



High Photosensitive Sol-Gel Hybrid Materials for Direct Photo-Imprinting of Micro-Optics

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Abstract. Sol-gel derived inorganic-organic hybrid materials (HYBRIMERS) were found to have high photosensitivity arising from large changes in refractive index and volume upon exposure to light. These materials combined different photosensitive mechanisms due to the presence of polymers and silica in the HYBRIMER structure. Photo-induced densification of a germanium-doped HYBRIMER gave an increase in refractive index accompanying a volume contraction. A methacrylate HYBRIMER was decomposed by long UV illumination, giving a low refractive index and resulting in a reduction in film thickness. Also, photo-initiators were locked inside the methacrylate HYBRIMER during illumination, giving a simultaneous increase in the refractive index and film thickness. Direct photo-imprinting using the photosensitive HYBRIMER was demonstrated for simple fabrication of gratings, microlens, and waveguides using a photomask, a phase mask, an interferometer, and laser writing.

Keywords: sol-gel, hybrid material, HYBRIMER, photosensitivity, photochemical self-development, micro-optics, grating, microlens, waveguide

1. Introduction

Micro-optical components, such as gratings, holograms, waveguides, microlenses, etc., with optical and/or topological surface modulation are becoming more important due to the increasing use of micro-optical elements in optoelectronics, optical computing and optical communication. The fabrication of microstructures has been achieved using various techniques and materials [1]. Conventional micro-fabrication technologies use a multi-step process that includes exposure of a photoresist film through a photomask, development, and wet or dry etching transfer of the optical structure into the substrate material [2]. However, the photosensitive materials can give simpler fabrication of micro-structured surfaces with refractive index and/or geometrical modulation just with light exposure. Optical patterning with refractive index modulation by light illumination has been seen in germanium-doped silica [3] and many photo-polymers

[4]. Light induced cross-linking in the molecular structure of a photo-polymer makes it resistive to etching, so that the developing process also creates micro-patterning [5]. A typical example of this photosensitive material is photoresist materials. Other types of photosensitive materials, such as azo-polymers, can create directly a micro-structured surface of refractive index changes and topological modulation upon light illumination [6, 7].

Recently, sol-gel derived inorganic-organic hybrids have been shown to be very photosensitive and thus suitable for the fabrication of micro-optics by photo-patterning [8–24]. In typical photosensitive sol-gel hybrids, selective photo-induced cross-linking was obtained, and micro-optical structures were created, by etching the unexposed area of film [8–10]. However, the structural development step still involved the use of organic solvents that may potentially decrease the surface quality of the optical elements. Moreover, it has been demonstrated that it is possible to fabricate directly

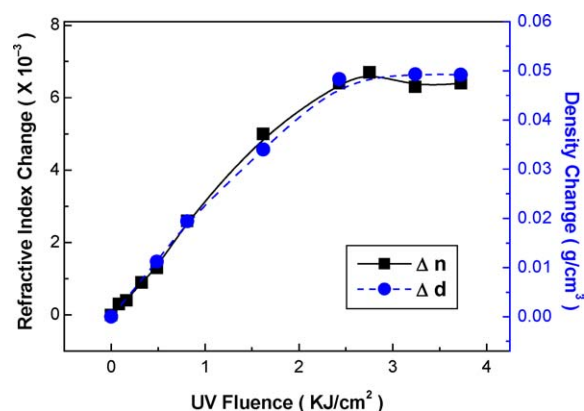


Figure 1. Increases in refractive index and density of germanium doped HYBRIMER by UV illumination.

optical structures in sol-gel hybrids by using only the exposure step [11–24]. This direct photo-imprinting enabled the simple and cheap fabrication of micro-optical structures with improved surface quality.

