INTERNATIONAL JOURNAL OF PRECISION ENGINEERING AND MANUFACTURING Vol. 16, No. 11, pp. 2427-2431 OCTOBER 2015 / 2427
DOI: 10.1007/s12541-015-0312-x ISSN 2234-7593 (Print) / ISSN 2005-4602 (Online)

Direct Fabrication of Nano-Wrinkled 3D Microstructures using Fitfully Accumulated Two-Photon Polymerization

Tae Woo Lim[1,2,#] and **Dong-Yol Yang**[1]

1 Korea Advanced Institute of Science and Technology, 291, Daehak-ro, Yuseong-gu, Daejeon, 34141, South Korea
2 The Institute of Display Research, Samsung Display, 84, Nongseo-ro, Giheung-gu, Yongin-si, Gyeonggi-do, 17113, South Korea
Corresponding Author / E-mail: twalways.lim@gmail.com, TEL: +82-42-350-3254, FAX: +82-42-350-5214

KEYWORDS: 3D microstructure, Wrinkling, Two-photon stereolithography

In this paper, we study the accumulated polymerization effect in the two-photon stereolithography process and its application. In the two-photon stereolithography process, less-polymerized material by insufficient dosing is generally removed by rinse material. The less-polymerized region of a voxel transforms into a fully-polymerized region in the voxel-by-voxel scanning process due to the accumulated dose. The parametric study of the accumulation effect for the widths of a voxel and a line pattern is investigated. Generally, accumulated polymerization from the scanning process has an influence on the increase of the pattern width smoothness of the space between each voxel. At a dose that is smaller than the dose generating a minimum size voxel, stochastic nano-patterns are generated by fitfully accumulated two-photon polymerization. Using the method of fitfully accumulated two-photon polymerization at a small dose, 3D micro-structures with nano-patterns are directly fabricated.

Manuscript received: July 23, 2015 / Revised: September 6, 2015 / Accepted: September 14, 2015

1. Introduction

Recent research works have shown the merits of nano/micro hierarchical structures, micro-structures with nano-structures on their surfaces, in diverse applications such as micro-sensors, optical devices, and micro-fluidic devices.[1-4] The large surface area to volume ratio stemming from the nano-structures increases the sensitivity of the micro-sensors, and the periodic sub-wavelength surface structures provide antireflection surfaces that are effectively applied to optical devices requiring high transmission. The superhydrophobicity induced by nano/micro hierarchical structures shows that wettability is strongly dependent on the surface geometry as well as on the chemical properties of a material. For the fabrication of nano/micro hierarchical structures, various strategies have been developed: a templated self-assembly process, a two-step photolithography process, a sequential process of photolithography and interference lithography, and a sequential process of photo lithography for microstructures and chemical or physical etching asperating of their surfaces.[5] However, relatively few studies have been devoted to the fabrication of nano-patterned 3D micro-structures.

A two-photon stereolithography process is one of the promising processes for direct 3D fabrication that has a resolution beyond the deflection limit of the laser beam.[6-8] The resolution of the process, which is based on a voxel-by-voxel or layer-by-layer stacking process, is determined by the geometry of a voxel (i.e. unit volume pixel). A lot of investigations into the process parameters for unit voxels have been conducted from analytical and experimental view points. However, the resolution in the beam direction of progress, the longitudinal length of a voxel, has not been sufficient for nano-scale patterning. In addition, the smoothness occurring in a voxel-by-voxel scanning process interrupts the nano-scale patterning on the surface of the 3D structures.

Until now, the influence of scanning parameters on the resolution of unit lines has received far less rigorous analysis. The parameters in the scanning process have been studied mainly for improvement of the effectiveness of the scanning process, with research having been done in such areas as reducing time and strengthening the structures. When the voxels are stacked densely for the smooth surface of 2D/3D microstructures, the resolution (i.e., width and height) of unit lines composing the contours can be affected by the accumulation of doses.

