Paper:

Fabrication and Composition Control of Three-Dimensional Dielectric Metal Microstructure Using Photocatalyst Nanoparticles

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Recently, three-dimensional microstructures have been attracting much attention because of their potential application to electromagnetic devices operating with specific frequencies such as THz wave. For suitability in such applications, the structures often need to have complex three-dimensional shapes, be smaller than or at least as small as the applied wavelengths, consist of metals or dielectric materials, and have certain electromagnetic characteristics such as high permittivity. Although there are several methods for fabricating micro-structures, few of them satisfy all of these conditions. We propose a new fabrication method for dielectric-metal three-dimensional structures with sizes of a few tens of micrometers. The main feature of our method is the extraction of metal using photocatalyst nanoparticles. Silver ions in solution are reduced to neutral silver by electrons from the photocatalyst nanoparticles. Experimental results show that our system can be used to fabricate three-dimensional structures, and we propose a new method for controlling the composition of the structures.

Keywords: microfabrication, photocatalyst, silver, dielectric, TiO_2

1. Introduction

Electromagnetic waves of certain frequencies, such as THz waves, have been shown to be especially valuable in fields such as biomedical imaging [1–4]. Although there are few devices that are suitable for controlling such waves, it has been reported that some structures such as a dielectric microcube with metal lines on its surface [5] or arrays of double helix metal wires [6] can serve as useful THz devices, sometimes in the forms of photonic crystals or meta-materials [7, 8]. For this purpose, the structure often needs to satisfy several conditions: it should have a three-dimensional shape, consist of metals or dielectric materials, be as small as or smaller than the applied wavelength, and have certain electromagnetic characteristics such as high conductivity or high permittivity. Although there are several methods for microfabrication [9, 10], no existing method meets all these requirements. For example, micro stereolithography is able to rapidly fabricate three dimensional structures [11, 12], but materials are basically limited to resins. Focused-Ion-Beam Chemical-Vapor-Deposition (FIB-CVD) can be applied to various materials [13], but the speed of fabrication is quite low and it requires large-scale systems.

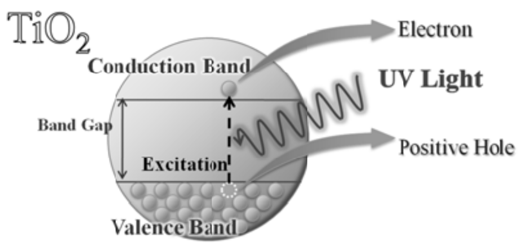


Fig. 1. Schematic of photocatalyst reaction.

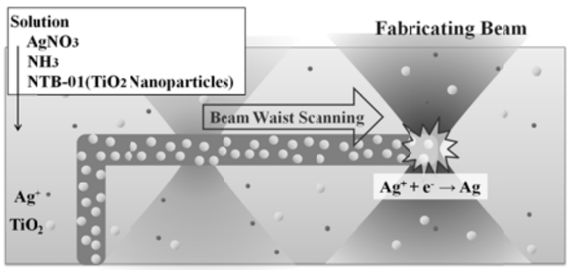


Fig. 2. Concept image of fabrication.

Therefore, we propose a new micro fabrication method that meets all the aforementioned requirements. The key feature of our method is the extraction of metal from solution with a photocatalytic reaction. A schematic image of the photocatalytic reaction is shown in **Fig. 1**. During the photocatalytic reaction, TiO_2 absorbs UltraViolet (UV) light, becomes excited, and emits an electron and a hole [14].

