Single-anchor support and supercritical CO_2 drying enable high-precision microfabrication of three-dimensional structures

Shoji Maruo[1,2*], Takuya Hasegawa[1], and Naoki Yoshimura[1]

[1]*Department of Mechanical Engineering, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501,Japan*
[2]*PRESTO, Japan Science and Technology Agency, Sanbancho Building, 3-5, Chiyoda-ku, Tokyo 102-0075, Japan*
**maruo@ynu.ac.jp*

Abstract: In high-precision two-photon microfabrication of three-dimensional (3-D) polymeric microstructures, supercritical CO_2 drying was employed to reduce surface tension, which tends to cause the collapse of micro/nano structures. Use of supercritical drying allowed high-aspect ratio microstructures, such as micropillars and cantilevers, to be fabricated. We also propose a single-anchor supporting method to eliminate non-uniform shrinkage of polymeric structures otherwise caused by attachment to the substrate. Use of this method permitted frame models such as lattices to be produced without harmful distortion. The combination of supercritical CO_2 drying and the single-anchor supporting method offers reliable high-precision microfabrication of sophisticated, fragile 3-D micro/nano structures.

OCIS codes: (120.4610) Optical fabrication; (190.4180) Multiphoton processes; (160.5335) Photosensitive materials

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1. Introduction

Multiphoton microfabrication techniques are being increasingly widely applied to produce various kinds of microdevices such as photonic crystals [1], microelectronic devices [2], and magnetic metamaterials [3], microfluidic devices [4,5], and micromechanical parts [6]. Recent progress in multiphoton process is summarized in several review papers [7,8]. The unique feature of the multiphoton process is the ability to make three-dimensional (3-D) microstructures at sub-100 nm resolution, beyond the diffraction limit of light. In the first demonstrations of 3-D fabrication using a multiphoton process, the resolution was in the order of micrometers [9], but has since attained 65 nm employing a multiphoton process with visible light [10]. Recently 40 nm resolution was also demonstrated by using photo-induced deactivation lithography [11]. In addition, sub-30 nm resolution has been achieved using bridge-like structures by exploiting photopolymer shrinkage [12].

The remaining challenge is improving the accuracy of 3-D fabrication in the production of practical microdevices. In the typical two-photon microfabrication processes, 3-D microstructures made from acrylic- or epoxy-type photopolymers are rinsed with ethanol or other liquids to remove unsolidified photopolymer. During the drying process after these rinses, surface tension causes the collapse of 3-D patterns [13]. To prevent the collapse and deformation, a method to increase the mechanical strength of polymeric microstructures using multi-path scanning of a laser beam was reported [13]. However, normal single-path scanning method is suitable for making complex 3-D micro/nano structures in a short time at intrinsic high resolution.

In this study, we utilize supercritical CO_2 drying to remove unsolidified photopolymer without causing unfavorable deformation or destruction [14]. Since supercritical fluid behaves as both a highly dense gas and a diffusible liquid, it has no gas-liquid interface. This property enables sophisticated 3-D micro/nano structures to be dried without suffering the damaging effects of surface tension. For this reason, the supercritical CO_2 drying process has been used in nanopatterning of photoresist [15] and surface micromachining [16]. Here, we have applied a supercritical CO_2 drying process to the extraction of 3-D polymeric microstructures produced by two-photon microfabrication. The supercritical CO_2 drying makes possible to fabricate fragile micro/nano structures with normal single-path scanning method.

However, even if we utilize supercritical CO_2 drying process, anisotropic deformation owing to shrinkage of photopolymer still remains. Since 3-D microstructures are attached to a substrate, the shrinkage rate of photopolymer is different in each part [17]. For example, in the

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fabrication of photonic lattices, the shrinkage of the top part is greater than that of the bottom part that is attached to the substrate [18,19].

To solve the problem, several approaches, including pre-compensation for deformation [18,19] and multi-anchor supporting method [20,21] have been reported. In this study, we employ a single-anchor supporting method to reduce deformation caused by anisotropic shrinkage of a 3-D microstructure [14]. In this method, since the microstructure is separated from the substrate and supported on a single anchor column, the resultant microstructure shrinks more uniformly compared with microstructures directly fabricated on a substrate. Compared with similar approach using multiple anchor supporting columns [20,21], our single anchor method has some advantages such as a minimum of additive columns, no use of long columns, and easy extraction of microstructures for practical use. Additionally, in the single-anchor supporting method, the pre-compensation of distortion is more effective at increasing fabrication accuracy, because the shrinkage of photopolymer is almost isotropic. Therefore the combination of single-anchor supporting method and supercritical CO_2 drying process makes it possible to fabricate precise 3-D microstructures using multiphoton microfabrication.

