

# Photochemical self-developing of doped sol-gel hybrid glass waveguides

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## ABSTRACT

Sol-gel hybrid glass (SGHG) films doped with various photoinitiators were prepared. Volatile photoinitiators are photolocked in SGHG matrix by photochemical reaction upon UV exposure. Refractive index and film thickness increases by UV exposure due to photoinduced polymerization and photolocking of high refractive index species. Using the photolocking of photoinitiators, channel waveguide was fabricated without using developing process step, which will be called photochemical self-developing.

**Keywords:** sol-gel hybrid glass, photolocking, photoinitiator, photochemical self-developing, channel waveguide

## 1. INTRODUCTION

Polymers have been investigating for use in planar optical waveguides because they exhibit low optical losses and easily construct channel waveguides.<sup>1,2</sup> Polymer channel waveguides can be fabricated in many ways. A direct photolithographic and etching fabrication technique is most appropriate since the polymers are very photosensitive and etching selective. Simpler technique of channel waveguide fabrication without etching process is using a photolocking of dopant inside the polymer matrix.<sup>3,4</sup> The polymers doped with volatile higher refractive index species can fabricate channel waveguide structure using photochemical reactions of dopants and/or polymer. The process that has sufficient resolution to make single-mode guides by direct photolithography, gives smooth interfaces and low optical losses to simply fabricate planar lightwave circuits.

Recently, sol-gel derived organic-inorganic hybrid materials have begun to receive attention for integrated optical applications.<sup>5,6</sup> The sol-gel hybrid glass (SGHG), like polymer, has a flexibility and versatility in composition and processing. Thick films over few microns can be deposited in a single step with low processing temperature below 200°C. Also, they are photosensitive for channel waveguide to be fabricated by photolithographic and etching process, and offer compatibility with both inorganic and organic dopants for active device applications. Most studies of the SGHG for integrated optics have used a photosensitive methacrylate-silica/zirconia system. Photoinduced polymerization of

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methacrylate can define channel waveguide and fabricate integrated optical components such as splitters, gratings, and wavelength multiplexers. Because the SGHG has versatility in process as in polymers, other channel waveguide fabrication techniques can be applicable to the SGHG. Thus, the simpler photolocking technique that can omit developing step can be used in the fabrication of the SGHG channel waveguides. Recently, we fabricated the channel waveguide of the benzyldimethylketal (BDK)-doped SGHG by direct laser writing and developing using photolocking of BDK in the SGHG matrix.<sup>7</sup> In this process, selective increase in the refractive index and thickness by light exposure can form the channel waveguide configuration. The BDK is mobile and volatile while photodecomposed benzoyl type radicals are not. Thus, the unreacted BDK thermally diffuse out to be evaporated during annealing and baking. On the other hand, the photodecomposed benzoyl type radicals are locked or fixed in the matrix remaining during annealing and baking. Thus, the higher thickness and refractive index can be obtained in the UV exposed area due to the locked photodecomposed benzoyl type radicals in the SGHG matrix. This process which is called photochemical self-developing will be applicable to the fabrication of channel waveguide.

In the present study, we investigated the photolocking behavior in the SGHG films doped with various photoinitiators. Also, we will demonstrate the photochemical self-developing process to fabricate the channel waveguide

## 2. EXPERIMENTAL

The SGHG whose composition has been already used in optical waveguide was prepared using methacryloxypropyltrimethoxysilane(MPTMS,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ), zirconium n-propoxide(ZPO,  $\text{Zr}(\text{OC}_3\text{H}_7)_4$ ), and methacrylic acid(MAA,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$ ) as precursors. Zirconium in the composition was used to increase refractive index as well as mechanical property of the films.<sup>6,7</sup> Firstly, MPTMS was hydrolyzed with 0.75 equivalents of  $\text{H}_2\text{O}$  in the presence of 0.05M HCl as a catalyst. ZPO was reacted with MAA in a molar ratio of 1:1 to avoid undesired precipitation of  $\text{ZrO}_2$  particles by chelating complex formation. After that, the chelated ZPO solution was added to the prehydrolyzed MPTMS solution and stirred for 1hrs to proceed hydrolysis and condensation. The mixed solution was reacted with additional water for 20hrs to complete the hydrolysis and condensation. Total amount of water was the 1.5 equivalents of total alkoxides in the solution. Benzyldimethylketal(BDK,  $\text{C}_6\text{H}_5\text{COC}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ ), Benzophenone(BP,  $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ ), or 2-Hydroxy-2-methylpropiophenone(DAROCUR1173,  $\text{C}_6\text{H}_5\text{COC}(\text{CH}_3)_2\text{OH}$ ) was used as a photolocking species as well as a photoinitiator. The prepared solution was then deposited on Si(100) wafers or thermally oxidized Si (12 $\mu\text{m}$  oxide thickness) substrates by spin coating method. Single coating yields approximately 4-5 $\mu\text{m}$  thicknesses of the films. The films were illuminated by UV lamp (1KW Hg -Xe lamp, 220-260nm, Oriel 82521) for different times. The UV illuminated films were dried at 70°C for a while depending on the used photoinitiators. Finally, the films were baked 150°C for 5 hrs. The refractive index and thickness of the films was determined by using a prism coupler (Metricon 2010) at wavelengths of 632.8 and 1550nm.