The schematic of our method using this reaction is shown in **Fig. 2**. First, we prepare a solution containing silver ions and TiO_2 nanoparticles. Then, TiO_2 is excited

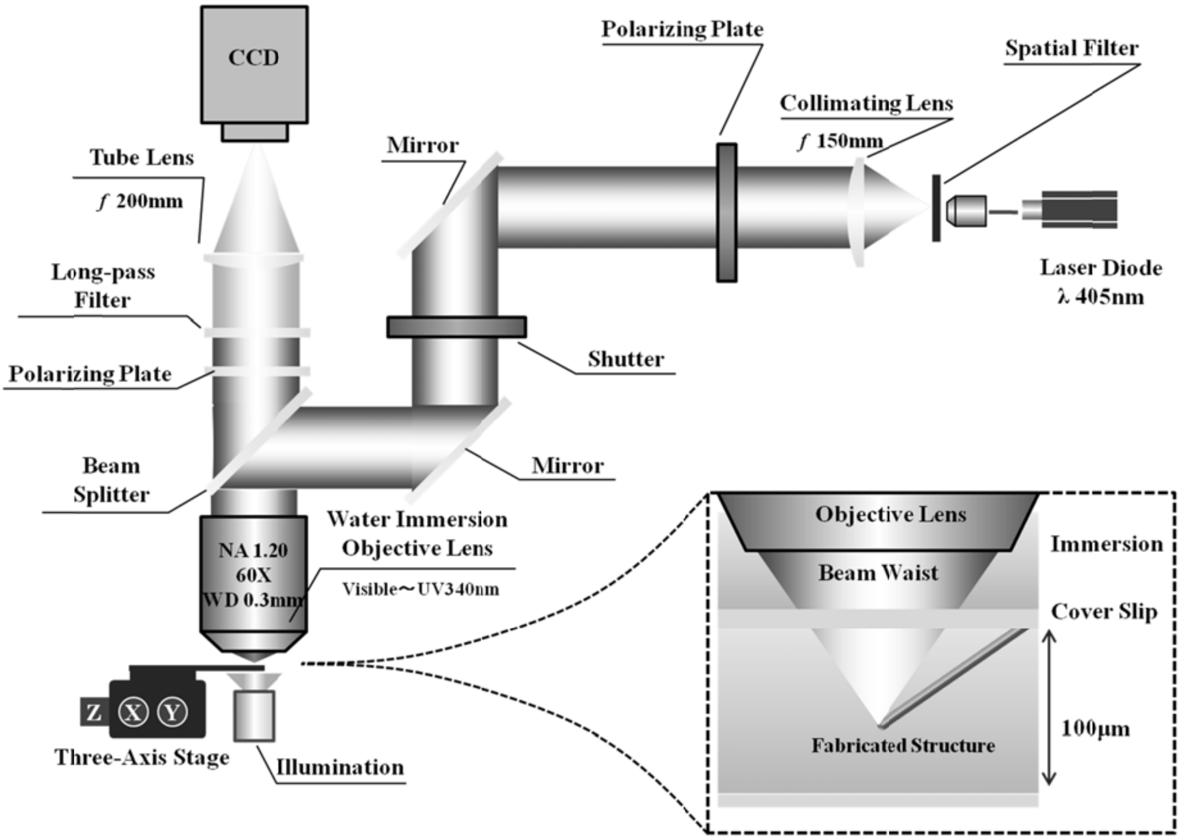


Fig. 3. Schematic of fabrication system.

by a concentrated UV beam, emits an electron, and a silver ion gains the electron and is reduced into a neutral silver atom. As this process occurs only in the vicinity of the beam waist, we can fabricate a three-dimensional structure by scanning the beam waist. As the UV process occurs simultaneously with the condensation of TiO_2 nanoparticles, the structure contains both silver and TiO_2. The two species spread randomly throughout the fabricated structures. Since structure designs are dominated by requirements for applications rather than for ease of fabrication, a method to control the composition of fabricated structure is needed.

In this paper, we report that after baking, silver was melted, and a three-dimensional TiO_2 structure could be fabricated. We also found that when we irradiated the baked structure with a UV laser in a solution including silver ions, the surface of the structure is covered with silver. Both of these results are desirable for fabricating structures and for developing new devices.