2. Supercritical CO_2 drying process of 3-D microstructures

2.1 Supercritical CO_2 drying process

We used a commercial apparatus for supercritical drying (Ryusyo Corp., SCRD401) in the following experiments. The supercritical drying process is as follows. (1) A polymeric microstructure is fabricated using a two-photon microfabrication system that we have developed [4]. (2) The resultant microstructure is immersed in glycol ether ester to remove the unsolidified photopolymer. (3) Glycol ether ester is replaced with hexane, because hexane is quite soluble in supercritical CO_2 fluid. (4) The microstructure immersed in hexane is put into the chamber of the supercritical apparatus, and supercritical CO_2 is pumped into the chamber at a flow rate of 30 ml/min for 30 minutes to dissolve the hexane. The temperature and pressure in the chamber are 40 °C and 12 MPa to maintain the CO_2 in supercritical condition. (4) After filling the chamber with supercritical CO_2, the pressure is reduced to 8 MPa in 20 minutes. (5) Finally, the flow of supercritical CO_2 is stopped and the pressure is gradually reduced to atmospheric pressure in 80 minutes. In our experiments, we mainly used a commercial epoxy-type photopolymer (SCR-701) provided by D-MEC Inc, Japan. In addition, we used a commercial photo-patternable inorganic-organic hybrid polymer (ORMOCOMP) provided by micro resist technology GmbH, Germany.

2.2 Natural drying and supercritical CO_2 drying of micropillar arrays

To demonstrate the validity of the supercritical drying process, 10-μm-high pillar array with diameter of 1μm were fabricated and dried using conventional natural drying and supercritical CO_2 drying. Figure 1 shows scanning electron microscope (SEM) images of the pillars . As shown in Fig. 1(a), with natural drying, the pillars collapsed due to surface tension while the rinse (glycol ether ester) was evaporating. In contrast, with supercritical CO_2 drying, no collapse was observed in any of the pillars.

2.3 Supercritical CO_2 drying of high-aspect ratio microstructures

In addition, we were able to fabricate a high-aspect-ratio (up to 100) submicron pillar and long cantilever using supercritical CO_2 drying. Figure 2(a) shows the high-aspect-ratio submicron pillar with a diameter of 500 nm and height of 50 μm. Figure 2(b) shows the cantilever with length of 40 μm and diameter of 200 nm. These results demonstrate that fragile micro/nano structures with a high aspect ratio, which are easily deformed or collapsed by surface tension during the washing process, can be fabricated by reducing the surface tension by employing supercritical CO_2 drying.

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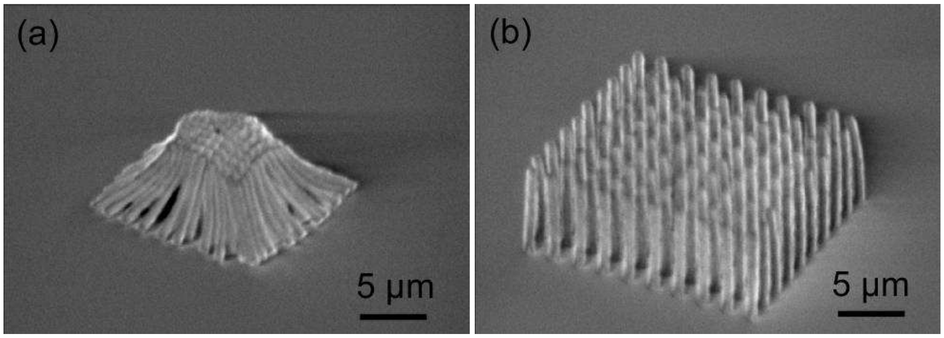

Fig. 1. Micro pillar array produced by natural drying and supercritical CO_2 drying. (a) natural drying. (b) supercritical CO_2 drying.

