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Corrected Article: "Ultraprecise microreproduction of a three-dimensional artistic sculpture by multipath scanning method in two-photon photopolymerization" [Appl. Phys. Lett 90, 013113 (2007)]

Dong-Yol Yang,[a] Sang Hu Park, and Tae Woo Lim
Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, South Korea

Hong-Jin Kong and Shin Wook Yi
Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 305-701, South Korea

Hyun Kwan Yang and Kwang-Sup Lee
Department of Polymer Science and Engineering, Hannam University, Daejeon 306-791, South Korea

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Ultraprecise fabrication of three-dimensional (3D) microstructures comes up to be one of the most important issues in two-photon induced photopolymerization. To date, it has been difficult to fabricate 3D microstructures without any deformation due to the surface tension between a rinsing material and solidified microstructures during the developing process: In general, the surface tension significantly affects the precision of the resulting 3D microstructures. To overcome this problem, the authors propose a simple and effective laser scanning method to reinforce the strength of 3D microstructures without loss of precision. Overall, a complex 3D artistic sculpture such as "The Thinker" was reproduced in the controlled ultraprecise form, which shows that the proposed method enables the fabrication of 3D patterns with dramatically improved precision and stability. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2692435]

The two-photon initiated photopolymerization (TPP) technology is considered a unique process, paving the way for the nano-microfabrication of three-dimensional (3D) complex microstructures and devices with a high spatial resolution reaching near 100 nm.[1–12] Following the pioneering work on TPP,[1] this technique has recently been utilized to fabricate 3D microstructures for various applications.[8–12] Additionally, new research reports on 3D applications of TPP continue to increase with higher throughput and greater functionality.[13–16] However, despite the powerful merits of TPP in 3D microfabrication, some fundamental issues still remain to be settled in terms of its practical use. The most important concern is a solution to the problem of 3D pattern deformations that result from surface tension on a developer during the developing process. However, there are few available reports concerning 3D pattern collapses. For these reasons, fundamental questions arise as to how the problem of pattern collapse can be solved or how its effects can be further minimized in 3D microfabrication. Here, we report an effective approach for the prevention of 3D pattern collapse without loss of resolution through the reinforcement of the strength of 3D microstructures, and we show the possibility of TPP for the ultraprecise fabrication of complicated 3D devices through the reproduction of a 3D artistic sculpture, "The Thinker," using the proposed method.

The cause of pattern collapse is generally known to be a cohesive force induced by the surface tension of a developing material during a drying process.[17,18] The driving force for collapse during the drying step can be expressed using the Young-Laplace equation $\Delta P = \sigma(R_1^{-1} + R_2^{-1})$; the symbols indicate the negative pressure difference (ΔP), the surface tension (σ) of the developer, and the two radii (R_1 and R_2) of surface curvature between structures.[16] A rinse material having a low surface tension for the reduction of collapse force generally costs more; therefore, a different means for increasing the mechanical strength of a pattern itself through a change of its structural parameters was sought.

Being different with the raster scanning method, only outer contours are scanned for polymerization, leaving the inside of contours as unpolymerized state by the contour scanning method (CSM). For this reason, CSM requires a relatively small number of voxels for 3D fabrication, and it is considered as a more effective 3D microfabrication based on TPP.[19] However, with CSM, the shell thickness of the solidified contours is generally very thin, approximately 150–200 nm due to a minimized voxel size that permits the precise fabrication; hence the fabricated microstructures by CSM can be deformed easily during the developing process. The mechanical strength of a structure is generally increased depending on the cube of its thickness, so the thickness of a 3D microstructure is an important factor for successful fabrication via CSM.

A simple method to thicken the contours of 3D microstructures in TPP is to increase the laser power (P) and exposure time (t) in the fabrication process. When the laser power is high, the threshold region for polymerization in a focal spot is rapidly increased, which leads to an enlargement

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[a] Author to whom correspondence should be addressed; electronic mail: dyyang@kaist.ac.kr