2. Fabrication System

We have been developing a microfabrication system based on the principle described above. We have previously verified that the system is suitable for fabricating complex three-dimensional complex structures [15], and have developed an in-process observation system for further study [16]. **Fig. 3** shows the schematic of the system. We use a 1.4-mW, 405-nm laser as a light source. The wavefront of the laser is conditioned using the spatial filter. A 1.20-NA objective lens focuses the laser into a cell which holds the fabrication solution; the cell is illuminated from the bottom. The illumination is collected by the objective lens, passes through a 50/50 beam splitter, and makes an image at CCD camera using infinity-corrected optical system, so we can achieve in process monitoring. The long pass filter is set before the CCD camera in order to reduce the intensity of the fabrication beam and to help observation.

The cell is composed of two cover slips that are separated by a 100-μm thick film. The film contains the fabrication solution. The solution consists of $AgNO_3$, and NH_3, – silver is actually forming the complex ion $Ag[NH_3]^{4+}$ in order to provide sliver ions – as well as the dispersion of brookite TiO_2 nanoparticles (NTB-01, Showa Titanium) which have 15 – 20 nm diameter. The solution concentration of each component is as follows: $AgNO_3$ is 0.009N, NH_3 is 9 wt%, and TiO_2 nanoparticles are 0.65 wt%. The cell is on the three-axis stage with 60-nm moving step such that we are able to scan the beam waist relatively. The picture of the actual system is shown in **Fig. 4**.

Since the structures are fabricated in the liquid phase, the surface tension of the solution will fracture the structure if simply dried out of solution. Thus, we apply a

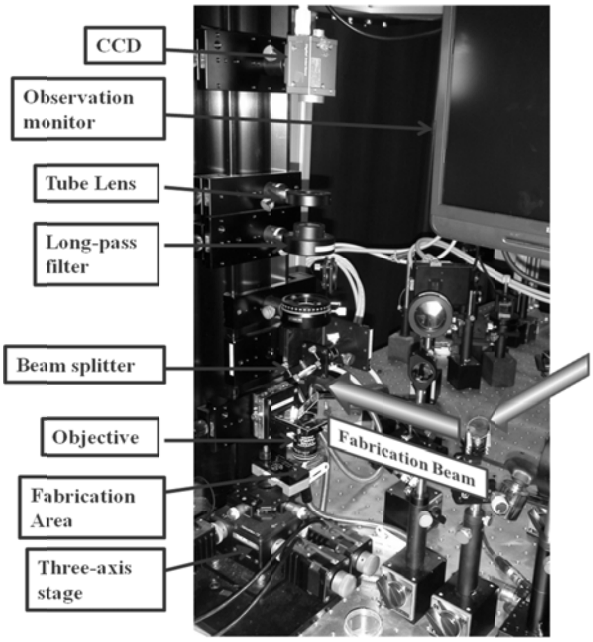
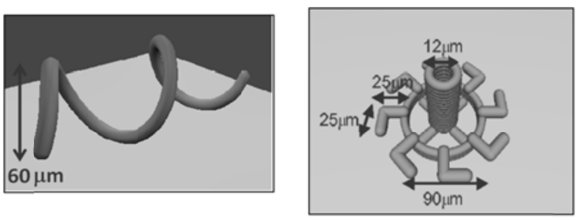
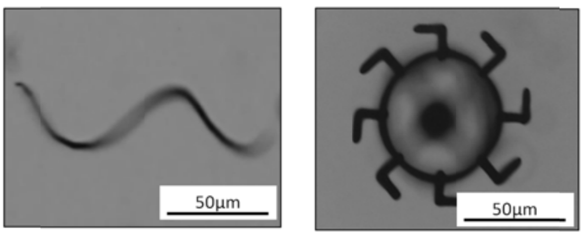


Fig. 4. Picture of fabrication system.



(a) Schematic images



(b) Microscopic images

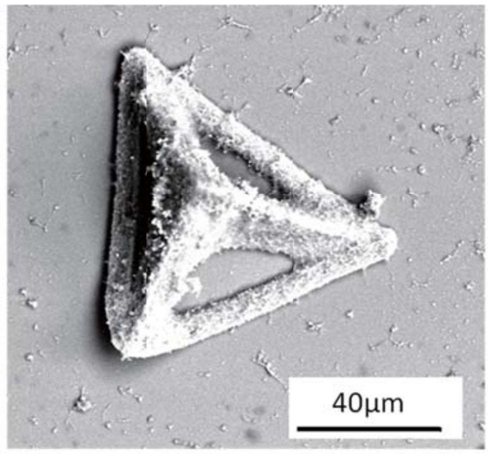
(A) Coil structure (B) Rotor structure

Fig. 5. Examples of fabricatie structures.