Highly photosensitive sol-gel hybrids that result in larger refractive index and topological changes upon light exposure can be designed by combining the different photosensitive mechanisms of silica (defect formation, densification) and polymers (polymerization, photochemical reaction, decomposition). Recently, we reported some different photosensitive mechanisms in the sol-gel hybrids (HYBRIMERS) to induce larger changes in both the refractive index and the volume for fabrication of micro-optical structures on the surface. In this paper, different types of highly photosensitive

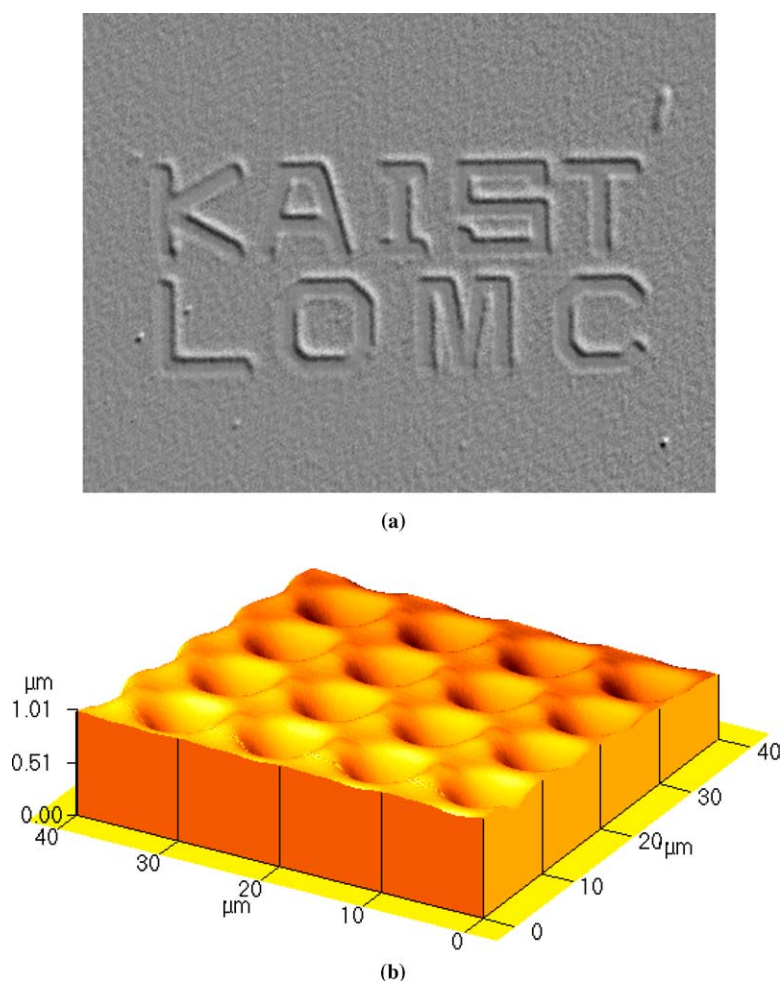


Figure 2. Direct photo-inscribed (a) letters (optical microscopy) and (b) microlens array (AFM) on germanium doped HYBRIMER by volume compaction.

HYBRIMER to be directly photo-imprinted are introduced, and the creation of micro-optical structure is demonstrated.

2. Photo-Induced Densification in Germanium Doped HYBRIMER [15–17]

Germanium-doped silica glass, which undergoes changes in refractive index with UV illumination, is used for the fabrication of grating devices used in optical communications. However, formation of a surface relief pattern is rare, as the refractive index changes occur through defect formation within the glass. The softness and porous structure of a HYBRIMER should enhance the photosensitivity of germanium-doped silica glass. A germanium-doped HYBRIMER, that consisted of a methyl-modified germano-silicate network, exhibited considerable photosensitivity. Large changes in its refractive index and the volume were seen upon illumination. It was demonstrated that this large change in refractive index was caused by photo-induced densification. The refractive index increase upon UV exposure of up to 10^{-2} can be estimated from the density increase in the Lorenz-Lorentz equation, as shown in Fig. 1 [15]. The Raman spectra confirmed the photo-induced densification from the reduction in the average inter-tetrahedral Si—O—Si bonding angle in the silica structure. Figure 2(a) shows direct photo-inscribed letters on the germanium-doped HYBRIMER [16]. Recently, larger and faster refractive index and volume changes were observed upon photopolymerization of methacryl radicals in a germanium-doped HYBRIMER [17]. Figure 2(b) shows a microlens array that was directly photo-imprinted using a binary photo-mask. The germanium-doped HYBRIMER has excellent optical qualities as well as good thermal and chemical stability. It was, therefore, suitable for the simple fabrication of effective micro-lenses and gratings.

