In-process visualization of laser-assisted three-dimensional microfabrication using photocatalyst nanoparticles

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KEYWORDS : Microfabrication, Three-Dimensional Visualization, Three-Dimensional Structure, Metal Structure, Photocatalyst

Recently microfabrication technology for Micro Electro Mechanical System (MEMS), Micro Total Analysis System (μ-TAS), and photonic crystal are being developed. Among a variety of microfabrication techniques one that can fabricate three dimensional metal structures in simple procedure is rarely seen. Because three dimensional (3-D) metal structures have not only mechanical functions but also electromagnetic functions, such a technique is desired. We have been developing a new technique for 3-D microfabrication which allows us to directly fabricate 3-D metal micro scale structures. Our technique is characterized by reduction of silver ions by photocatalysis of titanium dioxide (TiO_2) excited at a laser beam waist. For analysis and development of our microfabrication technique, we developed a microscope system which enabled us to observe the microfabrication process from the fabrication beam optical axis and its radial direction. We succeeded in visualizing the microfabrication process in 3-D. The visualization showed that when the beam waist was swept, the silver structure grew three-dimensionally following its path. The effect of substrate on the deposition condition was examined.

Manuscript received: July 15, 2009 / Accepted: August 15, 2009

NOMENCLATURE

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

1. Introduction

Recently microfabrication technology for Micro Electro Mechanical System (MEMS), Micro Total Analysis System (μ-TAS), and photonic crystal are being developed. Among a variety of microfabrication techniques, one that can fabricate 3-D structures in simple procedure is rarely seen. Because 3-D metal structures have not only mechanical functions but also electromagnetic functions, such a technique is desired.

One of the applicable techniques for 3-D microfabrication is one using laser. A technique using ultrashort pulse laser for fabricating 3-D metal structure was reported [1]. We have been developing a new technique for 3-D microfabrication using lower power continuous wave laser. Our technique is characterized by reduction of metal ions by photocatalysis of TiO_2. By using the photocatalytic action of TiO_2 on metal ions in solution, complex 3-D micro scale structures can be directory fabricated even with low power continuous wave laser. We

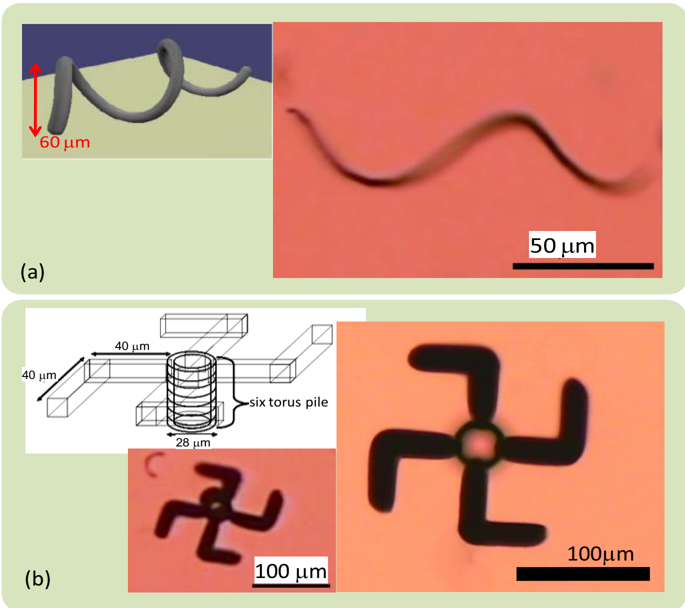

Fig. 1 Examples of micro scale structures fabricated by proposed method. (a) micro coil, (b) micro rotor

had already succeeded in fabricating 3-D silver structures with the size scale of several 10 μm [2]. Examples of 3-D silver structures we fabricated are shown in figure 1. Figure 1(a) shows our method can fabricate arbitrary 3-D shape, and figure 1(b) shows an example of application to a function device.

In this paper, for analysis and development of our microfabrication technique, we developed a microscope system which enabled us to observe the microfabrication process in 3-D. We succeeded in visualizing the microfabrication in 3-D. Observing the microfabrication process in three dimensionally, we discuss fabrication mechanism.