### 3. RESULTS AND DISCUSSION

#### 3.1 Photochemical reactions of photoinitiators

BDK, BP, and Darocur1173 were used as the photoinitiators to polymerize methacrylate monomers by UV exposure. BDK and Darocur1173 are decomposed to the radicals through  $\alpha$ -splitting while BP produces a radical by proton extraction when they are exposed to UV. These transitions are shown in Fig. 1.

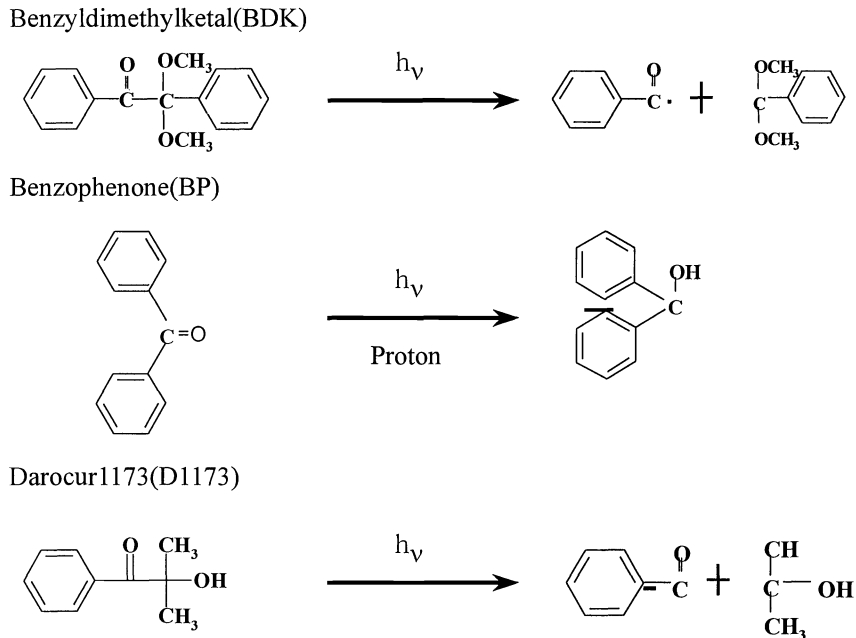


Fig. 1 Photochemical reactions of various photoinitiators

The photoinitiators used in this study are mobile and volatile to be removed by heating. On the other hand, the photodecomposed radicals are immobilized by photolocking in the SGHG matrix during UV exposure. The benzoyl radicals in BDK and Darocur1173 may be attached to methacrylate molecule as in case of BP or dimerize to form benzil molecule.<sup>4</sup> Using photolocking of the photoinitiators in the SGHG matrix, the channel waveguide can be fabricated as schematically represented in Fig. 2. The photoinitiator doped SGHG films are deposited and UV is exposed to pattern the channel waveguide. Upon UV exposure, the photoinitiator is decomposed not only to polymerize the SGHG matrix but also to be photolocked in the films. Then, the film is annealed to evaporate the photoinitiators in the unexposed area, which was not decomposed. Finally, the film is baked to be condensated and densificated. Thus, the UV exposed area create higher refractive index by photolocking of high refractive index photoinitiators as well as photoinduced polymerization. Also, the film thickness in the unexposed area decreases as the photoinitiators in the films are removed during annealing and baking the films. Thus, the channel waveguide can be easily fabricated by UV illumination without using developing process. Thus, this process is called the photochemical self-developing.

