Fabrication of Nano-precision PDMS Replica Using Two-photon Photopolymerization and Vacuum Pressure Difference Technique

Sang Hu Park, Tae Woo Lim, Dong-Yol Yang, Hong Jin Kong,† Ran-Hee Kim,‡ Kyoung-Soo Kim,‡ and Kwang-Sup Lee‡,*

Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
†Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
‡Department of Polymer Science and Engineering, Hannam University, Daejeon 306-791, Korea
Received March 25, 2004

Key Words : Two-photon polymerization, 3D microfabrication, Vacuum pressure difference, PDMS replica

It is undoubtingly believed that a revolution in miniaturization, in the field of microelectromechanical systems (MEMS), nano- and biotechnology etc., is under way. Multi-dimensional micro structures are fabricated by mainly two methods, such as laser rapid prototyping and lithography. Since it is a process that builds features layer by layer, rapid prototyping is a very slow process and is difficult to fabricate smaller objects.[1] On the other hand, the conventional lithographic technique requires an etching process that limits to build complicated figures. Recently, two-photon photopolymerization has attracted increasing attention as an innovative tool for micro- and nanofabrication due to its intrinsic multi-dimensional fabrication capability and sub-diffraction limited spatial resolution.[2,3] Two-photon absorption probability strongly depends quadratically on excitation beam intensity confining the process at the vicinity of the focus. Thus, by using two-photon excitation one can activate chemical and physical processes only for a tightly focused spot in the bulk medium with high spatial resolution. This substantial increase in structural complexity was only possible by using chromophores with high two-photon absorption cross-sections (σ). It is apparent that the synthesis of chromophores with even larger two-photon activity will unleash improvements in the capability and performance of a variety of two-photon absorption application including multi-dimensional nano- and microfabrication.

In this paper, we describe the synthesis of newly designed highly efficient two-photon chromophore and fabrication of three-dimensional nano-precision PDMS replica using vacuum pressure difference technique (VPDT) and two-photon photopolymerization. The two-photon absorbing chromophore **3** with long alkyl chain for improved solubility was synthesized using palladium catalyzed coupling reaction designed by Heck[4] from compound **1** and **2**. The compound **1** was obtained from Vilsmeier-Haack fomylation of triphenylamine followed by Wittig raction, and the 2,7-dibromofluorene was reacted with excess amount of ethylhexylbromide to give compound **2**. The resulting two-photon chromophore **3** was extensively purified before use as a light sensitizer/photoinitiator in two-photon photopolymerization.[5] The optical transparency of a chromophore at the wavelength of operation is crucial for successful 3D microfabrication with two-photonpolymerzation. As shown in steady-state absorption and emission spectra (Figure 1), the two-photon chromophore **3** has no absorption beyond 475 nm making itself ideal for two-photon application at the wavelength of 780 nm which is wavelength of our interest. Two-photon absorption cross-section of chromophore **3** at 780 nm was found to be $\sigma = 4.7 \times 10^{-48}$ cm^4s/photon with peak absorption at 411 nm.

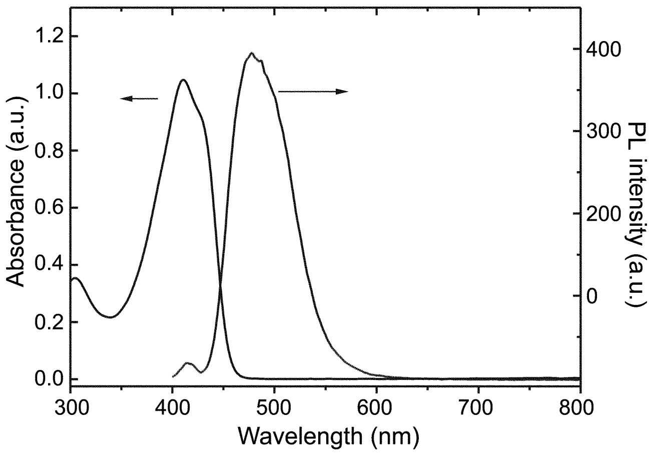
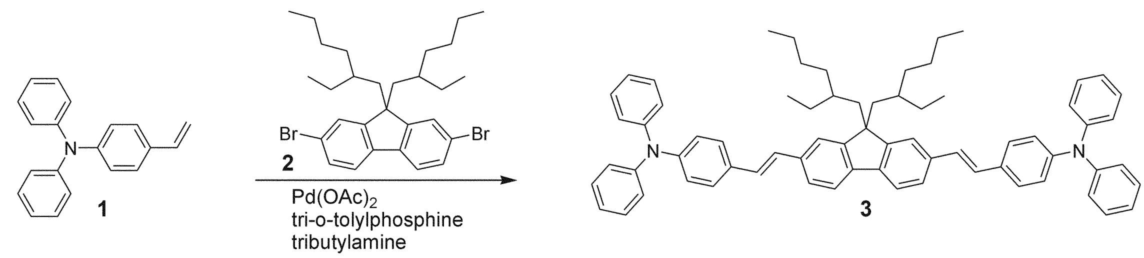


Figure 1. Steady state absorption and emission of two-photon chromophore 3.