3. Photo-Decomposition in a Methacrylate HYBRIMER [18–20]

Typically, organic polymers are susceptible to decomposition in UV light. Polymethylmethacrylate (PMMA) is decomposed and damaged by long UV illumination. Thus, a HYBRIMER composed of an Si—O—Si network with methacryl side groups

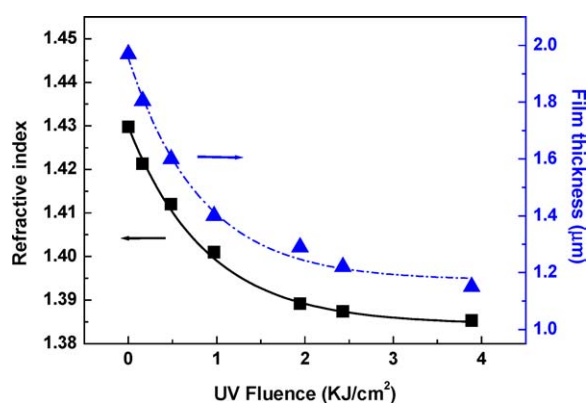


Figure 3. Decreases in refractive index and film thickness of methacrylate HYBRIMER containing perfluoroalkyl group by UV illumination.

should be susceptible to photo-decomposition induced changes in refractive index and film thickness. It was found that both the refractive index and film thickness of the methacrylate HYBRIMER decreased with growing UV influence [18, 19]. Moreover, the changes in the refractive index and the film thickness were enhanced with the addition of perfluoroalkyl groups as another organic modifier. Figure 3 shows the significant reduction in the refractive index and film thickness in the methacrylate HYBRIMER made by precursors of methacryl methoxysilane and perfluoroalkyl methoxysilane in a 3:1 ratio [18]. The measured refractive index of 1.3853 was very low in comparison with the refractive indices of perfluorinated polymers. Figure 4 illustrates that UV excitation of the carbonyl group led to decomposition of the methacryl chains in the HYBRIMER with formation of carbon and oxygen-containing volatile gaseous products [18]. This suggested that the removal of the high polar carbonyl groups and subsequent formation of pores inside the HYBRIMER might have resulted in a decrease in the refractive index. On the other hand, the loss of these organic groups and condensation of the Si—O—Si inorganic network upon UV illumination may have caused a reduction in the film thickness.

A surface relief pattern was directly imprinted on the methacrylate HYBRIMER using a photomask with a periodic pattern of $12 \mu\text{m}$, as is shown in Fig. 5(a) [18, 19]. Also, the KrF excimer laser through a phase mask can pattern the methacrylate HYBRIMER for fabrication of the diffraction grating, as shown in Fig. 5(b) [20].

