Preparation and Two-Photon Lithography of a Sulfur Containing Resin with High Refractive Index

Yasuharu Murakami*, Christopher A. Coenjarts**, and Christopher K. Ober**

**Hitachi Chemical Co., Ltd., Research and Development Center,
13-1 Higashi-cho 4-chome, Hitachi-shi, Ibaraki-ken, 317-8555 JAPAN*

***Cornell University, Materials Science & Engineering,
Bard Hall, Ithaca, NY, 14853-1501 USA*

A photonic crystal structure made with a thiirane resin (BT), which has high refractive index (1.68), has been prepared by two-photon lithography. This new brominated thiirane was prepared by the reaction of brominated epoxy (BE) and potassium thiocyanate. An iodonium salt/coumarin system was used as a photoacid generator for two-photon lithography. BT had a higher reactivity in this system than BE. A photonic crystal structure which is composed of a five layer “woodpile” structure was obtained using the BT/iodonium salt/coumarin resin.

Keywords: Micro-stereolithography, Two-photon lithography, Photonic crystal, High refractive index

1. Introduction

Micro-stereolithographic techniques [1] have attracted considerable interest for the fabrication of three-dimensional (3D) micro-structures. The type of micro-stereolithography which affords the highest resolution is two-photon lithography, [2] having a resolution below the diffraction-limit. The use of this technique enables one to create various micro- or submicro-structures, [2] such as micro-optics, micro-fluidics, micro-electro-mechanical systems (MEMS), and optical data storage devices.

The fabrication of 3D photonic crystals [3] with micro- and sub-micrometer lattice constants, which have a periodic variation of refractive index on a length scale comparable to the desired wavelength of operation, are a great technical challenge because they are difficult to fabricate by conventional fabrication techniques. Micro-stereolithography, especially two-photon lithography, offers interesting possibilities for the fabrication of 3D photonic crystals because of its high resolution and the diversity of structures which can be obtained.

While there are several reports on the fabrication

of 3D photonic crystals by two-photon lithography, [4] no reports on 3D photonic crystals with full photonic band gaps [3] have been reported because the photopolymers used as structural materials have relatively low refractive indexes (ca. 1.5). In order to produce a photonic crystal having a full band gap, the refractive index of the material which is used to prepare the photonic crystal structure needs to be extremely high. For example, a full band gap in diamond structure is achieved by using a structural material of which refractive index is greater than ca. 2.0 [4c] if the surrounding medium is air.

In this work, we focused on thiiranes, three membered cyclic sulfides, as a part of a photodefinable resin because these are expected to have not only high reactivity in various types of polymerizations, [5] such as cationic polymerization, polyaddition, and living polymerization, but also high refractive index due to the presence of a sulfur atom in the structure. In addition, in order to obtain extremely high refractive index (>2.0), thiirane resins can be an excellent matrix for the polymer nanocomposite with inorganic filler such as TiO_2 .

Although the use of epoxy resins for 3D lithography has been demonstrated, to the best of our knowledge, there has not been any report of using thiirane resins for 3D lithography.

In this paper, we describe the fabrication of micro-structures and a micro-ordered 3D photonic crystal structure by two-photon lithography with a thiirane resin derived from a brominated epoxy resin, which also has a high refractive index due to brominated aromatic moieties in the structure.

2. Experimental

2.1. Materials

The brominated epoxy resin (BE) was supplied by Nippon Kayaku Co., Ltd. Bis(4-tert-butylphenyl) iodonium camphorsulfonate (BBI-106) was purchased from Midori Kagaku Co., Ltd. 3-(2'-Benzimidazoly)-7- N,N- diethyl-amino-coumarin (C7) was obtained from Sigma-Aldrich Corporation.

2.2. Experimental process

2.2.1 Synthesis of Thiirane [6]

Potassium thiocyanate (KSCN) (12.6 g) and 10 ml of water were added to 15.0 g of brominated epoxy (BE) dissolved in 100 ml of 1,4-dioxane. The mixture was stirred for 24 h at room temperature. A new portion of KSCN (12.6 g) and 10 ml of water were added to the reaction mixture and stirred for 24 h at room temperature. The mixture was extracted with ethyl acetate, washed with water, and dried with MgSO_4 . The solution was concentrated *in vacuo* and added to isopropanol in order to precipitate the product. The product was purified by reprecipitation from THF/methanol.

