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Development of In-process Visualization System for Laser-assisted Three-dimensional Microfabrication using Photocatalyst Nano-particles

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Recently, microfabrication technology has been used to develop micro-electro-mechanical systems (MEMSs), micro-total analysis systems (μ-TASs), and photonic crystals. Various microfabrication techniques have been proposed; however, a technique that can be used to efficiently fabricate 3-D structures via a simple procedure has not been reported thus far. Because 3-D metal structures have not only mechanical functions but also electromagnetic functions, it is desirable to develop such a technique. Our research group is in the process of developing a new technique for 3-D microfabrication that involves the use of a lower power continuous wave laser. Our technique is characterized by the reduction of silver ions via the photocatalysis of titanium dioxide (TiO2) excited at the laser beam waist. For the analysis and development of our microfabrication technique, we developed a microscope system that enabled us to observe the microfabrication process along the fabrication beam optical axis and its radial direction. We successfully visualized the microfabrication process in 3-D. The visualization showed that when the beam waist was swept, the silver structure grew in 3-D following its path. The effect of the substrate on the deposition condition was examined.

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NOMENCLATURE

TiO_2 = Titanium dioxide
$AgNO_3$ = Silver nitrate
2-D = two dimension/tow dimensional
3-D = three dimension/three dimensional
UV = Ultra Violet

1. Introduction

Recently, microfabrication technology has been used to develop micro-electro-mechanical systems (MEMSs), micro-total analysis systems (μ-TASs), and photonic crystals. Various microfabrication techniques[1-6] have been proposed; however, a technique that can be used to efficiently fabricate 3-D structures via a simple procedure has not been reported thus far. Because 3-D metal structures have not only mechanical functions but also electromagnetic functions, it is desirable to develop such a technique.

Techniques that involve the use of lasers can be applied to 3-D microfabrication. A technique that uses an ultrashort pulse laser for fabricating 3-D metal structures was reported.[7] Our research group is in the process of developing a new technique for 3-D microfabrication that involves the use of a lower power continuous wave laser. Our technique is characterized by the reduction of metal ions via photocatalysis of TiO_2 nanoparticles in a liquid. The photocatalytic action of TiO_2 on metal ions in solution can be exploited to directly fabricate complex 3-D microstructures even with a low power continuous wave laser. In our laboratory, we successfully fabricated 3-D silver structures with sizes on the scale of several tens of micrometers.[8] Examples of the fabricated 3-D silver structures are shown in figure 1. Thus, our method can be used to fabricate arbitrary 3-D shapes (figure 1(a)) as well as functional devices (figure 1(b)).

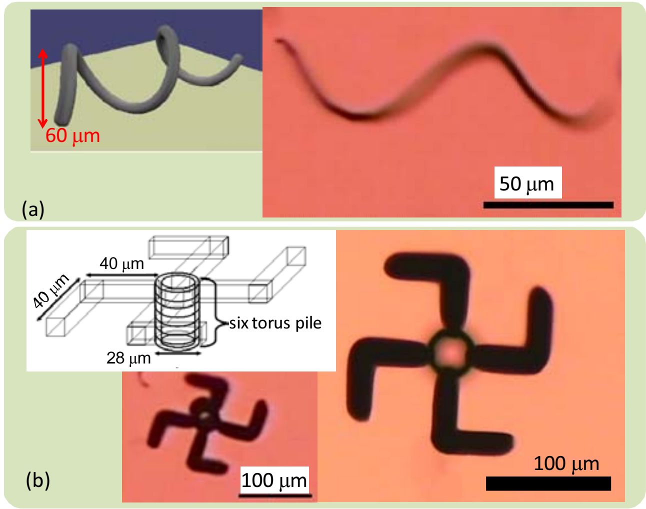

Fig. 1 Examples of microscale structures fabricated by the proposed method (a) Micro coil and (b) micro rotor

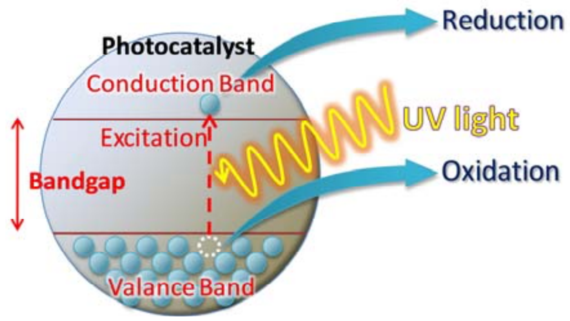

Fig. 2 Excitation of photocatalyst

Although we successfully fabricated 3-D silver structures, the mechanism underlying this microfabrication method is not clear. In particular, detailed analysis of the processes that lead to the formation of 3-D microstructures in the liquid is lacking. In order to analyze these essential processes, it is highly desirable to perform in-process visualization. Therefore, the purpose of this paper is to develop an in-process visualization system that allows us to carry out 3-D observations of the microfabrication process in the liquid and to discuss the basic fabrication characteristics on the basis of this in-process visualization.