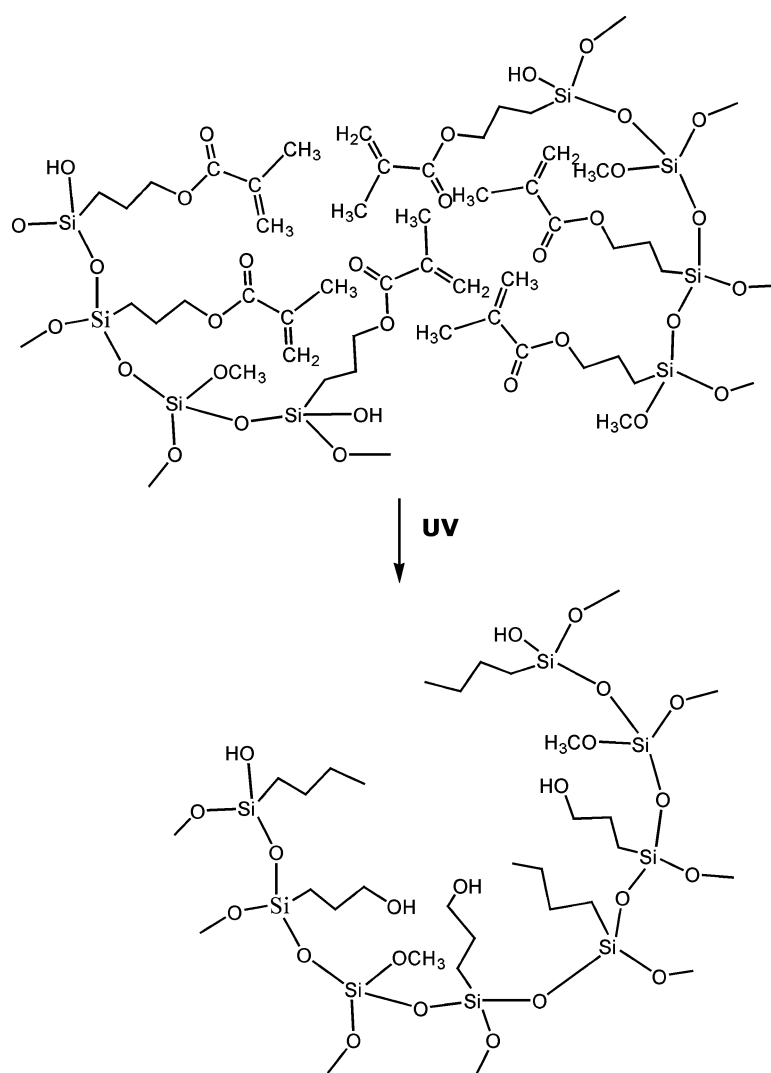


Figure 4. Schematic representation of decomposition of methacryl chains in methacrylate HYBRIMER being removed as volatile gaseous products and formation of pores inside the HYBRIMER by UV illumination.

4. Photolocking in Doped HYBRIMER [21–24]

HYBRIMERS doped with photochemical species are highly photosensitive to increases in refractive index as well as film thickness by photolocking of photochemical species with UV exposure. Upon UV illumination, photochemical species, such as photo-initiators, decompose and can be locked inside the HYBRIMER matrix with attachment or dimerization of photo-decomposed radicals. For example, in a benzylidimethylketal (BDK)-doped HYBRIMER containing methacrylate, the photo-induced change in refrac-

tive index and film thickness increased linearly with BDK content, as is shown in Fig. 6 [23]. It is also known that the photosensitivity was highly dependent on the identity of the doped photo-initiator.

Utilising this photosensitive mechanism, a channel waveguide was fabricated, as is schematically represented in Fig. 7 [22–24]. Photo-initiator-doped HYBRIMER films were exposed to UV light to pattern a channel waveguide. Upon UV exposure, the photo-initiator decomposed not only polymerizing the HYBRIMER but were also photo-locked into the HYBRIMER matrix. This made expanding the film to be

