

A Novel Microfabrication Technique for Three-Dimensional Metal Structures by Photocatalysis

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SUMMARY

Though there are a variety of microfabrication techniques, one that can fabricate three-dimensional metal structure by simple procedure is rarely seen. Given this fact, we suggest a new method for three-dimensional microfabrication that is characterized by photocatalytic deposition. The setup for this method consists of a wavelength 405nm laser diode, a numerical aperture 0.9 objective lens, and a motorized linear stage. With this setup, it was observed that a converging near-ultraviolet laser beam caused deposition of Ag at the beam waist in AgNO₃ solution including TiO₂ nanoparticles. Furthermore, we succeeded in fabricating a microbox and a microcoil by sweeping the beam waist in the solution.

INTRODUCTION

Microfabrication is one of the most important technologies in the manufacturing industry. Large Scale Integrated (LSI), Micro Electro Mechanical System (MEMS) or other electronic devices depend on it. On top of that, in biochemical fields, this technology is needed to manufacture cutting-edge devices such as Micro Total Analysis System (μ -TAS) and DNA Microarrays.

Therefore a lot of microfabrication techniques are under study, but one that can fabricate three-dimensional metal structure by simple procedure is rarely seen. Beyond that, apparatuses used for microfabrication tend to be expensive. For example, lithography requires complicated processes and the Focused Ion Beam (FIB) method is too expensive for mass-production.

Now we propose a new microfabrication technique that uses photocatalysis. In AgNO₃ solution including TiO₂ nanoparticles, it was observed that a converging laser caused photocatalytic reduction and Ag was deposited at its beam waist. Furthermore, we succeeded in fabricating a microbox and a microcoil by sweeping the beam waist in the solution.

PHOTOCATALYTIC OXIDATION-REDUCTION REACTION OF TiO₂

Our microfabrication technique is based on the theory of photocatalytic oxidation-reduction (redox) reaction. When a photocatalyst absorbs light energy that is greater than its bandgap

energy, electrons in the valence band transfer to the conduction band [1]. In this study, we selected a TiO₂ photocatalyst because it is very active and stable throughout the redox reaction. TiO₂ absorbs light with wavelength that is shorter than about 400nm, and then it generates pairs of holes and electrons. The holes are so oxidative that they can break apart the water molecules to form hydrogen gas and hydroxyl radicals. And the electrons can reduce oxygen molecules to form super oxide anions (Fig. 1).

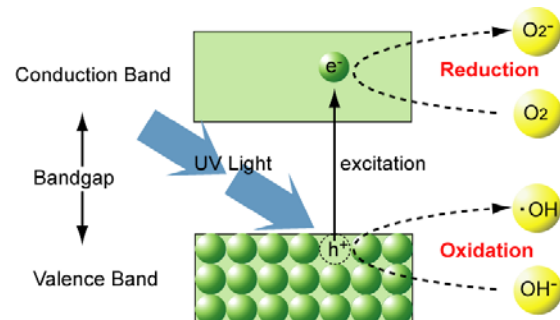


Fig. 1 Redox reaction of excited TiO₂. Electrons in the valence band are elevated to the conduction band by UV-light energy that is greater than bandgap energy.

If excitation of TiO₂ occurs in ionic solution of noble metal whose ionicity is lower than H⁺, reduction of the metal ions is possible. Actually, it was reported that when TiO₂ was illuminated with UV-light, it caused deposition of metal, such as Ag [2] and Pt [3].

CONCEPT OF MICROFABRICATION WITH PHOTOCATALYSIS

We thought that photocatalytic deposition of metal could be applied to three-dimensional microfabrication. The key point of our idea is to use a metal ion solution in which TiO_2 nanoparticles are dispersed. If a converging laser beam illuminates the TiO_2 nanoparticles in the solution, a cluster of metal will appear at the beam waist by the photocatalytic redox reaction. Therefore, by sweeping the beam waist, a three-dimensional structure would be formed along the path of the beam waist (Fig. 2).

