. However, the PS beads do not become completely flat; there are very small, narrow spaces between the beads, and these can be used as a template for metal patterning, as shown schematically in Fig. 3(b). The mixed solution of the gold plating solution and the reduction agent was impregnated into these spaces after the pretreatment of glass surface with SnCl_2 -trifluoroacetic acid mixed solution.¹⁴⁾ The spaces became filled with the solution, and uniform gold deposition was readily obtained after 15 min; this is shown in Fig. 3(c).

It was previously reported that metal deposition onto a glass substrate using polymer latex beads and sputtering resulted in the fabrication of a number of triangles arranged in a hexagonal pattern.¹⁵⁾ In our experiment, since metal deposition was obtained at surfaces in contact with the plating solution, metal was able to be deposited on all the regions of the substrate underneath the polystyrene beads except for the contact plane. However, areas where no deposition occurred were also found; these may be caused by the beads deforming so as to join together, forming a flat sheet that impedes the passage of the plating solution. That is, the spaces between the aggregated beads were filled with polystyrene through the deformation, and this polystyrene formed continuous layers in these areas. The thickness of the deformed beads was estimated to be from 15 to 20 μm , which was obtained by a 45° tilted SEM observation.

On the same slide glass, another gold pattern was found, which was much finer than the one described above. A reflection image from the optical microscope is shown in Fig. 4(a). A number of gold rings arranged in a hexagonal pattern and irregularly connected by thin lines were found over a wide area. It was difficult to control the number of lines emerging from a ring. The inner diameter of the gold

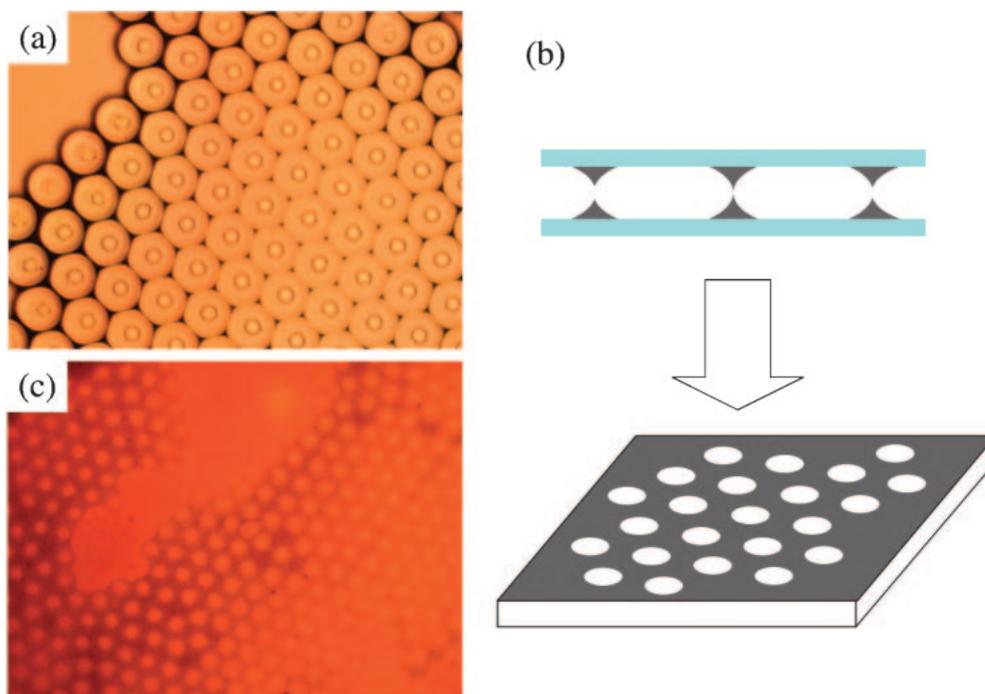


Fig. 3. (a) Transmission microscope image of crushed polystyrene beads. (b) Gold deposition process. The shaded part was filled by the gold plating solution. The polystyrene beads acted as a template, and a gold pattern was obtained. (c) Transmission microscope image of gold pattern fabricated by beads.