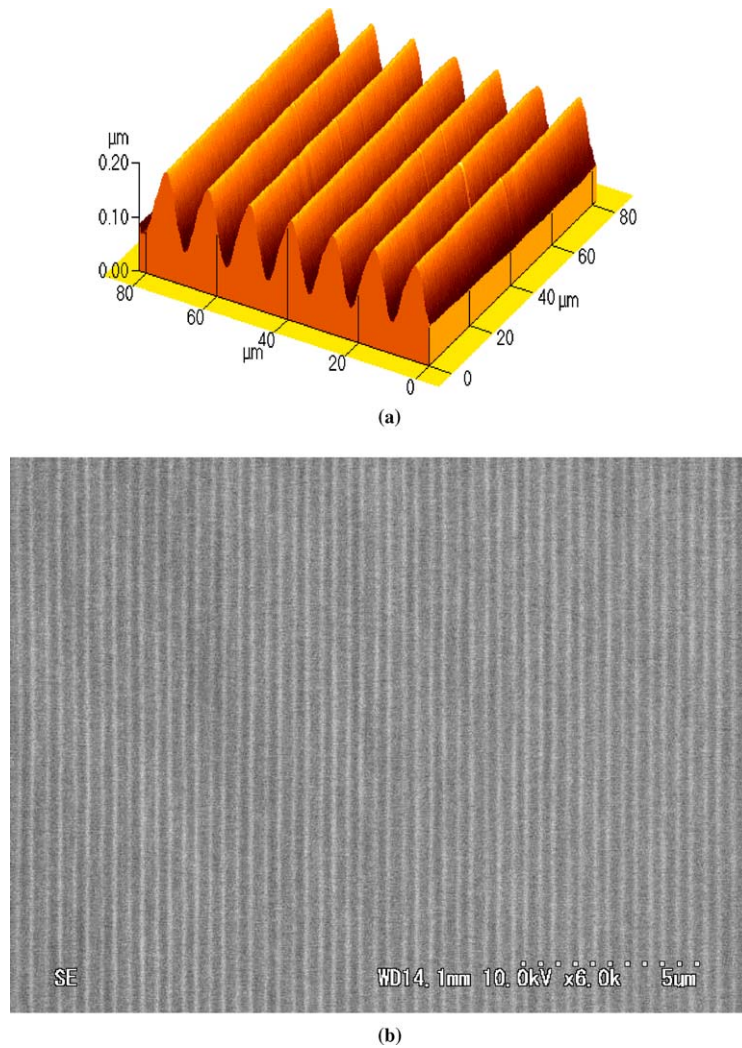


Figure 5. (a) AFM image of the surface relief pattern inscribed by UV lamp through a photomask with a $6\ \mu\text{m}$ opening, and (b) an SEM image of the diffraction grating inscribed by a KrF laser through a phase mask of $1\ \mu\text{m}$ period.

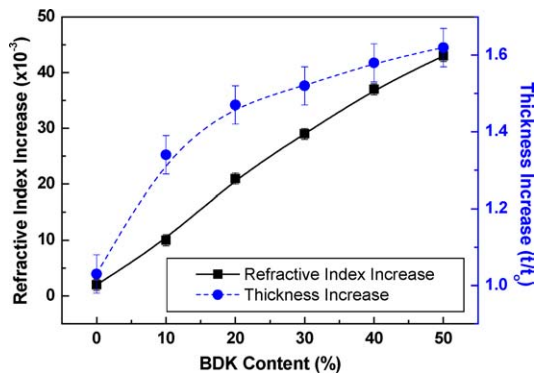


Figure 6. Photo-induced increases in refractive index and film thickness with BDK content (mol%).

patterned positively. Further, during annealing and baking, the mobile photo-initiators in the unexposed areas evaporated off. Thus, the area exposed to UV had both a higher refractive index and greater film thickness, directly fabricating a channel waveguide whilst avoiding the developing process. This process was termed photochemical self-development (PSD). Figure 8 presents an AFM image of the channel waveguide and the near-field mode profile fabricated by the PSD process with a photomask of $5\ \mu\text{m}$ opening on a BDK-doped HYBRIMER film [22]. Due to the diffusiveness of the BDK, the width of the waveguide channel was larger than the predefined photomask aperture. The shape of the single mode waveguide channel is gaussian, the

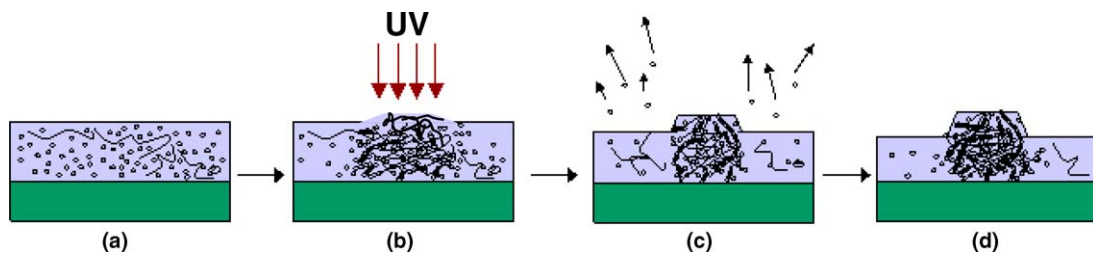


Figure 7. Schematic representation of photochemical self-development (PSD). (a) film coating, (b) photo-polymerization and photolocking of photo-initiators, (c) evaporation of photo-initiators by annealing, (d) condensation and densification of the film by baking.