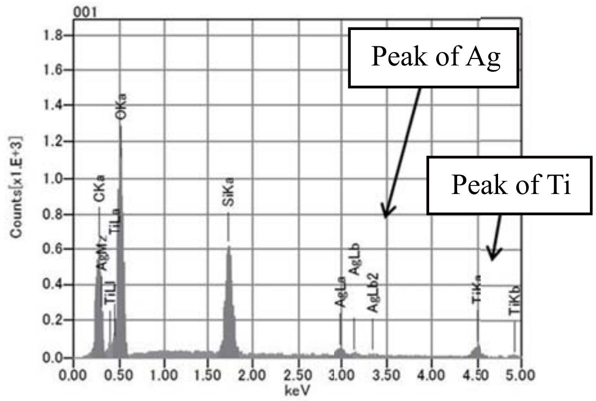
supercritical drying method [17] which brings the surface tension to near zero degree. The supercritical drying method allows us to further analyze the structures in vapor phase without damage during drying.

3. Characteristics of Fabricated Structure

Three-dimensional microstructures can be directly fabricated with the system we developed. Two examples are shown in **Fig. 5**. **Fig. 5(A)(a)** is the schematic of a coil-shaped structure with 60-μm diameter. **Fig. 5(A)(b)** is the optical-microscopic image of the coil structure that was actually fabricated. **Fig. 5(B)(a)** is the schematic of a more complicated structure, a micro-rotator structure with a cylinder and propellers. The diameter of the cylinder is 12 μm, the diameter of the bottom ring holding propellers is 90 μm, and the length of each propeller is 25 μm. **Fig. 5(B)(b)** is the optical-microscopic image of the rotator that was actually fabricated. The width of an element in the structure depends on the scanning speed of the beam waist. When scanned faster, the structure is thinner; when scanned slower, the structure is thicker. In this report, we scanned at 1 μm/s and the width is approximately 3 μm. As shown in these examples, this system made it possible to fabricate three-dimensional micro structures that are tens of micrometers in size.