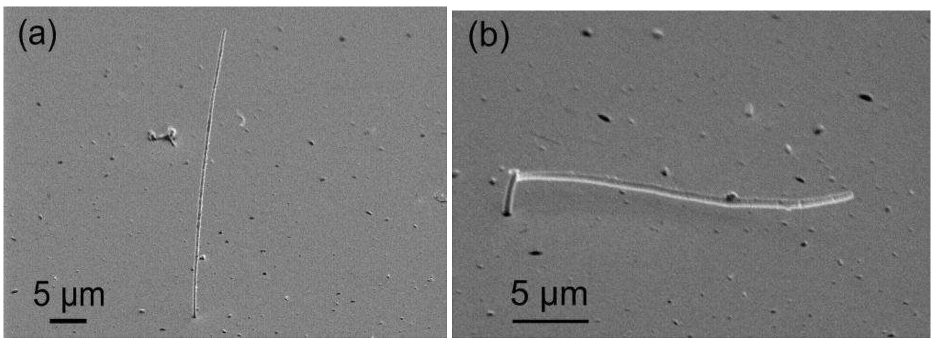

Fig. 2. High-aspect-ratio models. (a) Submicron pillar (diameter: 500 nm, height: 50 µm). (b) submicron cantilever (diameter: 200 nm, length: 40 µm).

3. Single-anchor supporting method for the reduction of non-uniform deformation

Non-uniform deformation due to the attachment of the polymeric microstructures to the substrate still appears, even if supercritical CO_2 drying is used for removing unsolidified photopolymer. To overcome this drawback, we use a single-anchor supporting method to reduce this distortion. In our method, we attach a single short anchor to the bottom part of the desired microstructure. The single anchor is used both to support the microstructure and to reduce non-uniform deformation. If two or more short anchors are attached to the structure, however, the structure is deformed owing to the attractive force exerted by the anchors. In contrast, although use of longer anchors also enables to reduce non-uniform deformation [20,21], the multiple anchors attached to the microstructures cause obstruction to practical use of 3-D microstructures.

As verification experiments of the single-anchor supporting method, cubic frame models with sides 5 µm long and different numbers of anchors were fabricated and their deformation in supercritical CO_2 drying evaluated. Each anchor was 1 µm long and 500 nm in diameter. Figures 3(a)-3(f) shows the experimental results of cubic frame models dried using supercritical CO_2. As shown in Figs. 3(a), 3(b), since the cubic frame with no supporting anchor was directly attached to the glass substrate, the top part of the cubic frame shrank to 68.5% while its bottom showed little shrinkage. This non-uniform shrinkage of the polymeric microstructure makes it difficult to produce sophisticated 3-D models with high reliability. In contrast, the cubic frame with a single anchor (Figs. 3(c), 3(d)) shrank uniformly, since the bottom part was able to shrink to the same extent as its top part. The shrinkage of the cubic frame with one anchor was 70.2% in this case. On the other hand, if two anchors were attached to a cubic frame, the bottom side attached to the anchors was unable to shrink as shown in Figs. 3(e), 3(f). These results indicate that single-anchor support is useful for reduction of non-uniform deformation due to shrinkage of polymeric microstructures due to

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attachment to the substrate. Uniform shrinkage can be easily compensated by adding an offset in a 3-D computer-aided design model.

Figure 4 shows a cubic frame models with sides 5 μm long and an anchor (diameter: 200 nm, height: 500 nm). Since supercritical CO_2 drying process reduces harmful surface tension, a submicron anchor can support a 3-D microstructure separated from a substrate. The combination of supercritical CO_2 drying process and the single-anchor supporting method makes it possible to provide precise 3-D microstructures with a minimum additive supporting part.