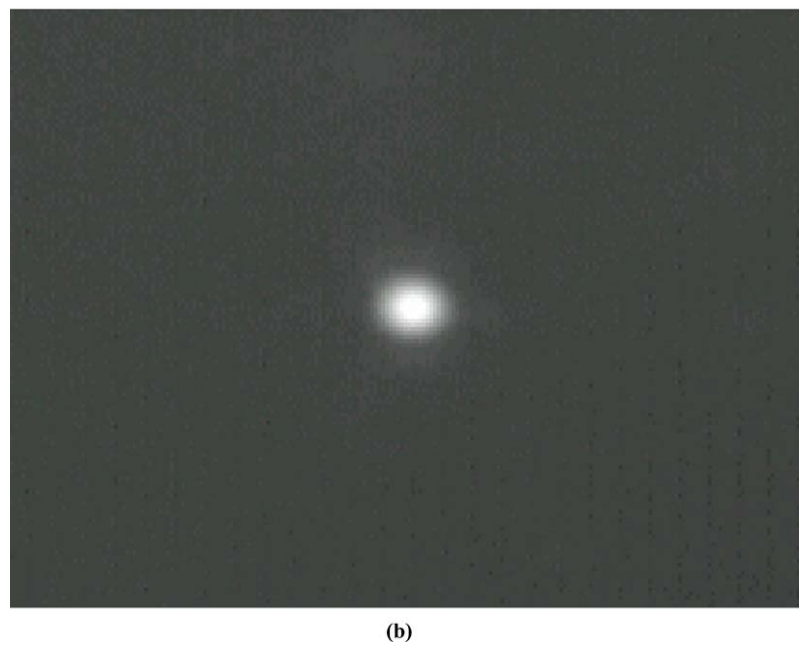
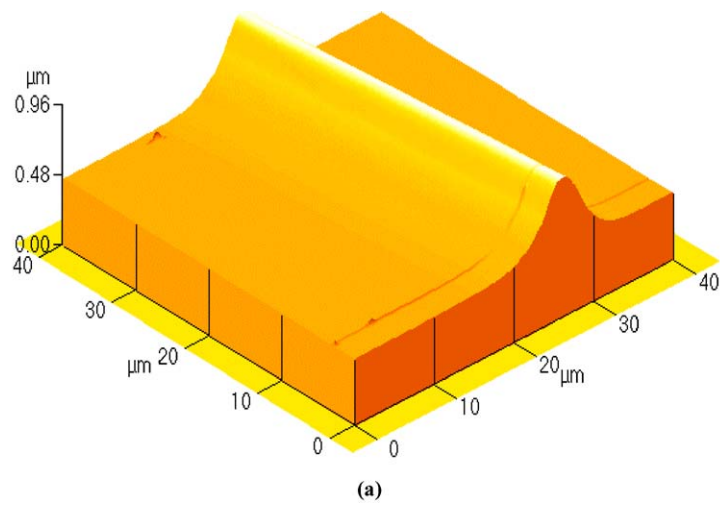


Figure 8. (a) AFM image and (b) near field mode profile of the channel waveguide fabricated by using a photomask with 5 μm opening.

same as that of a light beam. Also, the single mode ridge waveguides at $\lambda = 1.55 \mu\text{m}$ were formed without using a photomask and development process by direct laser exposure [23]. The PSD process on a HYBRIMER has the potential to fabricate very cheaply waveguide devices. At present, the most significant problem in the PSD process is relatively high optical propagation loss. However, this is being improved and was found recently to be less than 0.3 dB/cm at $\lambda = 1.3 \mu\text{m}$. In addition, the doped HYBRIMER has been directly written using a two-beam interferometer of a HeCd laser to fabricate grating devices.