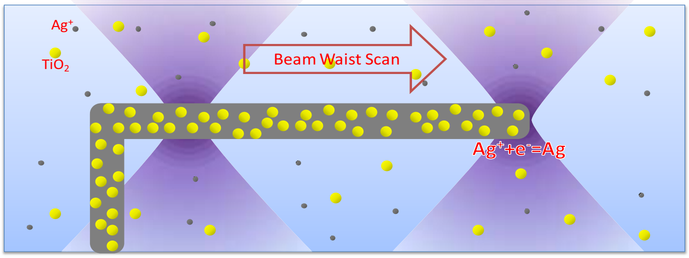

Fig. 3 Concept of microfabrication with photocatalysis.

2. Concept of Microfabrication with Photocatalysis

Our microfabrication technique is based on the theory of photocatalytic oxidation-reduction reaction. When photocatalyst absorbs light energy which is greater than its bandgap energy, it is excited and electrons in the valance band transfer to the conduction band (figure 2) [3]. This generates pairs of holes and electrons which accelerate other oxidation-reduction reactions. We selected a TiO_2 (Brookite) photocatalyst because it is very active and stable throughout the oxidation-reduction reaction. It was reported that when TiO_2 was illuminated with UV-light, it caused reduction of metal ions and deposition of metal such as silver [4] and platinum [5].

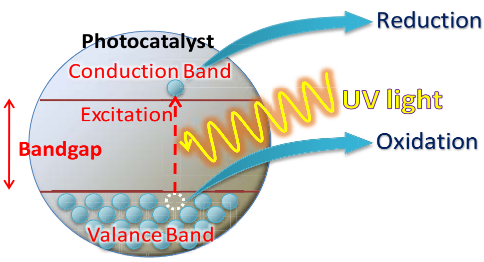

Fig. 2 Excitation of photocatalysit.

TiO_2 photocatalysis was used in two dimensional microfabrication [5][6]. In order to achieve 3-D microfabrication, we used suspension of TiO_2 nanoparticles. Although the absorption wavelength region of TiO_2 is limited to UV wavelength region, and visible light is hardly absorbed, we experimentally found that using a converging laser beam of wavelength 405 nm, it was possible to locally excite TiO_2 nanoparticles and reduce silver at the beam waist. Therefore scanning the beam waist in the solution as shown in figure 3, arbitrary silver 3-D structures can be fabricated.

3. Experimental Setup

Our microfabrication system is schematically shown in figure 4. Here we define xyz-axis as in figure 4. The system can be divided into three parts in terms of function. The first one is a microfabrication unit which forms converging fabrication beam and scans it. The second one and the third one are a top view in-process visualization unit and a side view in-process visualization unit which enable us to observe the fabrication from z-direction and y-direction respectively.

In microfabrication unit, the fabrication light source which excites TiO_2 is a wavelength 405 nm laser diode maximum output of which is 55 mW. The output light become collimated beam with a spatial filter and a collimator lens, and is focused in sample solution by a high numerical aperture objective lens. The sample solution is mounted on a motorized three-axis stage and it can be translated in 3-D relative to the beam waist.

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

The side view in-process visualization unit mainly consists of a long working distance objective lens, a long-pass filter, a tube lens, and a CCD camera. An infinity optical system is employed. To avoid the interference of 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.