The yield of BT was 12.8 g (80%). The degree of transformation to thiirane is 50% (± 5) as calculated from $^1\text{H-NMR}$ spectrum. δ 2.0-2.6 (m, $-\text{CH}_2-\text{S}-$, 6.0H), δ 2.4-2.8 (m, $-\text{CH}_2-\text{O}-$, 6.0H), 2.9-3.4 (m, $-\text{CH}-\text{S}-$ and $-\text{CH}-\text{O}-$, 6.0H), 3.5-4.2 (m, $\text{O}-\text{CH}_2-\text{C}$ and $\text{Ar}-\text{CH}_2-\text{Ar}$, 21.5H), 6.8-7.8 (m, Ar-H, 20H).

2.2.2 Two-photon lithography

A resin for two-photon lithography was prepared by blending 2 wt% of BBI-106 and 1 wt% of C7 into BE or BT resin. The resin films were prepared by blade casting from DMF on a glass plate. The films were baked at 90°C for 5 min.

The photosensitive films were exposed using a Ti:Sapphire femtosecond laser (Spectra-Physics Tsunami) as a light source, which delivers 750 nm laser pulses (~ 100 fs). The samples were mounted on a computer-controlled 3D translation stage. The incident beam was focused through an

oil-immersion objective with a numerical aperture of 1.35. By scanning the focal point of the laser beam through the film, 3D patterns were defined. The total exposure dose was determined by the laser power and linear scan speed of the stage. After exposure, the film was baked at 110°C for 5 min and developed in THF. The fabricated structure was observed by optical microscopy and scanning electron microscope (SEM).

2.3. Equipment

$^1\text{H-NMR}$ spectra were obtained using a Varian INOVA-400 spectrometer operating at 400 MHz. Absorbance and transmittance measurements were made with a UV-vis spectrometer. Refractive index measurements were made with Rudolph Ellipsometers at 830nm. Scanning electron microscope (SEM) images were taken with a LEICA 440 SEM.

3. Results and Discussion

3.1. Preparation of brominated thiirane

BT resin was synthesized from the reaction of a corresponding BE resin and KSCN. The yield of BT was 12.8g (80%). The degree of transformation to thiirane is 50% (± 5) as calculated from the $^1\text{H-NMR}$ spectrum. Figure 1 shows the chemical structures of these materials. The refractive indexes of BE and BT are 1.62 and 1.68, respectively.

Figure1. Structures of brominated epoxy and thiirane resins

3.2. Two-photon lithography

Figure 2. Absorption spectrum of BE/BBI-106/C7 mixture spin-coated on a glass plate.

We chose the iodonium salt/coumarin system as a photoacid generator for the curing of epoxy and thirane resins because this system was reported as being a highly efficient system for two-photon reactions [7]. Firstly, we compared the photoreactions of various resins: BE, BE/C7, BE/BBI-106, and BE/BBI-106/C7 systems.

Figure 2 shows the absorption spectrum of the BE/BBI-106/C7 mixture spin-coated on a glass plate. Since there is no absorbance from 600-900 nm, no single-photon processes are expected to occur under exposure in this wavelength range. Although any 3D images were not observed with BE, BE/C7, and BE/BBI-106 systems, a 3D image was obtained due to two-photon reaction using the BE/BBI-106/C7 system upon irradiation at 750 nm at a power of 0.95 mW. This power represents the minimum power at which a structure could be fabricated, i.e., the threshold power (P_{th}) [4b]. In all cases, damaged structures were observed at powers greater than 1.8 mW.

The fact that the images obtained are due to a two-photon reaction is also supported by the results of fabrication attempts under different laser oscillation modes, pulse vs continuous wave (CW). 3D fabrications were attempted using pulse mode (750 nm, pulse width: ~ 100 fs) and CW mode (750 nm) with the same mean laser power (1.44 mW). A structure was obtained using the pulse mode, but not the CW mode, as expected for a two-photon process which requires the high peak intensities associated with a pulsed laser.

A comparison of the reactivity of the BE and BT resins appears in Table 1. BT required lower powers to generate 3D images, suggesting that the thirane has a higher reactivity than that of the epoxy in the same oligomer backbone.

Table 1. Threshold and damaged powers of BE and BT^{a)}.

Resin	P_{th} (mW) ^{b)}	P_d (mW) ^{c)}	Dynamic range (P_d/P_{th}) ^{d)}
BE	0.95	1.80	1.90
BT	0.75	1.80	2.40

a) The fabrication of resins conducted using BBI-106/C7 with highly focused laser pulses at 750 nm. b) P_{th} is the power threshold. c) P_d is the power which damaged structures were observed. d) The ratio P_d/P_{th} shows the dynamic range for the resins.