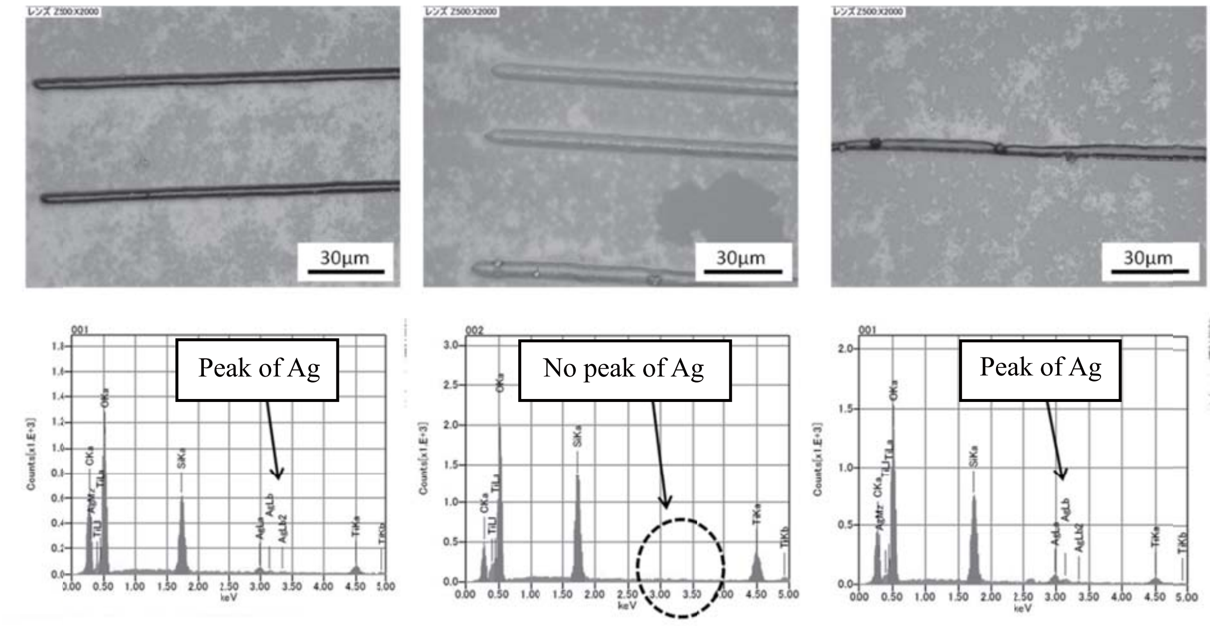
(a) SEM image



(b) Spectrum analysis by SEM-EDS

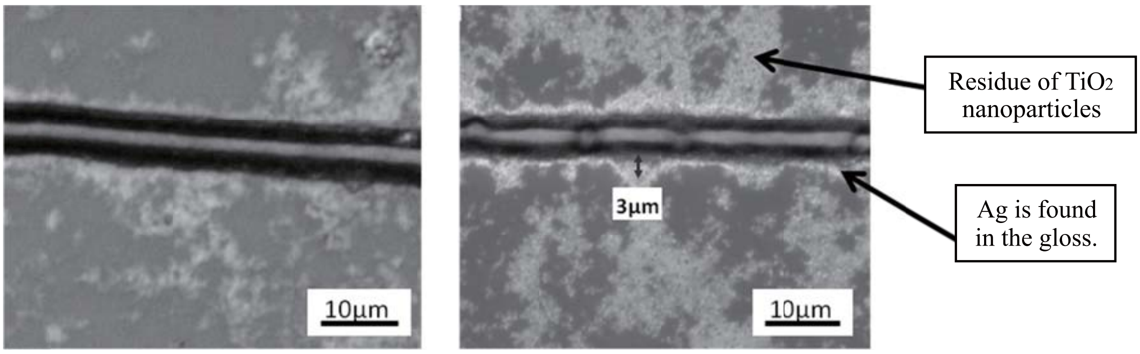
Fig. 6. SEM analysis of fabricated structures.

Figure 6 is a typical example of a structure brought out into vapor phase by the supercritical drying method. We observed it with SEM and determined its composition using energy-dispersive spectroscopy, SEM-EDS. **Fig. 6(a)** is the SEM image of the fabricated structure. **Fig. 6(b)** is the spectral analysis of the structure using SEM-EDS. The peak of Ag is detected at approximately 3.0 keV; similarly, the peak of Ti is approximately 4.5 keV, so the structure consists of both Ag and Ti.



Before Baking | Baking at 700°C | Baking at 450°C

Fig. 7. Baking temperature and change in composition.



Baking at 650°C, 10 min | Baking at 650°C, 20 min

Fig. 8. Baking time and change in compositon.

4. Composition Control by Baking

As described in section 3, the fabricated structure contains both Ti and Ag. However, the fact that metal and dielectric are spreading at random in the structure may make it difficult to control the properties and design characteristics of the structure. To solve this problem, we tried baking the structure. We found that we can separate Ag from Ti by baking the structure at 900°C for 20 minutes [18]. We then examined the thermal conditions of this reaction.

The samples that we prepared for this experiment are lines and spaces with a length of 200 μm and space width of 25 – 100 μm between each line. The substrate of these samples is heat-resistant coverglass that can resist baking at over 1000°C. Optical-microscopic images and SEM-EDS analysis of the samples before and after baking are shown in **Fig. 7**. Before baking, the lines look black, white residue is sticking on the substrate. The residue is mainly TiO_2 nanoparticles that were not used in the reaction and had been floating in the solution. SEM-EDS shows that the lines before baking contain both Ag and Ti. After baking at lower temperature, 450°C, no change was observed either by optical microscope or composition analysis using SEM-EDS. After baking at higher temperature, 700°C, a change is observed using both optical microscopy and SEM-EDS; the lines are relatively whiter and no Ag was detected. The color of TiO_2 is white so the change in composition is apparent as the change in color.