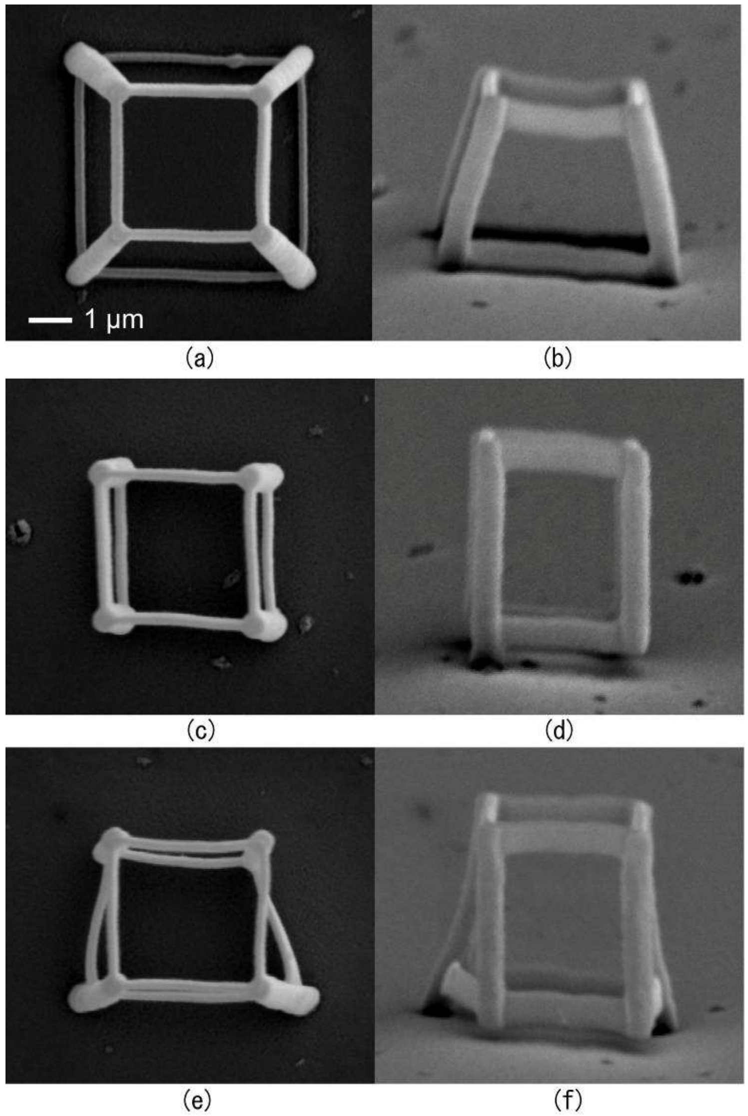

Fig. 3. Cubic frame models. (a), (b) top view and side view of a cubic frame model without anchors. (c), (d) top view and side view of a cubic frame model with a single anchor. (e), (f) top view and side view of a cubic frame model with two anchors.

To demonstrate the validity of the single-anchor supporting method for other materials, we used a commercial photopatternable inorganic-organic hybrid polymer (ORMOCOMP) provided by micro resist technology GmbH, Germany. Figures 5(a), 5(b) show lattice models with sides of 10μm without anchors and with an anchor (diameter: 1μm, length: 5 μm). The

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shrinkage of the lattice model made from ORMOCOMP is smaller than that of the epoxy-type photopolymer (SCR-701); nevertheless the single-anchor supporting method is effective in reducing non-uniform shrinkage. Therefore the single-anchor supporting method is useful for not only epoxy-type resins but also inorganic-organic hybrid materials.

A larger lattice model was produced using the single-anchor supporting method. Figure 6 shows a lattice model (30 × 30 × 15μm) made from SCR-701. In this case, an anchor with diameter of 1 μm and height of 1 μm was attached to the center of the bottom frame. In our experiments, the maximum size of a lattice model supported with an anchor is limited by mechanical strength of the photopolymer. By using other photopolymers with high mechanical strength, larger lattice model can be fabricated by the single-anchor supporting method.

Not only lattice models but also microrotors can be produced with high precision. Figure 7 shows SEM images of microrotors (diameter: 10 μm) produced without anchors and with an anchor. Although the blades of the microrotor fabricated on a substrate are deformed due to non-uniform shrinkage, the microrotor supported an anchor was successfully fabricated without non-uniform deformation. These results demonstrate that this method can be used for making a wide variety of 3-D microstructures such as photonic crystals, master models for imprinting and molding, and micromechanical parts with high precision.

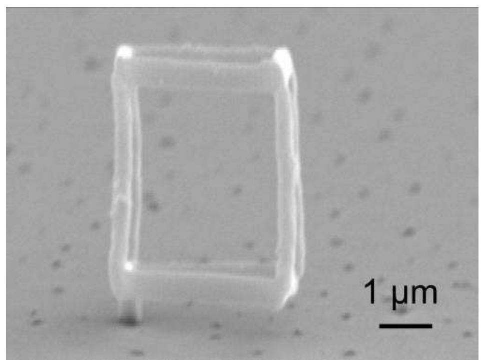

Fig. 4. A cubic frame model with a submicron anchor (diameter: 200nm, length 500 nm).