The smallest resolved dimension was determined by analysis of the test structure shown in Figure 3. This test structure is composed of a base structure [29.8 μm (length), 6.6 μm (width), and 1.0 μm (height)] and lines on the base

structure with different width of line and space, 0.21/0.21 μm (1/1pixel), 0.43/0.43 μm , 0.64/0.64 μm , 0.85/0.85 μm , 1.07/1.07 μm , respectively. The smallest dimension of BE/BBI-106/C7 system and BT/BBI-106/C7 system were both 0.21 μm in this system (Table 2).

Table 2. The smallest resolved dimension of BE and BT by two-photon lithography^{a)}.

Resin	Smallest dimension (μm)	Exposure condition
BE	0.21	213 $\mu\text{m/s}$ @1.44mW
BT	0.21	213 $\mu\text{m/s}$ @1.19mW

a) The fabrication of resins conducted using BBI-106/C7 with highly focused laser pulses at 750 nm.

Figure 3. The SEM image of a microstructure on a glass plate fabricated by two-photon lithography using BT/BBI-106/C7 resin with highly focused laser pulses at 750 nm.

Figure 4. The SEM image of a photonic crystal structure fabricated by two-photon lithography using BT/BBI-106/C7 resin with highly focused laser pulses at 750 nm.

Figure 4 shows a "woodpile" type photonic crystal structure having an average periodicity of 1 μm using the BT/BBI-106/C7 resin. The structure is composed of five layers of 0.5 μm spaced parallel resin rods. Each line width is about 300 nm.

which is much smaller than the wavelength of light that was used for the fabrication.

4. Conclusion

A new brominated thiirane (BT) with a high refractive index (1.68) was prepared. This resin has a higher reactivity than the corresponding brominated epoxy resin. A 3D photonic crystal type structure which is composed of five layer "woodpile" structure was obtained using the thiirane/iodonium salt/coumarin resin.

Acknowledgements

The authors would like to appreciate Dr. W. Zipfel (Cornell University, Applied & Engineering Physics), Dr. C. Bayles (Cornell University, Nanobiotechnology center), and Dr. Tianyue Yu (Cornell University, Materials Science & Engineering) for many useful discussions.

References

1. For example; V. K. Varadan, X. Jiang, and V. V. Varadan, "Microstereolithography and other Fabrication Techniques for 3D MEMS", John Wiley & Sons Ltd. (2001).
2. (a) W. Denk, J. H. Stricker, and W. W. Webb, *Science* **248** (1990) 73. (b) E. S. Wu, J. H. Stricker, W. R. Harrell, and W. W. Webb, *Proc. Soc. Photo-Opt. Instrum. Eng.* **1674** (1992) 776. (c) S. Maruo, O. Nakamura, and S. Kawata, *Opt. Lett.* **22** (1997) 132. (d) S. Maruo and S. Kawata, *J. Microelectromech. Syst.* **7** (1998) 411. (e) W. Zhou, S. M. Kuebler, K. L. Braun, T. Yu, C. K. Ober, J. W. Perry, and S. R. Marder, *Science* **296** (2002) 1106. (f) T. Yu, C. K. Ober, S. M. Kuebler, W. Zhou, S. R. Marder, and J. W. Perry, *Adv. Mater.* **15** (2003) 517.
3. (a) E. Yablonovitch, *Phys. Rev. Lett.* **58** (1987) 2059. (b) J. Joannopoulos, R. Meade, and J. Winn, *Photonic Crystals*, Princeton University Press, Princeton, NJ (1995).
4. (a) H. Sun, S. Matsuo, and H. Misawa, *Appl. Phys. Lett.* **74** (1998) 786. (b) S. M. Kuebler, M. Rumi, T. Watanabe, K. Braun, B. H. Cumpston, A. A. Heikal, L. L. Erskine, S. Thayumanavan, S. Barlow, S. R. Marder, and J. W. Perry, *J. Photopolym. Sci. Technol.* **14** (2001) 657. (c) V. Mizeikis, H. Sun, A. Marcinkevicius, J. Nishii, S. Matsuo, S. Juodkazis, and H. Misawa, *J. Photochem. and Photobiol.* **145** (2001) 41.
5. (a) J. K. Stille and J. A. Empen, *Chem. Sulfides, Conf.* (1968) 125. (b) A. Kameyama, Y. Kimura, and T. Nishikubo, *Macromolecules* **30** (1997) 6494. (c) A. Kameyama, K. Shimotsuma, and T. Nishikubo, *Macromol. Rapid Commun.* **15** (1994) 335.
6. R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.* **26** (1961) 3467.
7. C. Li, L. Luo, S. Wang, W. Huang, Q. Gong, Y. Yang, and S. Feng, *Chem. Phys. Lett.* **340** (2001) 444.