In this work, we investigate the effect of accumulated dose on the two-photon stereolithography process. The characteristics of accumulated two-photon polymerization in a voxel-by-voxel scanning process are studied. Of special interest is the fact that stochastic nano-patterns were generated by fitfully accumulated two-photon

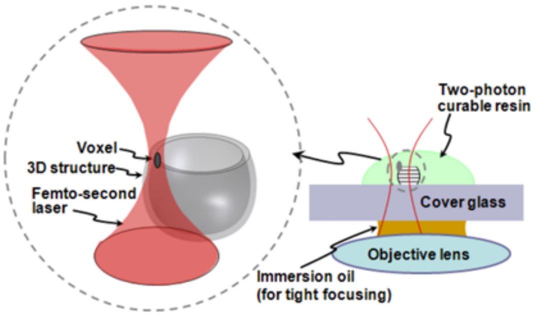


Fig. 1 Schematic illustration of the two-photon stereolithography process. 2D and 3D microstructures are fabricated through a voxel-by-voxel stacking process using Galvano mirrors and a layer-by-layer stacking process using a piezoelectric stage, respectively

polymerization at a dose that is smaller than the dose needed to generate a voxel of a minimum size. Using the method of fitfully accumulated two-photon polymerization, 3D micro-structures with nano-patterns are directly fabricated.

2. Experimental Details

2.1 System and materials

A femtosecond laser system with related optical instruments was employed in the TPS procedure. A Ti:Sapphire laser mode-locked at 80 MHz and with a 780 nm wavelength (with pulses of less than 100 fs) was utilized as the light source. The laser was closely focused into the volume of the resin using a high numerical aperture (NA: 1.4, with immersion oil) objective lens. The dose for the photocuring reaction at each voxel was controlled by the process parameters of the laser power and the exposure time.

A voxel-by-voxel stacking process was performed by a beam-scanning method using Galvano mirrors. The overlapping distance was set at 30 nm, considering the voxel size of 100 nm scale. Since the focus moves almost immediately, with a response time smaller than 0.1 ms, total doses were controlled by laser power and exposure time for each position. The interval between each exposure was controlled using an optical shutter of Galvano mirror type. 3D microstructures are fabricated through a layer-by-layer stacking process using a piezoelectric stage, as shown in Fig. 1. The two-photon curable resin used in this work was a mixture of SCR500 (JSR) and photosensitizers (0.1 wt %); for effective TPA, a two-photon chromophore (BOPF-TP) was used. Its chemical formula is C81H80N2O2, and it consists of 4,4’-(1E,1’E)-2.2’-(9,9-bis(4-(octyloxy(phenyl)-9Hflourene-2,7-diyl)bis (ethene-2,1-diyl)bis(N,N-diphenylaniline).[6]

2.2 Voxel and scanning process

In the two-photon stereolithography process, the radicals are generated by two-photon absorption, and then they combine with monomers to initiate a chain polymerization reaction. The density of the radicals becomes higher in proportion to the square of photon intensity as they approach the center of the focus of a laser beam with Gaussian distribution. When a unit volume pixel (i.e., voxel) is generated by a single exposure at a point, three different regions are defined according to the density of the radicals and the oxygen, as illustrated in Fig. 2(a): a fully-polymerized region (FPR) with high-weight polymers (solid state); a less-polymerized region (LPR) with low-weight polymers (solid-liquid mixed state); and a non-polymerized region (NPR, liquid state). After the scanning process, the remains in the less-polymerized region and the non-polymerized region are generally eliminated by using a rinsing material in the development process. However, the characteristic regions defined in a single exposure change during the voxel-by-voxel scanning process due to the increase of radical density in the LPR stemming from the accumulated dose. When line patterns are fabricated by overlapping the voxels, therefore, the line width becomes larger than the voxel size due to the accumulated polymerization in the LPR, as shown in Fig. 2(b).