For further analysis, we baked line samples at 650°C, for different amounts of time. **Fig. 8** shows the results of baking the sample for 10 – 20 minutes. With 10 minutes of baking, no change could be observed by optical microscope imaging. We also observed with SEM-EDS, and Ag is found in the lines. Through 20 minutes of baking, the residue near the lines starts to look shiny, reflecting the observation light from the optical microscope. The

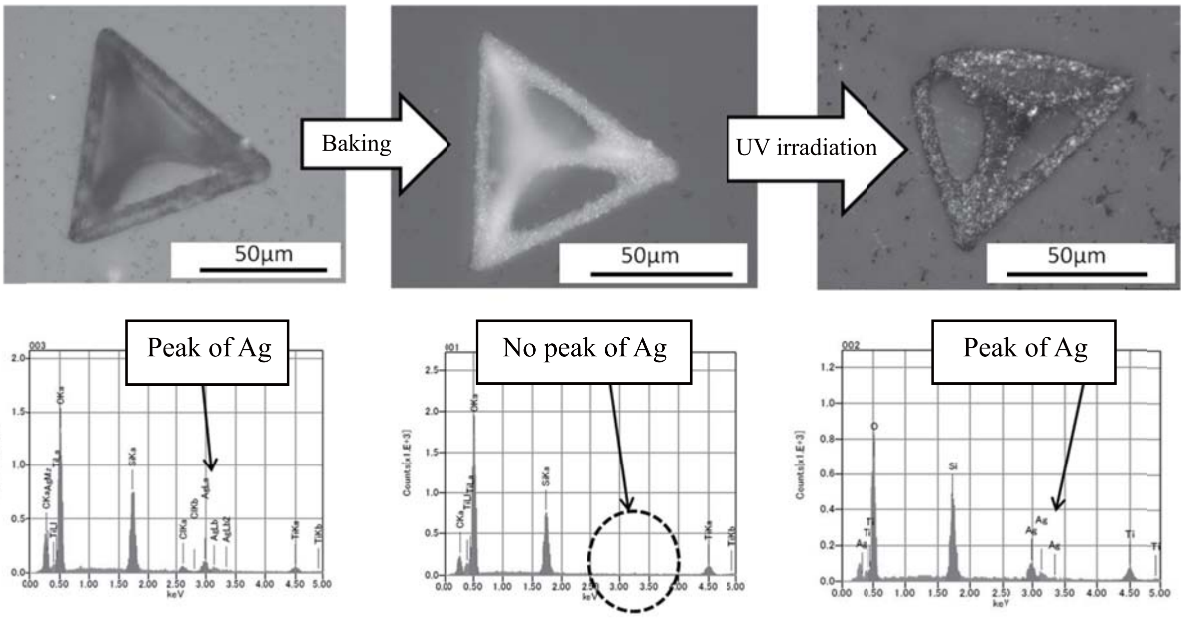


Fig. 9. Covering TiO_2 structure with silver.

spatial range of this gloss is approximately 3 μm from the line edge. By using SEM-EDS, we found that Ag is in this region, and the peak of Ag in the lines is weaker than before baking. We also baked the sample for a longer time, 30 minutes. The resulting gloss is wider, approximately 10 μm from the edge, the lines are whiter, and the SEM-EDS peak of Ag in the lines is weaker than when baking for 20 minutes.