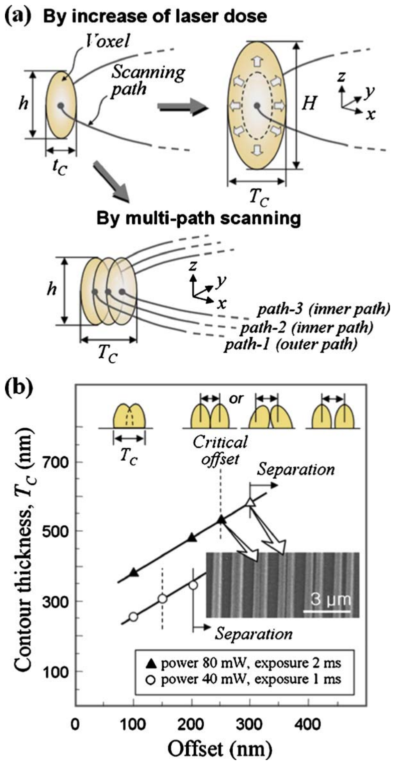

FIG. 1. (Color online) (a) Schematic illustration of the difference between two approaches to increase contour thickness: by increase of laser dose and by multipath scanning. In case of the increase of laser dose, the contour thickness is reinforced from the initial thickness, t_C to T_C, and accordingly the height of contour becomes larger (from h to H) as well. In multipath scanning, only the wall thickness is formed to T_C without increase in voxel height. (b) The variation of the contour thickness with respect to offset for two cases of laser power of 80 mW and exposure time of 2 ms and laser power of 40 mW and exposure time of 1 ms. The inserted SEM image shows the separation between two lines fabricated when the offset is larger than a critical value (in this case, 250 nm).

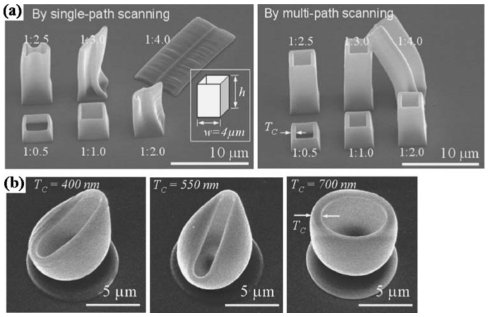

FIG. 2. SEM images of the fabricated hollow rectangular columns obtained by (a) a single-path scanning method (SPS) and a multipath scanning method (MPS). A column has a width of 4 μm and diverse heights from 2 to 16 μm. (b) SEM images of the fabricated microcups by SPS and MPS methods under the condition of laser power of 90 mW and exposure of 1 ms. The offset was 150 nm, and the contours were tried with single-, double-, and threefold-scanning paths from left to right.

of the voxel size. Moreover, when the exposure time is longer, the voxel size gradually grows depending on the exposure time, based on the radical expansion to the outside of an initially formed voxel.[20] The relationship between voxel shape, such as diameter (d) and height (h), and process parameters are given as follows:[21] $d(P,t)\propto[\ln(P^2t)]^{1/2}$ and $h(P,t)\propto[(P^2t)^{1/2}-1]^{1/2}$. Although these approaches permit the improvement of strength by enlarging the contour thickness (T_C), they are not suitable for an ultraprecise fabrication of complicated 3D microstructures due to the large voxels. Essentially, the height of a voxel is enlarged depending on the increase of a laser dose from h to H [see Fig. 1(a)], and also, an extra shape appears due to the growth of a voxel diameter, which becomes obstacles for precise fabrication in the approach of a layer-by-layer accumulation. The multipath scanning (MPS) method is an alternative for an effective and precise reinforcement of strength of 3D microstructures without the reduction of a resolution, as illustrated in Fig. 1(a). The multipath is obtained strictly from two-dimensional (2D) sliced data by using a Voronoi diagram.[22] After constructing the dividing lines in an outer contour, offsetting is carried out to generate a new interior contour by connecting intersection points on the dividing vectors. From the reiteration of this procedure, three or more scanning paths can be generated precisely in the interior of sliced data with the controlled distance of offset. Therefore, the target thickness of a contour can be obtained readily by controlling the offset distance between contours and the number of inner contours in the MPS. For evaluating the optimal offset between contours, a variation in the reinforced contour thickness according to various offsets was investigated in case of double-scanning paths [see Fig. 1(b)]. When an offset was more than 250 nm, a geometrical separation between contours occurred, which indicates that two adjacent contours were not joined together; therefore, the innercontour does not contribute to the improvement of the strength of microstructures. From these results, the offset of approximately 200 nm is found to be a reasonable value in the given laser dose (laser power of 80 mW and exposure time of 2 ms). However, the optimal offset is not a fixed value but varies depending on the exposed laser dose.

Preliminary examples, six hollow rectangular columns having various aspect ratios of 0.5, 1.0, 2.0, 2.5, 3.0, and 4.0, respectively, were fabricated using single-path scanning (SPS) and double-path scanning by the MPS method, in order to verify the effects on the enhancement of strength by the increase of T_C in a 3D microfabrication. Each was fabricated under the identical conditions of the laser power of 80 mW and the exposure time of 2 ms, and the offset used in the MPS method was set at 200 nm. In the results shown in Fig. 2(a), the maximal aspect ratio of a column created completely by the SPS method, of which the thickness was nearly 360 nm, was found to be 1.0; however, the other columns having higher aspect ratios were distorted during the developing process due to their low mechanical strength. However, when a double-scanning path by the MPS method was utilized, the columns with the T_C of 560 nm and aspect ratio limited to 3.0 preserved their shapes precisely without distortion after the developing process. To show explicitly the relationship between the strength and the thickness of a hollow rectangular column, a dimensionless shape factor (K) was defined. The K can be obtained using the geometrical parameters of the driving force (F) for collapse derived from the Young-Laplace equation, as $K=[[2(a+b)]^2/ab](h/c)$. Here, c is a characteristic length of the section (in this case, let $c=\sqrt{a^2+b^2}$). The K is proportionally dependent on the aspect ratio of a structure and the arc length of an outer contour. However, in the fabrication of hollow rectangular columns, the completely created columns having a maximum aspect ratio (1.0 for SPS and 3.0 for MPS) show the K values as 11.32 and 33.97, respectively. This signifies that the strength of the column patterns is reinforced three times by