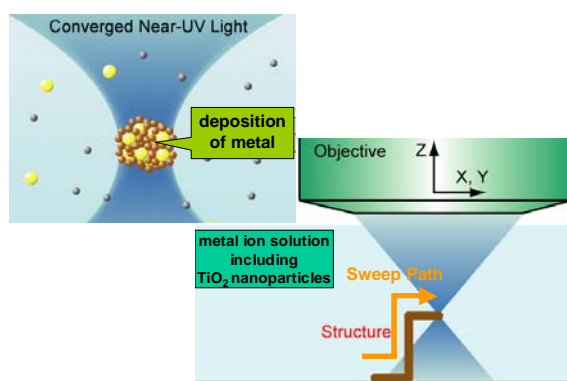


Fig. 2 A metal structure formed by beam waist sweep. In metal ion solution, excited TiO_2 nanoparticles deposits the metal at the beam waist of a converging laser beam. Therefore, by sweeping the beam waist within the solution, any shapes of three-dimensional structures will be fabricated.

EXPERIMENTAL SETUP

To realize our conception, we set up a fabrication system, which is illustrated by Fig. 3. The light source of the system is a wavelength 405nm laser diode whose maximum output is $55 \text{ mW} / \text{cm}^2$ (LDM Series Blue, Omicron Laserage). Its exit aperture is connected with a single-mode optical fiber with a $3.3\mu\text{m}$ diameter (LDM-405 FAS, Omicron). The end point of the fiber can be positioned by a motorized linear stage under computer control (LINEAR-BALL GUIDE, SURUGA SEIKI Ltd.). With this stage, it is possible to position the fiber end by $2 \mu\text{m}$.

After going through the fiber, the light is gathered together to a parallel beam by a collimating lens with a focal length 48 mm, and a 8 mm effective diameter (06GLC205, MELLES GRIOT). Via a beam splitter, the laser beam enters a 40x objective with a 0.9 numerical aperture (CFI S Fluor 40x, NIKON). By the

objective, the laser beam is converged at a point on the sample stage.

And a CCD camera enables observation of the fabrication process in real time. To avoid CCD saturation, a dichroic mirror is inserted in front of the CCD imaging lens.

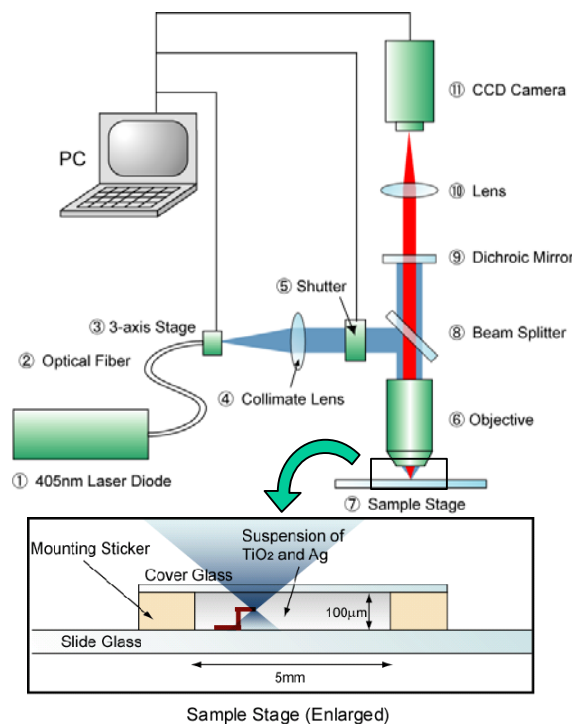


Fig. 3 Diagram of our experimental setup. The laser diode on the left side of the diagram provides a wavelength 405nm laser beam. Via an optical fiber, a collimating lens, a beam splitter and an objective, the laser is converged at a point on the sample stage on the right side of the diagram. The fiber end can be positioned by a computer-control stage, so that it is possible to manipulate the beam waist with the computer.

FEASIBILITY OF PROPOSED METHOD

With the setup mentioned in previous section, we tested the feasibility of the proposed microfabrication method. In this report, we used AgNO_3 solution as a metal ion solution. This was because Ag has the lowest electric resistivity among all metals so that microstructure of Ag should be worthy for electric usage. On top of that, Ag microstructure may be applied to optical devices because Ag nanoparticles show unique optical properties such as photochromism that is based on surface plasmon resonance [4].

The first step was preparation of a sample, AgNO_3 solution in which TiO_2 nanoparticles

were dispersed. We used suspension of brookite TiO_2 nanoparticles with a 10 nm diameter on the average (NTB-1, Showa Denko K.K), and 0.1 mol / l AgNO_3 solution. They were mixed at the same rate. Then a drop of the mixture was clipped between a slide glass and a cover glass.