2. Concept of Microfabrication with Photocatalysis

Our microfabrication technique is based on the theory of photocatalytic oxidation–reduction reactions. When a photocatalyst absorbs light having energy greater than its bandgap energy, it is excited and electrons in the valance band are transferred to the conduction band (figure 2).[9] This generates electron–hole pairs that accelerate other oxidation–reduction reactions. We selected a TiO_2 (Brookite) photocatalyst because it maintains considerably high activity and stability throughout the oxidation–reduction reaction. It was reported that under illumination with UV light, TiO_2 caused reduction of metal ions and deposition of metals such as silver[10] and platinum.[11]

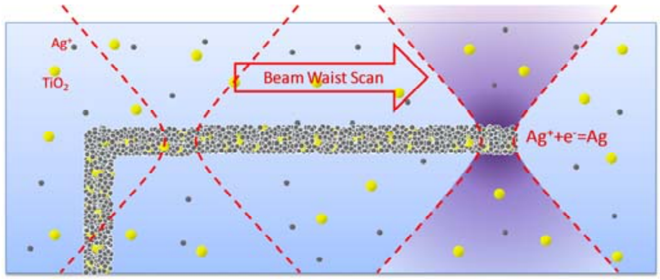

Fig. 3 Concept of microfabrication with photocatalysis

TiO_2 photocatalysis was previously used in 2-D microfabrication.[11,12] In order to achieve 3-D microfabrication, we used a suspension of TiO_2 nanoparticles. Although absorption in TiO_2 is limited to the UV region and visible light is hardly absorbed, our experiments revealed that by using a converging laser beam with a wavelength of 405 nm, it was possible to locally excite TiO_2 nanoparticles and reduce silver at the beam waist. Therefore, by scanning the beam waist in the solution (figure 3), arbitrary 3-D silver structures can be fabricated.

3. Experimental Setup

Figure 4 shows a schematic diagram of our microfabrication system, with the x, y, and z axes defined as shown. The system can be divided into three parts in terms of function. The first one is a microfabrication unit that forms the converging fabrication beam and scans it. The second and third ones are the top view and side view in-process visualization units that enable us to observe the fabrication process from the z- and y-directions, respectively.

In the microfabrication unit, the fabrication light source used to excite TiO_2 is a laser diode that emits light at a wavelength of 405 nm with a maximum output of 55 mW. The output light is collimated via a spatial filter and collimator lens and is focused on the sample solution by a high numerical aperture objective lens. The sample solution is mounted on a motorized three-axis stage and it can undergo 3-D translational motion relative to the beam waist.

The top view unit mainly consists of an objective lens, dichroic mirror, tube lens, and CCD camera. The objective lens is shared with the microfabrication unit.

The side view unit mainly consists of a long working distance objective lens, longpass filter, tube lens, and CCD camera. An infinity optical system is employed. To avoid interference between the two objective lenses, a long working distance objective lens is used in this unit. The microfabrication process can be observed with epi-illumination or transillumination.

The sample solution contains TiO_2 nanoparticles; consequently, when the microfabrication process is observed, light scattered by TiO_2 nanoparticles affects the observation. To clearly visualize the microfabrication process, it is necessary to suppress this effect appropriately. For this purpose, a dichroic mirror and longpass filter were inserted in the top view and side view units, respectively.

The fabrication region (height = ~100 μm) lies between a glass substrate and a cover slip. The glass substrate is coated with gold.