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

The fabrication region is between a glass substrate and a cover

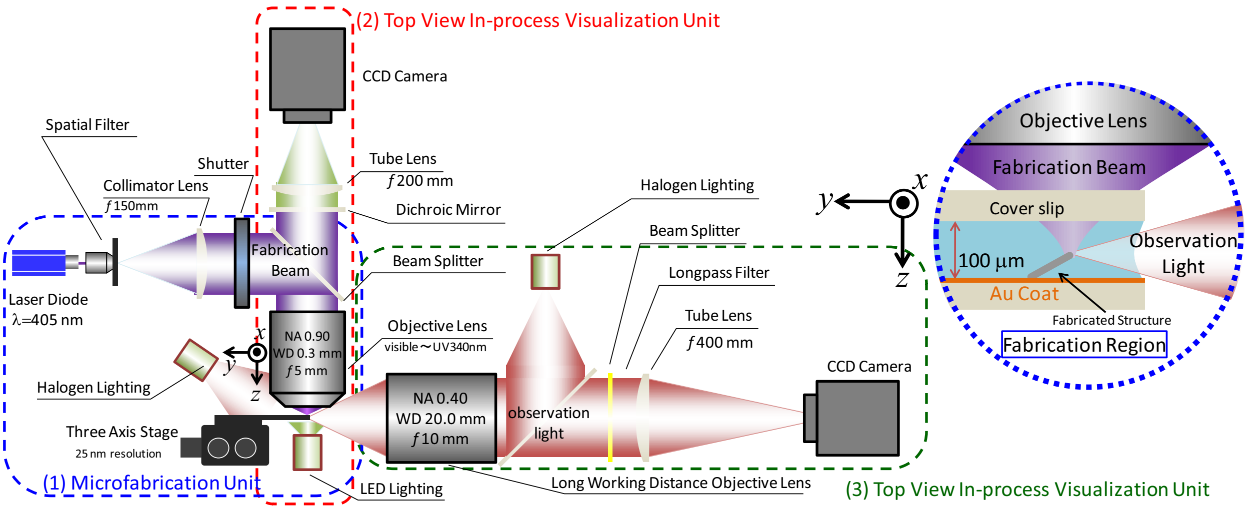

Fig. 4 Experimental setup for microfabrication and microscopic in-process visualization.

slip, and its height is about 150 µm. The glass substrate is coated with gold. When the microfabrication is observed with the side view in-process visualization unit, it is observed through interface between the sample solution and the atmosphere which is maintained by surface tension.

4. In-Process Visualization Experiment

4.1 Side View Observation of Scattered Light by TiO_2 Nanoparticles

Before observing the microfabrication process, fabrication beam was observed as scattered light by TiO_2 nanoparticles, with the side view in-process visualization unit. Figure 5 is a typical image of scattered light observed with the side view in-process visualization unit. The tight beam waist focused by the NA0.9 objective lens, was seen as scattered light by TiO_2. This shows feasibility of the side view in-process visualization 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.

4.2 Observation of Microfabrication Process

The microfabrication process was observed with the side view and top view in-process visualization units. The obtained images are shown in figure 6. In figure 6(A) the beam waist was scanned in z-direction, and in figure 6(B) the beam waist was scanned in x-direction. In each figure, (a) is a side view and (b) is a top view. The fabrication condition is shown in table 1. As shown in the figure 6, it was seen that the structures were growing and scattering light at their growing point. Therefore we succeeded in visualizing the microfabrication in 3-D.

From this observation it was confirmed that deposition of silver was three dimensionally localized and the micro scale structure grew three dimensionally following the beam waist scan.

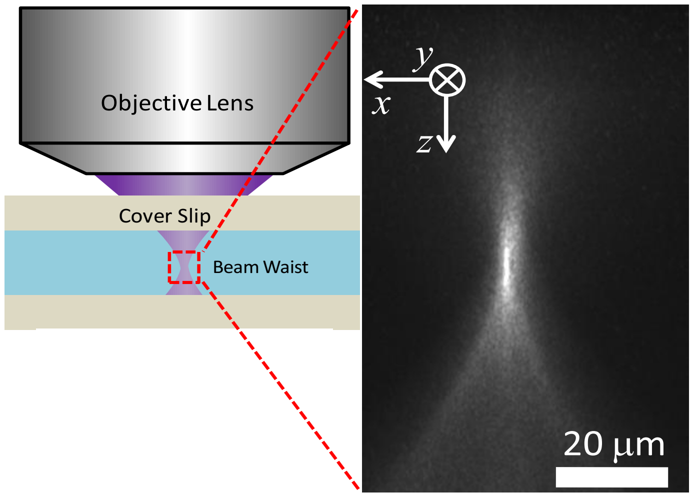

Fig. 5 A typical image of scattered light by TiO_2 nanoparticles observed with the side view in-process visualization unit.