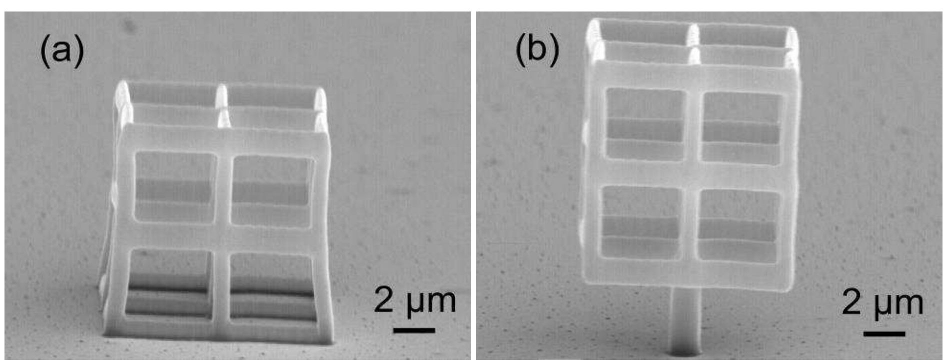

Fig. 5. Lattice models made from ORMOCOMP. (a) Lattice model without anchors. (b) Lattice model with an anchor.

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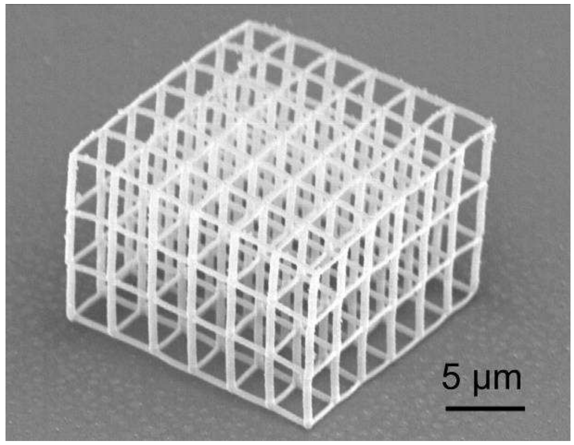

Fig. 6. A large lattice model produced by the single-anchor supporting method.

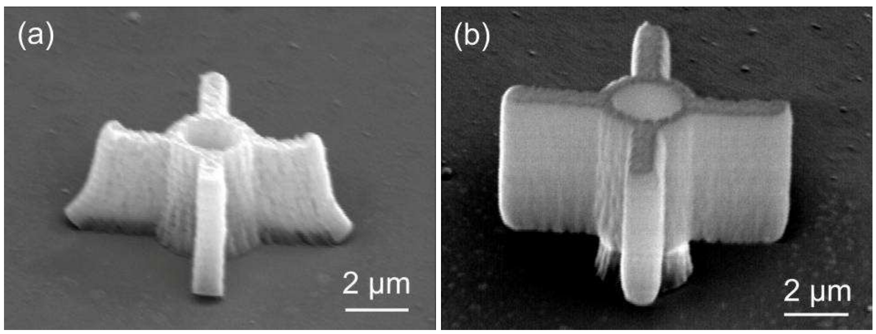

Fig. 7. Microrotor models produced by the single-anchor supporting method. (a) Microrotor without anchors (b) Microrotor with an anchor.

4. Conclusions

In summary, we applied supercritical CO_2 drying to remove unsolidified photopolymer in the two-photon microfabrication process. Supercritical CO_2 drying makes it possible to obtain fragile 3-D micro/nano structures without the surface tension of the rinse causing them to collapse. Furthermore, we propose a single-anchor supporting method to reduce the non-uniform deformation of 3-D microstructure caused by attachment to the substrate. Since pinpoint support with a single anchor allows uniform shrinkage of a polymeric microstructure by releasing it from the substrate, the resultant microstructure shrinks uniformly. The combination of supercritical CO_2 drying and the single-anchor supporting method is a promising way of reliably producing sophisticated 3-D micro/nano structures such as photonic crystals, master molds for micro transfer molding [22], and mechanical microparts. In addition, pinpoint fixation with an anchor makes it easy to release the resultant microstructures from the substrate. This feature is also suitable for transporting the resultant 3-D microstructures to the desired position by release and additive bonding [23]. The assembly of complex 3-D micro/nano structures plays an important role in producing practical devices consisting of various elements such as photonic, electronic and mechanical components.

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