5. Summary

A HYBRIMER that contains organic molecules and/or a polymer network based on an inorganic silica network prepared by a sol-gel process can be used as an optical material. Combining the different photosensitive mechanisms of polymers and silica can enhance the photosensitivity of the HYBRIMER. Photo-induced densification, photo-decomposition, and photolocking in the HYBRIMER can result in large changes in both refractive index and volume. Direct photo-imprinting on the HYBRIMER was applied to simplify the fabrication of micro-optical elements like gratings, microlens and waveguides. The direct fabrication of micro-optics has significant application in future optical interconnection technologies.

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References

1. H. Nishihara, M. Haruna, and T. Suhara, *Optical Integrated Circuits* (McGraw-Hill, New York, 1989).
2. E.J. Gratix, Proc. SPIE **1992**, 266 (1993).
3. K.D. Simmons, S. LaRochelle, V. Mizrahi, G.I. Stegeman, and D.L. Griscom, Opt. Lett. **16**, 141 (1991).
4. T.J. Trout, J.J. Schmieg, W.J. Gambogi, and A.M. Weber, Adv. Mater. **10**, 1219 (1998).
5. M. Eisner and J. Schwider, Opt. Eng. **10**, 2979 (1996).
6. N. Zetsu, T. Ubukata, T. Seki, and K. Ichimura, Adv. Mater. **13**, 1693 (2001).
7. N.K. Viswanathan, D.Y. Kim, S. Bain, J. Williams, W. Liu, L. Li, L. Samuelson, J. Kumar, and S.K. Tripathy, J. Mater. Chem. **9**, 1941 (1999).
8. J.T. Rantala, P. Ayras, R. Levy, S. Honkanen, M.R. Descour, and N. Peyghambarian, Opt. Lett. **23**, 1939 (1998).
9. P. Ayras, J.T. Rantala, R. Levy, M.R. Descour, S. Honkanen, and N. Peyghambarian, Thin Solid Films **352**, 9 (1999).
10. J.T. Rantala, R. Levy, L. Kivimaki, and M.R. Descour, Electron Lett. **16**, 530 (2000).
11. B. Darracq, F. Chaput, K. Lahlil, Y. Levy, and J.P. Boilot, Adv. Mater. **10**, 1133 (1998).
12. S. Pelissier, D. Blanc, M.P. Andrews, S.I. Najafi, A.V. Tishchenko, and O. Parriaux, Appl. Opt. **38**, 6744 (1999).
13. J.T. Rantala, A.H.O. Karkkanen, J.A. Hiltunen, M. Keranen, T. Kololuoma, and M.R. Descour, Opt. Express **8**, 682 (2001).
14. A.H.O. Karkkanen, J.M. Tamkin, J.D. Rogers, D.R. Neal, O.E. Hormi, G.E. Jabbour, J.T. Rantala, and M.R. Descour, Appl. Opt. **41**, 3988 (2002).
15. J.H. Jang, D.J. Kang, and B.S. Bae, J. Am. Ceram. Soc. **87**, 155 (2004).
16. J.H. Jang, D.J. Kang, and B.S. Bae, MRS Symp. Proc. **780**, Y5.10.1 (2003).
17. J.H. Jang, D.J. Kang, and B.S. Bae, MRS Symp. Proc. **780**, Y5.10.1 (2003); J.U. Park, W.S. Kim, and B.S. Bae, J. Mater. Chem. **13**, 738 (2003); J.U. Park, E.S. Kang, and B.S. Bae, MRS Symp. Proc. **780**, Y3.7.1 (2003); D.J. Kang, J.U. Park, B.S. Bae, J. Nishii, and K. Kintaka, Opt. Express **11**, 1144 (2003).
18. O.H. Park, J.I. Jung, and B.S. Bae, J. Mater. Res. **16**, 2143 (2001).
19. B.S. Bae, J.I. Jung, and O.H. Park, Proc. SPIE **4279**, 101 (2001).
20. B.S. Bae, O.H. Park, R. Charters, B. Luther-Davies, and G.R. Atkins, J. Mater. Res. **16**, 3184 (2001).
21. J.I. Jung, O.H. Park, and B.S. Bae, J. Sol-Gel Sci. & Tech. **26**, 897 (2003).