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

Table 1 The 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

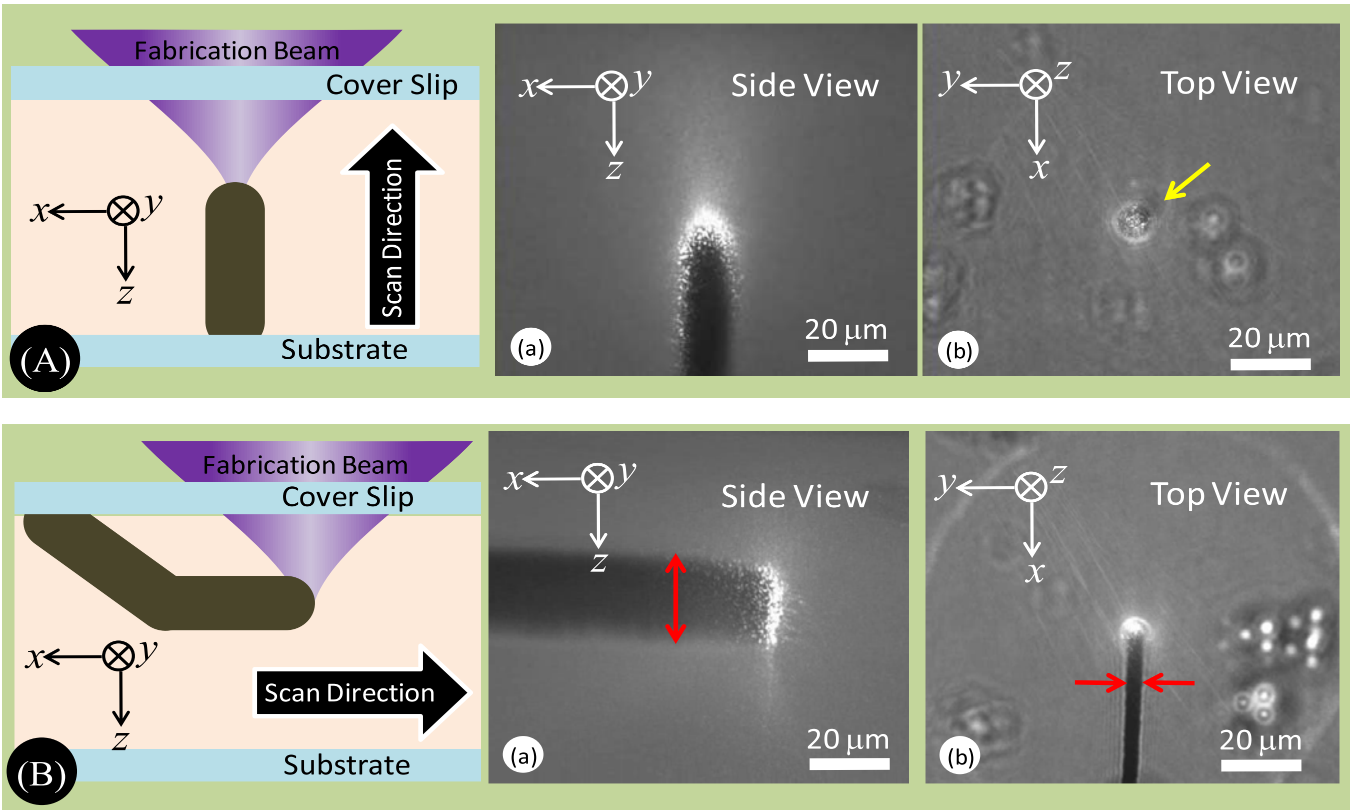

Fig. 6 In-process visualization of proposed microfabrication method. (A) z-direction scan, (B) x-direction scan, (a) side view, (b) top view

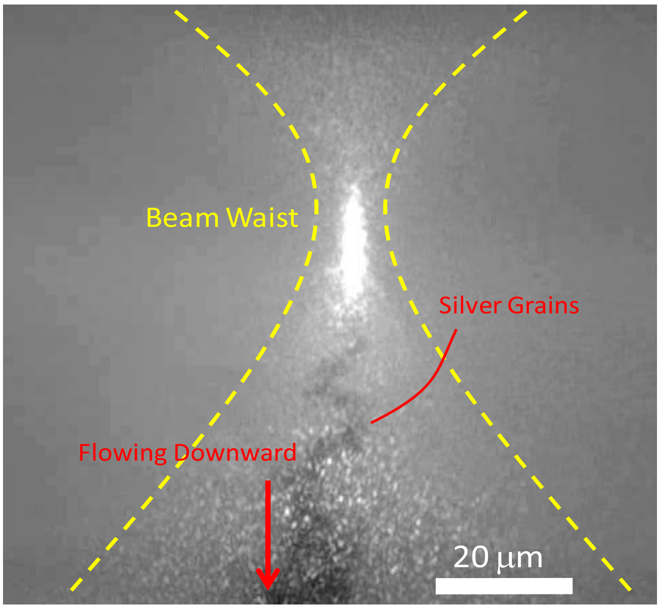

Fig. 7 Observation of deposition at the beam waist.