When the sample was illuminated at $7\text{mW} / \text{cm}^2$ with our setup, a dark spot with a $10\text{ }\mu\text{m}$ diameter appeared in the sample solution (Fig. 4 (a)). And we swept the beam waist at $2\text{ }\mu\text{m} / \text{sec}$ during illumination, a line was formed along the sweep path of the beam waist (Fig. 4 (b)).

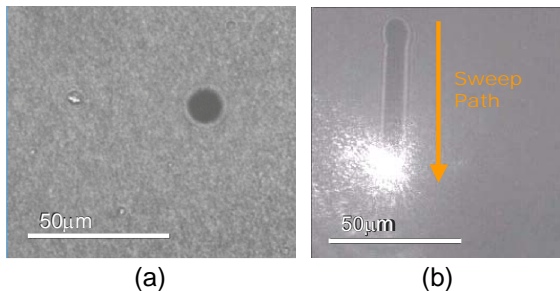


Fig. 4 (a) A photograph of a dark spot that appeared after near-UV laser illumination with our setup. The diameter was about $10\text{ }\mu\text{m}$. (b) A line that was formed along the sweep path of the beam waist.

To investigate composition of the deposited substance, we analyzed it with an X-Ray Diffraction (XRD) Spectroscopy apparatus. Fig. 5 shows the analysis result. The diffraction angles at which the spectrum peaks appear match those of Ag and TiO_2 . This means that the deposited substance was composed of Ag and TiO_2 , therefore the proposed microfabrication method turned out to be feasible.

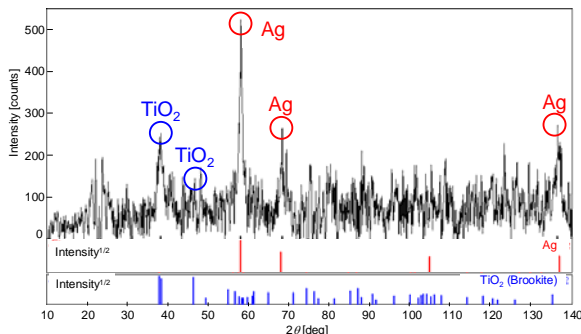


Fig. 5 XRD analysis of the deposited substance that was obtained with our setup. X-ray diffraction patterns of Ag and TiO_2 are attached at the foot of the obtained pattern. The diffraction angle 2θ at which a spectrum peak appears matches that of Ag and TiO_2 .

RELATIONSHIP BETWEEN LINE WIDTH AND SWEEPING VELOCITY

It is important to figure out the characteristics of the proposed microfabrication, so we examined how sweeping velocity v would influence the line width of deposited Ag w at a certain light intensity. As a result, it was observed that w monotonously decreased with increasing v . Fig. 6 shows variations in w versus v at $7\text{mW} / \text{cm}^2$. Then it turned out that w was approximately proportional to $v^{-1/2}$. This can be explained with the hypothesis that deposited metal grows with geometric similarity, and its amount is linear with exposure. If deposited Ag grows similarly, cross section area of the line S is proportional to $w^{1/2}$. And if amount of deposited Ag has linearity with exposure, S is proportional to v^{-1} because the time period in which a certain cross section can receive exposure energy is proportional to v^{-1} . Therefore w is proportional to $v^{-1/2}$, so that it is possible to control line width by sweeping velocity.