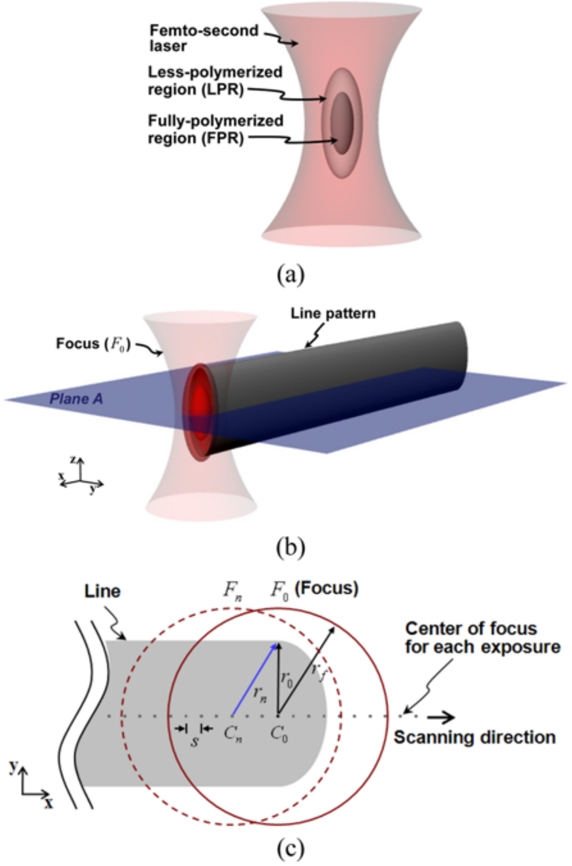


Fig. 2 Schematic illustrations of (a) three different regions (a fully-polymerized region with high-weight polymers, a less-polymerized region with low-weight polymers, and a non-polymerized region) which are generated by a single exposure at a point, and (b) a line pattern with the width larger than the width of a voxel owing to the accumulated polymerization. (c) The line pattern and focuses of the cross-section in the plane A of (b)

Fig. 2(c) shows the relative position of a line pattern and corresponding foci. C_n is the center of the focus (F_n). In a single exposure, the probability of two-photon curing in the fabrication of a voxel is characterized by the following equation, since the probability of two-photon curing depends on the exposure time (t_e) and on the square of the intensity and exposure time.

$$\psi \propto (H(0)\exp(-2r^2/r_t^2))^2 \cdot t_e \qquad (1)$$

where r_f, r and $H(0)$ are the radius of the focus, the distance from the center of the focus and the beam intensity at the center axis in the focus plane, respectively.

In Fig. 2(c), B_0 is the point where the contour of a line intersects the line passing through C_0 in a normal direction of the scanning direction, at which the intensity at the distance of r_n from the center (C_n) for each focus (F_n) is exposed. When the laser beam is exposed with the unit moving distance of S, the probability of two-photon curing at B_0 is increased as accumulated by each exposure, of which r_n is smaller than r_t. The accumulated probability at the point B_0 becomes the threshold probability ψ_{th} (the minimum probability for two-photon curing), as given in Eq. (2).

$$\psi_{th} \propto \alpha \sum_{n=-\gamma}^{\gamma} [H(0)\exp(-2((d/2)^2+(ns)^2)/r_t^2)]^2 \cdot t_e \qquad (2)$$

where d is the diameter of the line pattern. Therefore, a much larger width of line pattern compared to a single voxel is estimated.

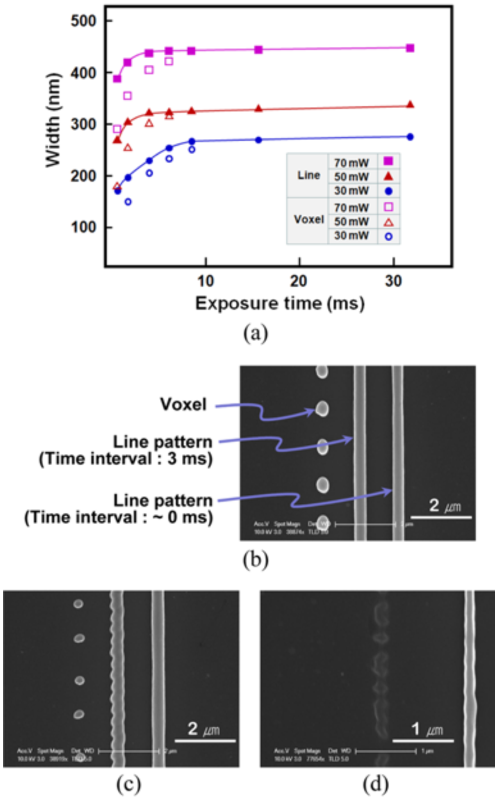
However, the time interval between each exposure on the line pattern is an important parameter in the voxel-by-voxel stacking process considering the chemical reaction of radicals and radical quenching materials. Present oxygen and other radical quenching materials combine with initiated radicals and convert them to nonradical species or radicals with very low reactivity that are not able to undergo propagation. The radical quencher concentration in a resin changes the threshold for polymerization because the polymerization reaction will not propagate until the number of quenching molecules is significantly reduced. While accumulated polymerization occurs in the voxel-by-voxel stacking process, the concentration of quenching materials in the LPR changes due to diffusion. Therefore, the line width and the roughness of a line pattern would be influenced by the time interval. In this work, the difference between the widths of a voxel and line pattern according to the laser power and exposure time was experimentally compared. In addition, line patterns were fabricated with and without time intervals to investigate the effect of the time interval.