These results indicate that silver had melted out of the structure during baking. The critical temperature of this reaction is estimated to be approximately 650°C. However, the melting point of bulk Ag is 962°C, so the Ag had melted at a temperature much lower than the melting point. Generally speaking, the melting point of a material reduces as its size gets smaller, especially at nanoscale sizes. This phenomenon is called melting-point depression. The Ag is expected to exist in the structure as nanoparticles or some other small form other than bulk. According to a thermodynamic approach, the melting temperature T_M of a spherical particle is calculated from the following equation [19], which is known as the Gibbs-Thomson equation,

$$T_M = T_B \left(1 - \frac{4\sigma_{sl}}{H_f \rho d}\right) \quad \text{. . . . . (1)}$$

where T_B is the melting temperature of the bulk material, σ_{sl} is the solid-liquid interface energy, H_f is the heat of fusion, ρ is the density of material, and d is the diameter of the particle. As Eq. (1) shows, the smaller particle, the lower the melting temperature.

Assuming that Ag is forming nanoparticles that have a smooth surface, the solid-liquid interface energy of Ag is assumed to be 0.143 J/m^2, as determined in 1983 [20]. Substituting this value to Eq. (1), Ag particles with 1.8-nm diameter would result in the observed melting at 650°C. This value and the applicability of the model to fabricated structures could be verified with further analysis.

5. Verifying Possibility of Further Control in Composition

As described in section 4, with baking at greater than approximately 700°C, silver is molten down and the baked structure consists of only the TiO_2 photocatalyst. This means that if we put the baked structure into the solution which contains silver ions and irradiate the structure with UV light, we may be able to fabricate a structure that has a dielectric core and silver surface, which is a desirable structure for optical or electromagnetic devices. In order to examine the possibility of this process, we fabricated the structure, removed it to vapor phase by supercritical drying, baked it at 900°C for 20 minutes, put it into $AgNO_3$ (aq) solution, and irradiated it with a 325-nm He-Cd laser.

Figure 9 shows the optical-microscope images and spectral analysis of the structure in each step of the process. We fabricated a triangular pyramid with each edge 60 μm long. After drying, the structure consists of both silver and TiO_2. After baking it at 900°C for 20 minutes, the spectral analysis shows that the silver melted out from the structure. This result indicates that we can fabricate three-dimensional micro structures with high permittivity, which is applicable to some electromagnetic devices.

After the baking step, we put the baked structure into a sample cell composed of two cover slips holding $AgNO_3$ aq inside. We found that the baked structure has higher durability than that of the structure before baking such that this step does not break the structure. For quantitative evaluation, we measured the Young's modulus through an indentation test using a Vickers penetrator. The Young's modulus of the structure before baking was approximately 3.6 GPa – almost same value as that of polystyrene: 3 – 3.5 GPa – while the Young's modulus of the baked structure was approximately 22 GPa – close to that of concrete: 20 – 30 GPa. This value is smaller than that of either bulk Ag or TiO_2 – 83 GPa and 290 GPa, respectively – but it is high enough to bear the surface tension of the solution and maintain a three-dimensional shape.

Finally, we irradiated the sample with a 325-nm He-Cd laser. The power of the laser was adjusted to 10 mW. The irradiated structure seems to be covered with black material in the optical-microscope image, and the peak of Ag is detected through spectral analysis; we can conclude that the irradiated structure is coated with Ag. This result indicates the possibility that we can fabricate a structure with a dielectric core and metal surface.

6. Conclusions

We developed a new method for fabricating three-dimensional micro structures. The essential feature of our method is the reduction of silver ions to silver using TiO_2 nanoparticles. The size of the fabricated structures is of the order of tens of micrometers, and they consist of silver and TiO_2. We proposed a novel method for controlling the composition of the structure using baking and UV irradiation. When baking at temperatures above approximately 700°C, silver is melted; consequently, the baked structure contains only TiO_2. By irradiating the baked structure with a 325-nm laser in a silver-ion solution, the surface of the structure becomes covered with silver. The results obtained by baking and UV irradiation indicate that we are able to control the composition of structures and fabricate either three dimensional TiO_2 structures or structures with a TiO_2 core and a silver surface. In the future, we will verify the possibility of applying such structures to THz wave devices by studying the details of other process characteristics including accuracy and process resolution, and other materials suitable for this method.

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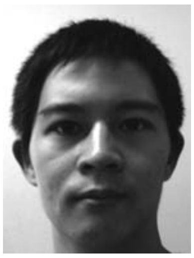

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