As a laser system, a 780 nm wavelength mode-locked Ti:sapphire laser with 80 MHz repetition and less than 100 femtosecond pulse width was used for microfabrication. SCR resin which consists of urethane acrylate monomers and oligomers was mixed with two-photon photoinitiator (0.1 wt%). Then, laser was focused by a 1.24 NA (numerical aperture) objective lens. The laser focal spot was scanned in three dimensions by computer controlled Galvano-scanner with 24 nm resolution for *x* and *y* and by pizezoelectric *z* stage with 100 nm resolution. A micro structure was obtained by raster graphics type voxel matrix scanning (VMS) scheme, which is now proposed to produce easily a 2D micro-object from a bitmap format figure.[6] To get an insight

*Corresponding Author. Fax: +82-42-626-8841, e-mail: kslee@hannam.ac.kr



Scheme 1

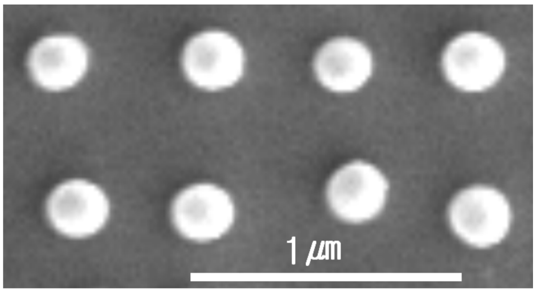


Figure 2. SEM image of fabricated voxels in the condition of laser power, 5mW and exposure time, 2 ms.

into facility of VMS scheme, we have prepared array of voxels with 200 nm diameter. The size of voxel is dependent on laser power and irradiation time. Figure 2 shows the voxels fabricated with 5 mW laser power and 2 ms of irradiation time. The fabricated 2D micro-object is shown in Figure 3b along with its original bitmap image (Figure 3a). This clearly shows that the VMS technique is capable of transferring a bitmap image into a nearly identical 2D micro-object with 200 nm resolution by two-photon photopolymerization. After successful fabrication of 2D micro-object we were interested in preparing polydimethylsiloxane (PDMS) mold which is widely used to make microstructures for bio-MEMS. A 10 : 1 mixture of the PDMS prepolymer, Sylgard 184A and the curing agent, Sylgard 184B was placed in a vacuum chamber and degassed for 30 min. The mixture was poured onto the micro-object substrate while maintaining vacuum, then vacuum was released. This later release of vacuum will assure filling of the small voids which may be present between PDMS and micro-object. Generally, it is not necessary to perform such a process under the vacuum environment when one wants to make PDMS molds with several tens of micro scale. However, even the smallest void between PDMS and micro-object will deform the resulting PDMS in the process of fabricating molds with higher precision. The PDMS mold was easily peeled-off from micro-object after curing the prepolymer for 2 hour at 70 ^{o}C (Figure 3c). Before making the PDMS replica using PDMS mold, a thin layer of gold (30 nm) was deposited on the micro-object to insert surface incompatibility. As shown in Figure 2d, this technique allowed us to replicate the identical structure from the micro-object fabricated with two-photon photopholymerization and PDMS mold.

In summary, we have designed and synthesized highly active two-photon chromophore for two-photon excitation. Using this chromophore as a light sensitizer/photoinitiator the 2D micro-object was successfully fabricated by two-photon induced photopolymerization with voxel matrix scanning (VMS) scheme. The vacuum pressure difference technique facilitates fabrication of a PDMS mold from an obtained micro-object, and the nano-precision PDMS replica was prepared from the PDMS mold.

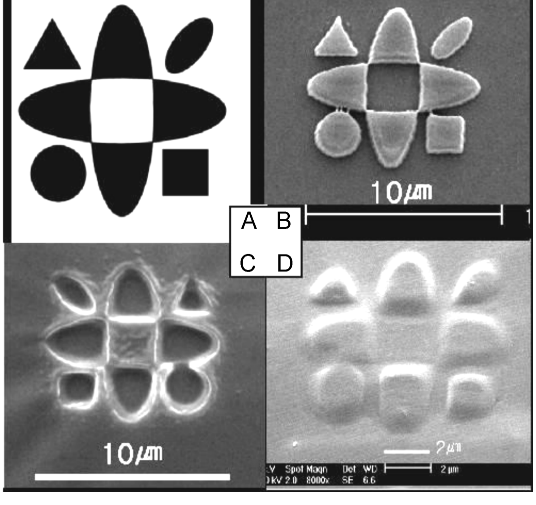


Figure 3. (A) Bitmap image, (B) 2D micro-object fabricated by two-photon photopolymerization, (C) PDMS mold, (D) PDMS replica.

Acknowledgments. This research was funded by Center for Nanoscale Mechatronics & Manufacturing of 21st Frontier Project Supported by Ministry of Science & Technology in Korea. K.-S. Lee, one of us, is also gratefully acknowledged R&D Program for NT-IT Fusion Strategy of Advanced Technologies for their financial support.

References

1. Maruo, S.; Kawata, S. *J. Micro Electro Mechanical Systems* **1998**, *7*, 411.
2. Kawata, S.; Sun, H.-B.; Tanaka, T.; Takada, T. *Nature* **2001**, *412*, 667.
3. Sun, H.-B.; Takada, T.; Kim, M.-S.; Lee, K.-S.; Kawata, S. *Appl. Phys. Lett.* **2003**, *83*, 1104.
4. Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133.
5. ^{1}H-NMR ($CDCl_3$): 7.1-7.7 (m, 34H), 7.1 (d, 4H), 2.1 (m, 4H), 0.5-1.0 (m, 30H), FT-IR (KBr pellet, cm^{-1}): 2950-2800 (alip. C-H), Elemental Analysis: C 89.18, H 7.81, N 3.01 cal. C 89.21, H 7.80, N 2.99 found.
6. Yi, S. W.; Lee, S. K.; Kong, H. J.; Yang, D.-Y.; Park, S.; Lime, T.; Kim, R. H.; Lee, K.-S. unpublished results.