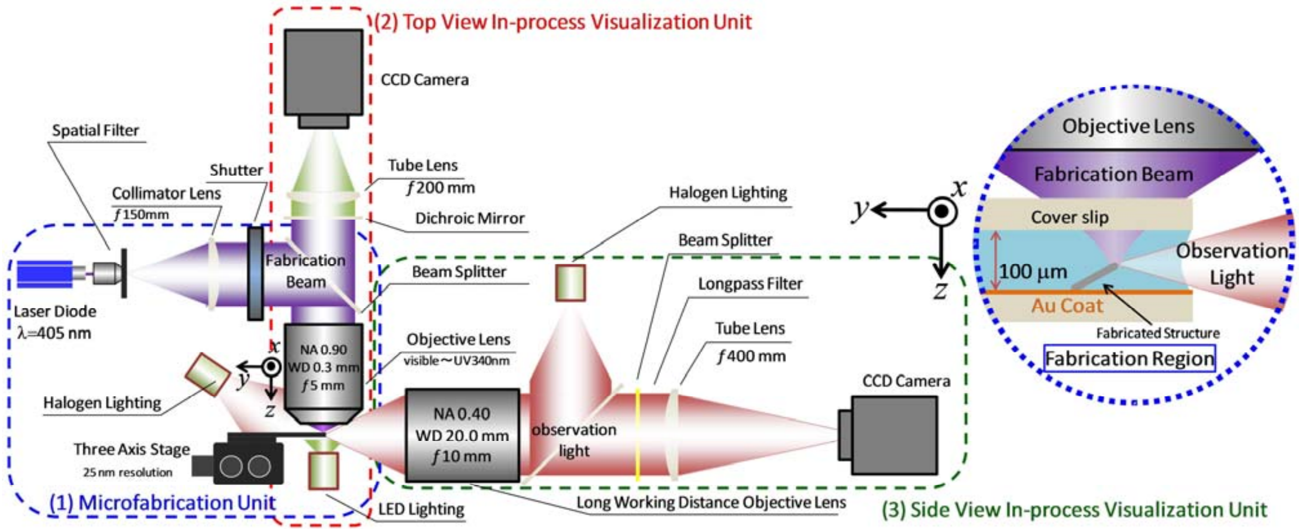

Fig. 4 Experimental setup for microfabrication and microscopic in-process visualization

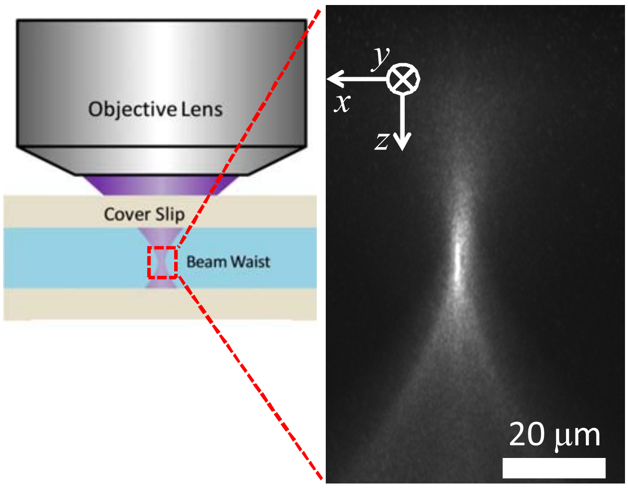

Fig. 5 Typical image of light scattered by TiO_2 nanoparticles as observed with the side view unit

When the microfabrication process is observed with the side view unit, it is observed through the interface between the sample solution and the atmosphere; this interface is maintained by surface tension.

4. In-Process Visualization Experiment

4.1 Side View Observation of Light Scattered by TiO_2 Nanoparticles

Prior to visualization of the microfabrication process, the fabrication beam was observed as light scattered by TiO_2 nanoparticles with the side view unit. Figure 5 shows a typical image of scattered light observed with the side view unit. The tight beam waist focused by the NA0.9 objective lens was seen as light scattered by TiO_2. This shows the feasibility of the side view unit. Figure 5 also shows that we can localize light energy at the beam waist in a sample solution. Therefore, if the sample solution contains silver ions, it is expected that TiO_2 nanoparticles are excited locally and silver ions are reduced at the beam waist.

Table 1 Fabrication conditions

Sample solution	TiO_2 particle size 10-20 nm	0.7 wt%
	$AgNO_3$	0.01 mol/l
	NH_3	9 wt%
fabrication beam power (measured before objective lens)		2 mW
scan velocity	z-direction	1.5 μm/s
	x-direction	1.0 μm/s

4.2 Observation of Microfabrication Process

The microfabrication process was observed with the side view and top view units. The images obtained from the visualization are shown in figure 6. The beam waist was scanned in the z-direction (figure 6(A)) and the x-direction (figure 6(B)). In each figure, (a) shows the side view and (b) the top view. The fabrication conditions are listed in table 1. To prevent the aggregation of TiO_2 in the sample solution, the sample pH was controlled by adding NH_3 solution. As shown in figure 6, the structures were found to be growing and scattering light at their growth point. Thus, we successfully visualized the 3-D microfabrication process.