3. Results and Discussion

3.1 Accumulated two-photon polymerization

Voxels and two types of line patterns (i.e. without time interval and with time interval of 3 ms) were fabricated using the same process conditions of unit dose: laser power from 30 to 70 mW and exposure time from 1 to 32 ms. The line widths for both types were almost the same as those in the overall conditions, and the time interval dominantly influenced just the roughness in the conditions of small doses.

Fig. 3(a) shows the widths of voxels and line patterns (without time interval). Fig. 3(b)~3(d) shows the SEM images of the voxels and line patterns. The widths of the voxels were almost the same as the widths of the line patterns in the condition of long exposure time (longer than 16 ms) as shown in Fig. 3(b). As the exposure time is reduced, the difference between the widths of a voxel and a line pattern became larger as shown in Fig. 3(c). The width of a line was about 1.5 times larger than that of a voxel at the exposure time of 1 ms. In the conditions of low laser power (30 mW) and short exposure time (1~2 ms), a uniform line pattern was obtained though no voxels were fabricated as shown in Fig. 3(d). It is thought that only LPR exists during a single exposure in that condition and the LPR transforms into FPR due to the accumulated dose. These characteristics mean that the variation of the characteristic regions (FPR, LPR, NPR) occurs in a manner significantly dependent on the exposure time, and that the relative area of the LPR is large at a small dose.



(a)

(b)

(c) (d)

Fig. 3 (a) The widths of voxels and line patterns (without time interval). (b)~(d) SEM images of voxel (left), line patterns by voxel scanning method (middle) and continuous scanning method (right). Laser power and exposure time were (b) 70 mW and 32 ms, (c) 70 mW and 2 ms, and (d) 30 mW and 1 ms, respectively. The line patterns fabricated without time interval are uniform in all conditions. However, the voxels and the line patterns fabricated with the time interval of 3 ms are non-uniform at small exposure time. Especially at a small dose of 30 mW and 1 ms, a voxel is not fabricated and stochastic line pattern is fabricated by the accumulated polymerization

However, the characteristic of the accumulation effect was dependent on the time interval. In the case of a line pattern fabricated with a time interval of 3 ms, two characteristic groups of conditions were observed. In the conditions of long exposure times larger than 4 ms, smooth line patterns were fabricated and the widths were not dependent on the time interval. At a small exposure time, significantly different line patterns were observed according to the presence of the time interval, though the total doses for each type are commensurate. The line patterns that were fabricated with the time interval of 3 ms had very rough surfaces, as shown in Fig. 3(c). The abrupt increase of the roughness at short exposure time is not due to small voxel width compared to overlapping distance but, rather, is due to non-uniform accumulated polymerization. For example, the line pattern in the condition of 70 mW, 1 ms is more rough than the line pattern in the condition of 50 mW, 32 ms though the voxel width in the condition of 70 mW, 1ms is larger than the voxel width in the condition of 50 mW, 32 ms, as shown in Fig. 3(b) and 3(c). The roughness increases at a very small dose where relatively large area of LPR is generated and the significant variation of the characteristic regions (FPR, LPR, NPR) occurs. The increased non-uniformity results in stochastic patterns, as shown in Fig. 3(d). Therefore, the roughness can be controlled through the scanning parameters as well as through the voxel distance, and it can be used in direct fabrication of 3D hierarchical structures with higher resolution of the voxel size.