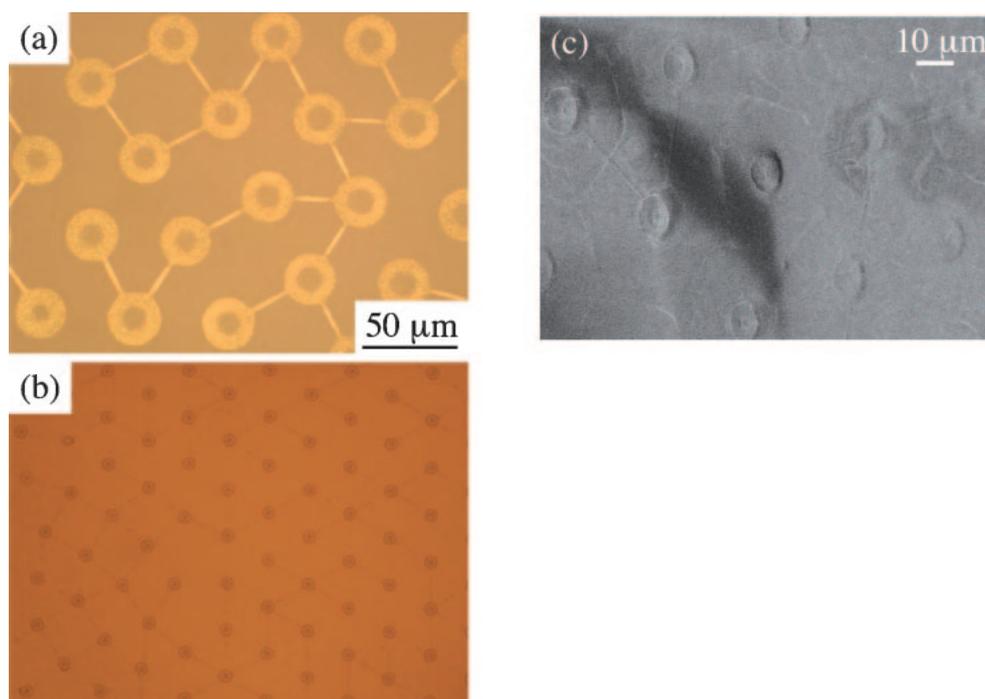


Fig. 4. (a) Reflection microscope image of finer gold pattern formed on glass plate. (b) Reflection microscope image of pattern formed on the glass plate and removed from polystyrene bead layer before gold deposition. (c) SEM image of 45°-tilted polystyrene template used for gold patterning.

rings was about 10 μm, and the distance between the centers of the rings was about 50 μm, which is almost the same as the diameter of the spherical polystyrene beads. The size of the inner, non deposited areas varied, although the outer diameters were almost constant at 30 μm. Therefore, the width of the gold rings was not constant, which may be due to irregularities in the polystyrene bead template.

We considered the possibility that this fine pattern was also formed as a result of spaces between the beads and the glass slide. To confirm this, the glass slide used to compress the beads and the crushed beads were observed before gold deposition. The same pattern of rings connected by lines was observed on the glass slide that was removed from the layer of beads, as shown in Fig. 4(b). From this image, we

assumed that the same pattern would exist on the beads. The surface of the layer of beads was observed by SEM and the result is shown in Fig. 4(c). The same pattern was found there, as expected. Therefore, we can infer that the pattern on the beads was transcribed onto the slide glass, thus acting as a template for this patterning. The width of the lines connecting each ring was found to be approximately 1 μm , which is much finer and more complex than that of the previous gold pattern. It is noted that fine, complex metal patterns with a scale of about one micrometer can be readily obtained by electroless plating.

Looking to the future, this electroless plating method may be a strong tool for metal coating or metal fabrication in nanoengineering applications. The advantage of this method is not only a uniform metal deposition onto surfaces of complex structures, but also the ability to fill metal into narrow spaces of complex structures over a wide region. Moreover, the metal deposition can be controlled by adjusting the reaction conditions, including the concentration of the plating solution and the reduction agent, the temperature, and the reaction time. Therefore, these conditions should be carefully optimized for the target application, according to the desired pattern size, type of substrate, and other factors.

Although this method can be used for fine metal

patterning, we believe that the most advantageous application of our electroless plating may be to three-dimensional metal microfabrication.

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