From this observation, it was confirmed that the deposition of silver was localized in 3-D and that the microscale structure underwent 3-D growth following the beam waist scan.

The deposition region was longer in the z-direction than in the x- and y-directions (figure 6(B)). This may correspond to the light intensity distribution and the excitation region of TiO_2 (figure 5). This means that it is important to control the 3-D light intensity distribution of the beam waist for fabricating high-definition structures.

4.3 Discussions about Effect of Substrate

In our experiments, we knew that in order to fabricate continuous structures following the beam waist scan, the deposition should start on the cover slip or on the substrate. To analyze the effect of the substrate, the deposition process was observed when the beam waist was set about 50 μm above the substrate. A typical image obtained with the side view unit is shown in figure 7. It was

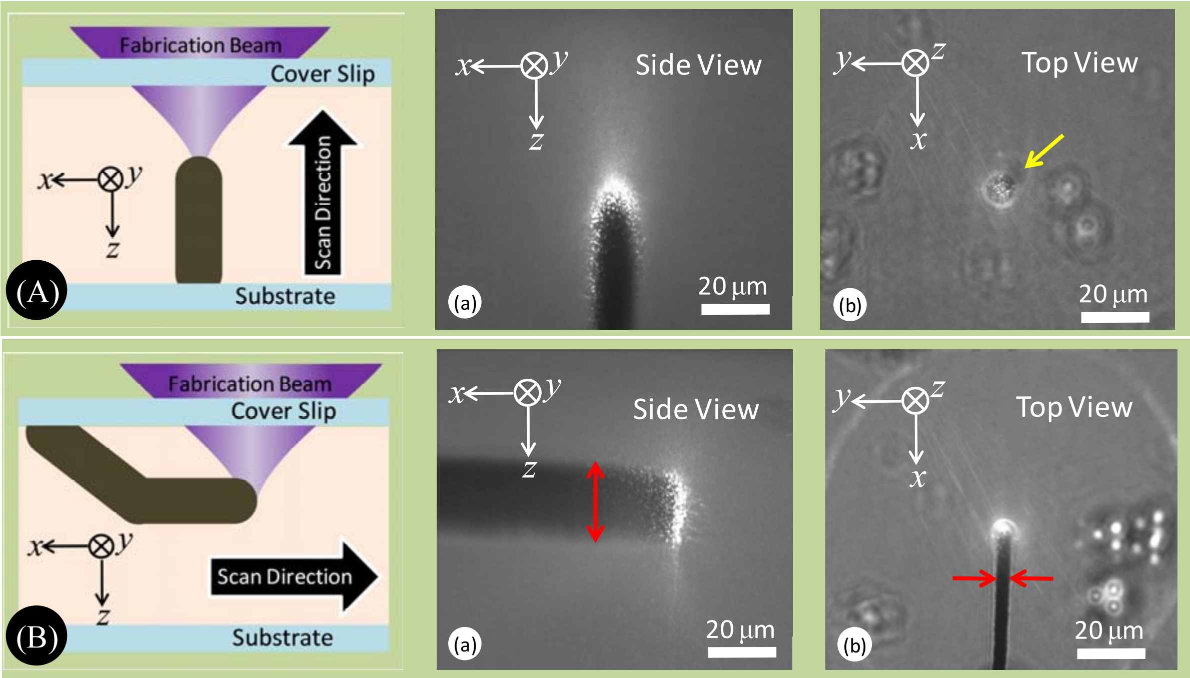

Fig. 6 In-process visualization of proposed microfabrication method (A) z-direction scan, (B) x-direction scan, (a) side view, and (b) top view