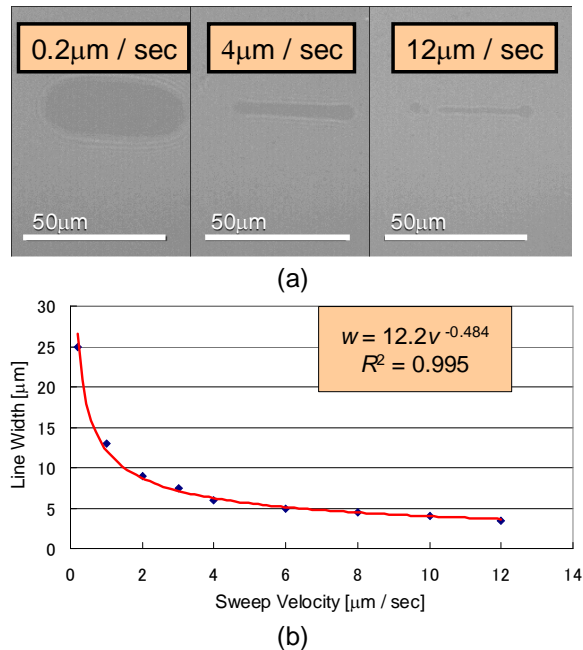


Fig. 6 (a) Three photographs of line-shaped deposited Ag. They were deposited at $7\text{mw} / \text{cm}^2$. Line width w decreases as sweeping velocity v gets faster. (b) Plot of w versus v . Under the condition of fixed light intensity, w was approximately proportional to $v^{-1/2}$.

DEMONSTRATIONAL FABRICATION OF THREE-DIMENSIONAL MICROSTRUCTURE

Here we tried to fabricate two different types of structures as a demonstration. One structure

was a microbox shown in Fig. 7 (a). It is a cuboid with sides of 60 μm , 60 μm , 30 μm , and two decoration circles suspended in the squares. The other was a microcoil with a 60 μm diameter and a 12 μm pitch, which is shown in Fig. 7 (b).

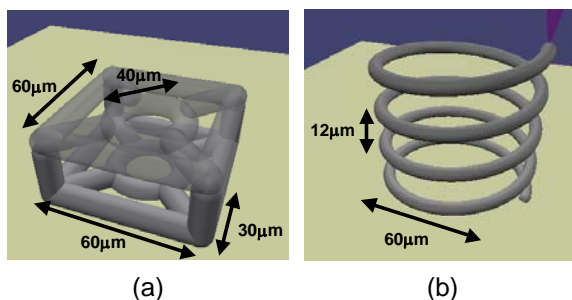


Fig. 7 Design of three-dimensional structures for demonstrational fabrication. (a) A microbox with sides of 60 μm , 60 μm , 30 μm , and two decoration circles suspended in the squares. (b) A microcoil structure with a 60 μm diameter and a 12 μm pitch.

We prepared the sample in the same way as the previous sections. The two structures were fabricated on a slide glass. In this experiment, the laser output was 7mW / cm², and the sweeping velocity was 2 μm / sec.

The microbox was shown in Fig. 8 (a). The frame of the microbox structure was fabricated completely along the sweep path. The microbox wasn't too weak to collapse immediately. It was seen that when the microbox came off the slide glass, it turned over in the solution with its shape kept. Thus parts of the microbox were combined with some strength.

The microcoil was fabricated by sweeping the beam waist in a spiral (Fig. 8 (b)). Presently, the maximum number of pitches is just two, so we'll try to fabricate longer coil in the further study.

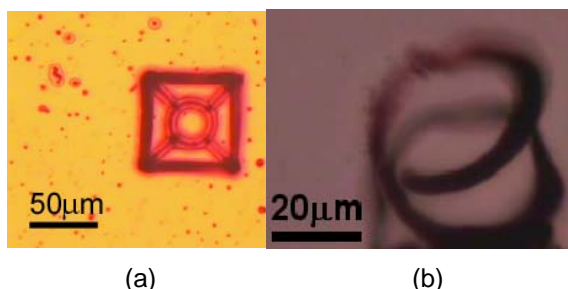


Fig. 8 (a) A microbox with 60 μm x 60 μm bottom and top, and four 30 μm columns. Sweep path of the beam waist completely matches the frame of the microbox. (b) A microcoil with a 60 μm diameter and a 12 μm pitch.

CONCLUSION

In conclusion, we have shown the feasibility of the new microfabrication technique based on photocatalytic deposition Ag. First, we actually set up a microfabrication system with a wavelength 405nm laser diode and a 0.9 numerical aperture objective.

Then, with our setup it was possible to cause deposition of Ag at the beam waist. If the beam waist was swept in the sample solution, deposited Ag formed a structure along the sweep path of the beam waist.

And inspection of the relationship between line width w and sweep velocity v made it appear that w was proportional to $v^{1/2}$. Therefore the line width was controllable by the adjustment of the sweep velocity.

Finally, we succeeded in fabricating two types of three-dimensional structures, a microbox and a microcoil. In particular, the microbox was strong enough to rotate in the solution without being broken. From now on, we'll search for how to fabricate smaller, stronger and more complicated structures.

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