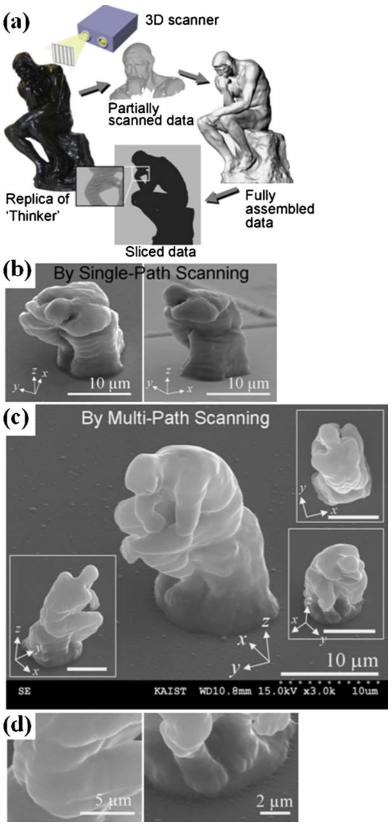

FIG. 3. (Color online) (a) Procedures of creation of CAD data using a 3D scanner based on white-light interferometer: original replica of "The Thinker," partially scanned 3D points data, fully assembled STL data, and 2D sliced data using a homemade program (the inset of sliced data is partially magnified data). The total number of layers is 667 layers. (b) SEM images of failed "micro-Thinker" (by single-path scanning method) due to the flow and surface tension of a developing material. (c) SEM images of reproduced micro-Thinker by double-scanning path. The insets are the same micro-Thinker with various view angles, and the scale bars are 10 μm. (d) Partially magnified images of micro-Thinker: skins displaying muscles, two feet, and toes can be found.

the increase of thickness from 360 to 560 nm (only a 66% increase) via MPS. As shown in Fig. 2(b), when a double scanning is not enough to preserve the exact shape of a microcup, three and more scanning paths can be utilized to improve its strength. Thus, it is proven that the MPS method is effective in increasing the strength of 3D microstructures without additional efforts. The photocurable resin used in this work was a mixture of a commercially available resin, SCR500 (Japan Synthetic Rubber) and the two-photon absorbing chromophore (0.1 wt %).[14,20]

With the aim of evaluating the usefulness of the MPS method, a more complex 3D microstructure (micro-Thinker) was fabricated. The original sculpture of The Thinker (Le Penseur) with a height of 186 cm was designed and created by the artist Rodin in 1880. Since his creation, this may be the first trial for the fabrication of The Thinker in microsize that includes nanoscale details. As depicted in Fig. 3(a), the 3D computer-aided design (CAD) data of this artistic workpiece were obtained by scanning a replica of the sculpture made under license. Following this, the scanned 3D coordinates were transformed into stereolithography (STL) data, and it was sliced with a uniform slicing thickness of 30 nm along the z axis to generate a 2D layer data set for accumulation. When the SPS method was utilized for this reproduction, all trials failed in the precise fabrication during the developing process due to the low strength of the structure [see Fig. 3(b)]. For the precise and stable fabrication of the "micro-Thinker," double scanning via the MPS method was applied with an offset of 150 nm, which was an optimal value under the laser power of 40 mW and exposure time of 1 ms/voxel. The micro-Thinker was created, scaled down to 1:93 000 as compared with the original sculpture by Rodin. Figures 3(c) and 3(d) show scanning electron microscope (SEM) images of the fabricated micro-Thinker via MPS where the posture, appearance, and even the fine details of the muscles can be noted.

In summary, for overcoming the problem of the 3D pattern collapse, we have proposed and demonstrated the MPS method, with the intention of enhancing the physical strength of the 3D microstructures. With the MPS method, the contour thickness of a 3D microstructure is controlled simply but effectively using multipaths and offsets without loss of resolution, which enables a precise 3D microfabrication. Using the MPS, a reproduction of The Thinker, as a complex example, was created precisely at 20 μm in height through the use of the actual-size 3D data of the original The Thinker. The finding of a relationship between the physical strength and 3D pattern collapse shows the importance of the precise fabrication of complex 3D microstructures or devices, and the MPS method improves the ability of TPP as a promising 3D precise microfabrication tool.

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