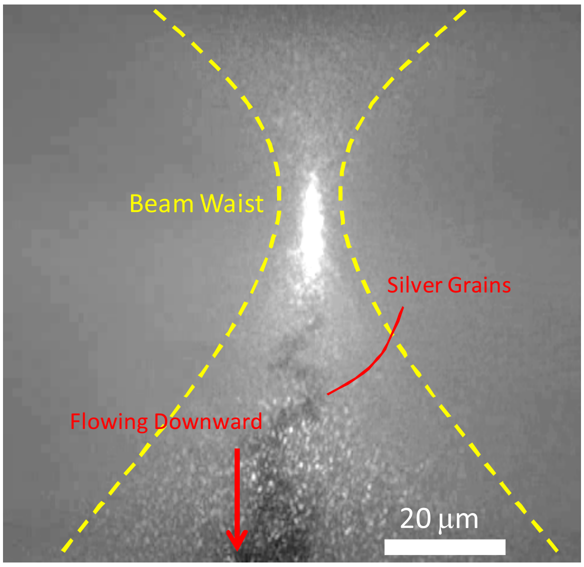

Fig. 7 Observation of deposition at the beam waist

observed that a continuous structure was not fabricated, i.e., below the beam waist, silver grains appeared in a discontinuous manner and flew downward.

Next, the deposition processes for different distances between the beam waist and the substrate were compared. The fabrication beam power and the sample solution density were the same as given in Table 1. These visualization experiments showed that the deposition condition depended to a considerable extent on the distance between the beam waist and the substrate. Three important cases are shown in figure 8. When the distance was less than about 20 μm, continuous deposition on the substrate was observed (figure 8(a)(b)). When the distance was greater than about 20 μm, continuous deposition was not observed, but many grains of silver were found (figure 8 (c)).

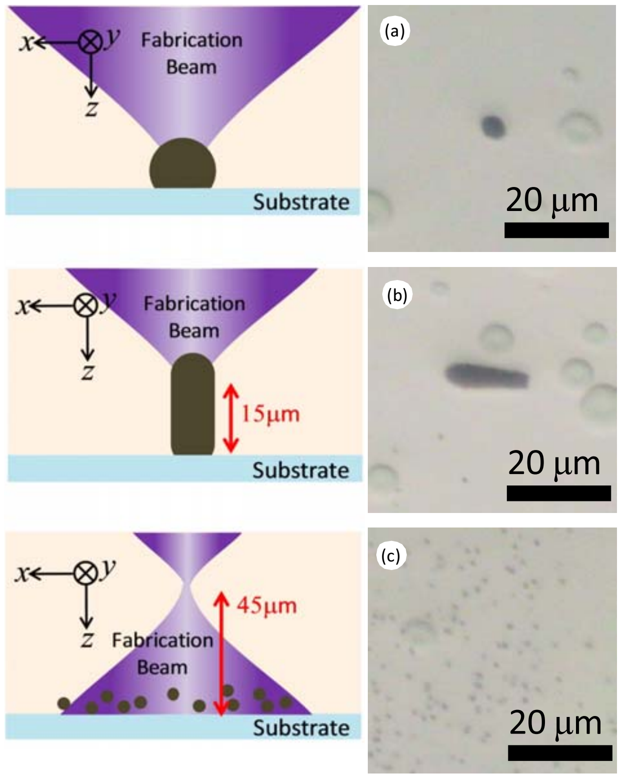

Fig. 8 Effect of substrate on deposition condition. The distances between the beam waist and the substrate are 0 μm, 15 μm, and 45 μm in (a), (b), and (c), respectively. The exposure times are 10 s, 10 s, and 100 s in (a), (b), and (c), respectively. The images on the right side are taken using the top view unit. In (b), the image was taken after the structure was laid down

These results show that the substrate considerably affects the deposition condition and that the deposition condition depends on the distance between the beam waist and the substrate. For continuous deposition, in particular, the distance must be lesser than a certain value. This suggests that some fixed substance such as the substrate or a deposited structure is necessary near the beam waist to ensure continuous deposition. This phenomenon seems relevant to the thermal conditions, fluid dynamical conditions, or optical conditions around the beam waist. We will endeavor to examine these conditions in more detail in future studies.

5. Conclusions

We developed a microscope system that enabled us to observe the microfabrication process along the fabrication beam optical axis and its radial direction. We successfully visualized the microfabrication process in 3-D. From this observation, it was confirmed that the deposition of silver was localized in 3-D and that the microscale structure underwent 3-D growth following the beam waist scan.

The effect of the substrate on the deposition condition was examined. It was found that the deposition condition depends on the distance between the beam waist and the substrate and that for continuous deposition, the distance must be lesser than a certain value. In future studies, we will analyze the fabrication conditions required for achieving continuous deposition.

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