4.3 Discussions about Effect of Substrate

We knew experimentally that 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 in-process visualization unit is shown in figure 7. It was observed that continuous structure was not fabricated, but below the beam waist silver grains discontinuously appeared and flew downward.

Next the deposition processes were compared when the distances between the beam waist and the substrate were different. Three important cases of the results 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 over about 20 μm, continuous deposition was not observed, but many grains of silver were found (figure 8 (c)).

These results show the substrate considerably affects the deposition condition, and the deposition condition depends on the distance between the beam waist and the substrate. Especially for continuous deposition, the distance has to be shorter than a certain distance. This suggests that some fixed substance is necessary near by the beam waist for continuous deposition. This phenomenon seems relevant to thermal condition, fluid dynamical condition, or optical property condition around the beam waist. We want to examine these conditions in more detail in future.

5. Conclusions

We developed a microscope system which enabled us to observe the microfabrication process from the fabrication beam optical axis and its radial direction. We succeeded in visualizing the microfabrication in 3-D. From visualization it was confirmed that the deposition of silver was localized three dimensionally and the micro scale structure grew three dimensionally following the beam waist scan.

The effect of 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 for continuous deposition the distance has to be shorter than a certain distance. We want to analyze the fabrication condition for achieving continuous deposition more in future.

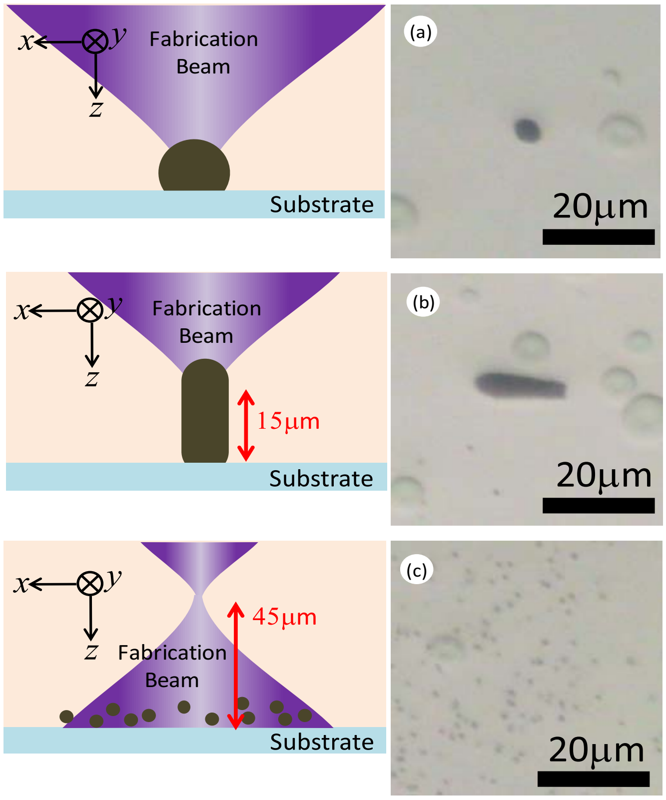

Fig. 8 Effect of substrate on deposition condition. The distances between the beams waist and the substrates are 0 μm, 15 μm, and 45 μm in (a), (b), and (c) respectively. The exposure times are 10 s, 10 s, and 100 s in (a), (b), and (c) respectively. The pictures in the right side were top view. In (b)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

ACKNOWLEDGEMENT

The authors thank Dr.Yasushi Kuroda of Showa Titaniumu Co. Ltd. providing brookite TiO2 nanoparticles This work was partially supported by JSPS under the Grant-in-Aid for Scientific Research (B) , NEDO under the Industrial Technology Research Grant Program, and TEPCO Research Foundation.

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