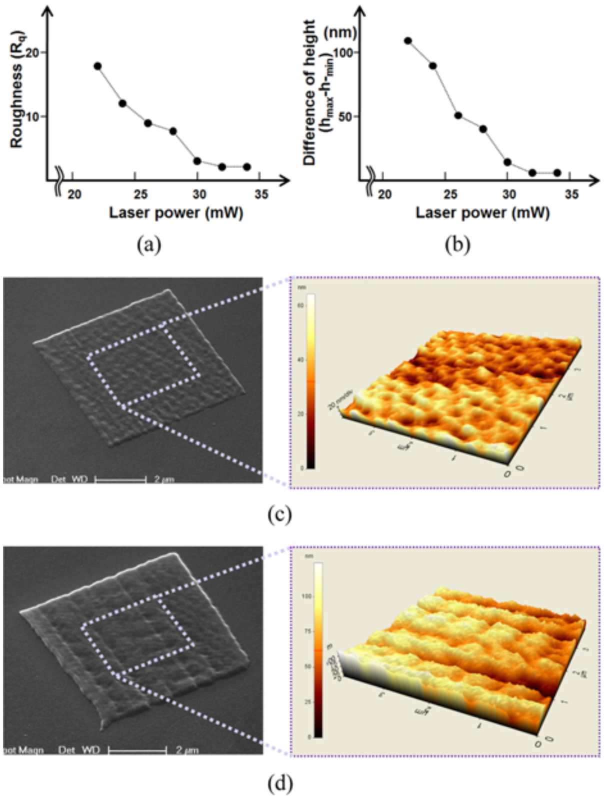
3.2 Nano-wrinkled surface by fitfully accumulated polymerization

Square plates were fabricated using the voxel-by-voxel scanning method for the observation of the surface roughness at the low laser dose as shown in Fig. 4. Since the surface becomes very thin at the low laser power, three layers with a layer distance of 100 nm were piled up for the closed surface. The scanning parameters of the voxel distance and the line distance were set at 30 nm. The exposure time and the interval were set at 1 ms and 3 ms, respectively. The laser power was set starting from 22 mW, which is the minimum value for generating plates, to 34 mW, which is the minimum laser power generating voxels.

Fig. 4(a) and 4(b) show the surface roughness (root mean square average) and difference of the maximum and minimum heights of the surfaces according to the laser power, respectively. The surface is almost flat for laser power over 30 mW due to the smoothness induced by the accumulated polymerization between the voxels. However, the surface roughness of the plates increases sharply as the laser power decreases below the laser power of 30 mW, as shown in Fig. 4(a). In addition, the pitch size as well as the surface roughness is strongly dependent on the laser power, as shown in Fig. 4(b). The pitch size of the wrinkled surfaces becomes larger at the smaller laser power. That is, the roughness and the pitch size are relatively tunable in the process of fitfully accumulated two-photon polymerization though the shape of the nano-patterns is not controllable. Therefore, the method of fitfully accumulated two-photon polymerization can be useful for the direct fabrication of 3D microstructures with stochastic nano-patterns.

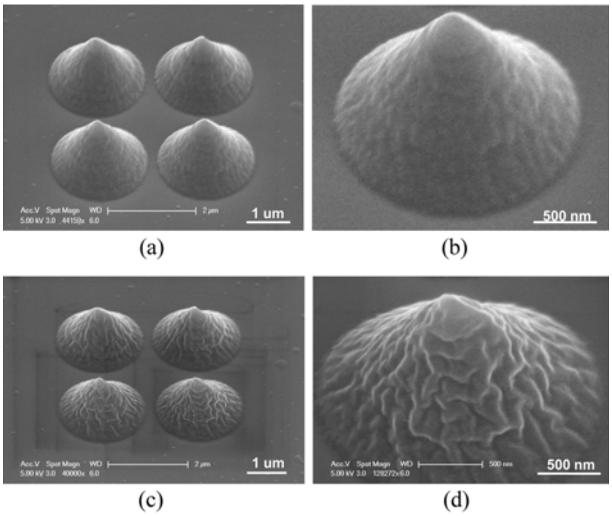
3.3 3D micro-structures with nano-wrinkles

Cone array patterns were fabricated using the method of the fitful accumulation process as an example of 3D nano/micro hierarchical structure. Contour scanning type, which is generally used in a scanning process to reduce the fabrication time, was used. The multi-path scanning method was used to prevent any non-fabricated area on the surface of the structure and any distortion stemming from the rinse material during the developing process.



(a) (b) (c) (d)

Fig. 4 (a) The surface roughness (root mean square average) and (b) the difference of the maximum and minimum heights of the surfaces according to the laser power. The laser power was set from 22 mW to 34 mW. SEM and AFM images of the square plates fabricated at the laser powers of (c) 22mW and (d) 26mW



(a) (b) (c) (d)

Fig. 5 SEM images of cone structures which are fabricated at the laser powers of (a), (b) 30 mW and (c), (d) 24 mW

Fig. 5 shows the SEM images of the fabricated structures at the laser powers of 30 mW and 24 mW. Voxel distance was set at 30 nm; three contours were scanned with a distance of 100 nm for each layer; and layer distance was set at 30 nm. The exposure time and time interval were set at 1 ms and 3 ms, respectively. It was possible to fabricate a 3D nano/micro hierarchical structure directly, as shown in Fig. 5(c) and 5(d). A nano-wrinkled surface was observed at a low laser power. Generally, in the case of the deformation due to the rinse material, the geometry of the structures is distorted. However, the fabricated structures shown in Fig. 5(a)~5(b) show the same geometry of cone shape. Therefore, it is confirmed that wrinkling occurs not due to the deformation of the structure by the surface tension of the rinse material in the developing process, but due to the non-uniform polymerization in the local area.

4. Conclusions

In this work, we studied the effect of accumulated polymerization in the two-photon polymerization process. The line patterns, which were fabricated by the voxel-by-voxel scanning process, showed almost the same widths of voxels at the large exposure time and laser power. When the exposure time was reduced below 10 ms, the difference between the widths of the voxels and the line-patterns became larger. The increased width of the lines was about 1.5 times that of the voxels at the exposure time of 1 ms. The different characteristics of the line patterns according to the presence of a time interval of 3 ms were observed below the exposure time of 4 ms. At low laser power and exposure time, at which less polymerization is generated by a single exposure, stochastic nano-patterns were generated by fitfully accumulated two-photon polymerization. In addition, the roughness and the pitch size are relatively tunable, though the shape of the nano-patterns is not controllable. Using the method of fitfully accumulated two-photon polymerization, it was possible to fabricate a 3D nano/micro hierarchical structure in a single process using the fitful accumulation process.

REFERENCES

1. Li, W., He, D., and Bai, J., “The Influence of Nano/Micro Hybrid Structure on the Mechanical and Self-Sensing Properties of Carbon Nanotube-Microparticle Reinforced Epoxy Matrix Composite,” Composites Part A: Applied Science and Manufacturing, Vol. 54, pp. 28-36, 2013.
2. Kang, M.-S., Joo, S.-J., Bahng, W., Lee, J.-H., Kim, N.-K., and Koo, S.-M., “Anti-Reflective Nano- and Micro-Structures on 4H-SiC for Photodiodes,” Nanoscale Research Letters, Vol. 6, No. 1, pp. 1-4, 2011.
3. Cha, T.-G., Yi, J. W., Moon, M.-W., Lee, K.-R., and Kim, H.-Y., “Nanoscale Patterning of Microtextured Surfaces to Control Superhydrophobic Robustness,” Langmuir, Vol. 26, No. 11, pp. 8319-8326, 2010.
4. Jo, H.-B., Choi, J., Byeon, K.-J., Choi, H.-J., and Lee, H., “Superhydrophobic and Superoleophobic Surfaces using ZnO Nano-in-Micro Hierarchical Structures,” Microelectronic Engineering, Vol. 116, pp. 51-57, 2014.
5. Lee, C. H., Jung, P. G., Lee, S. M., Park, S. H., Shin, B. S., et al., “Replication of Polyethylene Nano-Micro Hierarchical Structures using Ultrasonic Forming,” Journal of Micromechanics and Microengineering, Vol. 20, No. 3, Paper No. 035018, 2010.
6. Yang, D.-Y., Park, S. H., Lim, T. W., Kong, H.-J., Yi, S. W., et al., “Corrected Article:”Ultraprecise Microreproduction of a Three-Dimensional Artistic Sculpture by Multipath Scanning Method in Two-Photon Photopolymerization” Applied Physics Letters, Vol. 90, No. 7, Paper No. 079903, 2007.
7. Lim, T. W., Son, Y., Yang, D.-Y., Kong, H.-J., and Lee, K.-S., “Selective Ablation-Assisted Two-Photon Stereolithography for Effective Nano-and Microfabrication,” Applied Physics A, Vol. 103, No. 4, pp. 1111-1116, 2011.
8. Lim, T. W., Son, Y., Jeong, Y. J., Yang, D.-Y., Kong, H.-J., et al., “Three-Dimensionally Crossing Manifold Micro-Mixer for Fast Mixing in a Short Channel Length,” Lab on a Chip, Vol. 11, No. 1, pp. 100-103, 2011.