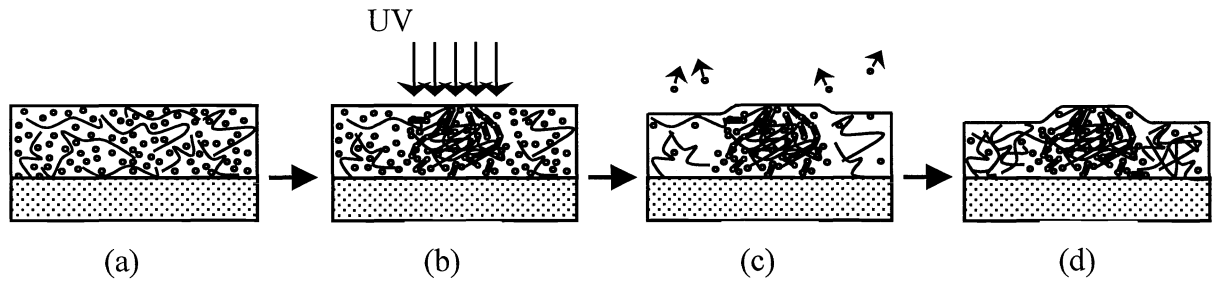


Fig. 2 Schematic representation of photochemical self-developing by photolocking of photoinitiators

(a) film coating (b) photoinduced polymerization and photolocking of photoinitiators by UV exposure (c) evaporation of photoinitiators by annealing (d) condensation and densification of the film by baking

### 3.2 Photoinduced change in refractive index and film thickness

Fig. 3 shows the refractive index increase by UV exposure at the wavelengths of 633nm and 1550nm as a function of UV exposure comparing with the undoped SGHG film. The refractive index of the undoped SGHG is not varied during UV illumination. On the other hand, the refractive index increases with increasing UV dose in the doped SGHG films by photoinduced polymerization as well as photolocking of the photoinitiators in the films as described before. For the BDK (30mole%)-doped SGHG film, the refractive index change is greatest up to  $3.0 \times 10^{-2}$  at 633nm and  $2.5 \times 10^{-2}$  at 1550nm. It is because high content of the BDK is photodecomposed into two high refractive index aromatic radicals to be photolocked in the films. The refractive index increase in the SGHG doped with BP (20 mole%) is high at 633nm comparable to the BDK-doped one but is much less at 1550nm. This implies the SGHG photolocked with BP presents large refractive index change depending on wavelength. Also, the refractive index increase is slower than the others since the photochemical reaction of the BP is not favorable. On the other hand, the SGHG film doped with Darocur1173 shows less refractive index increase because the Darocur1173 contains an aromatic radical to be photolocked in the film.

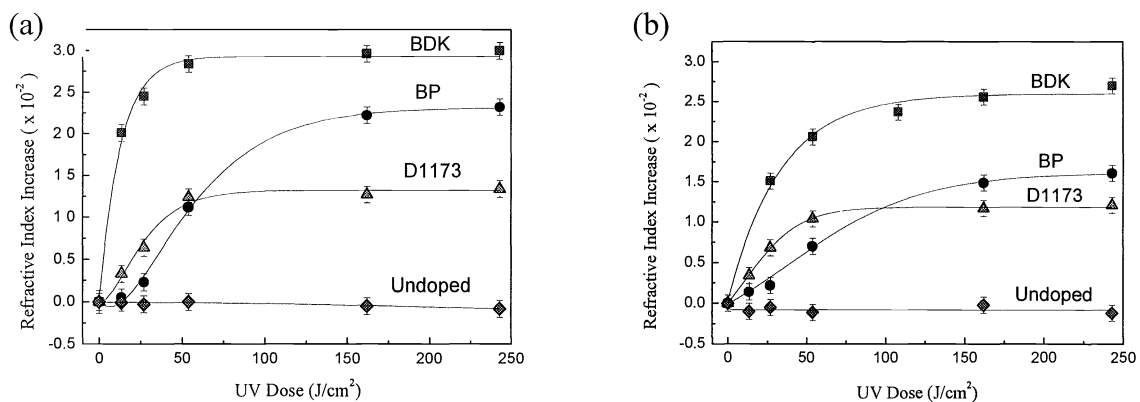


Fig. 3 Refractive index increase at wavelengths (a) 633nm and (b) 1550nm of undoped and doped films by UV exposure (30mol% BDK, 20mol% BP, and 30mol% Darocur1173 are doped)

Fig. 4 presents film thickness change that is normalized by the film thickness of the unexposed film depending on UV exposure. Thickness of the undoped SGHG film is not changed regardless of UV exposure. However, the BDK-doped SGHG film shows the greatest film thickness increase up to 1.5 that indicate the film thickness of the unexposed and the UV exposed films is approximately  $4\mu\text{m}$  and  $6\mu\text{m}$ , respectively. On the other hand, the BP or Darocur1173-doped SGHG films make less film thickness change. Fig. 5 shows the variation of refractive index profiles in undoped and doped SGHG

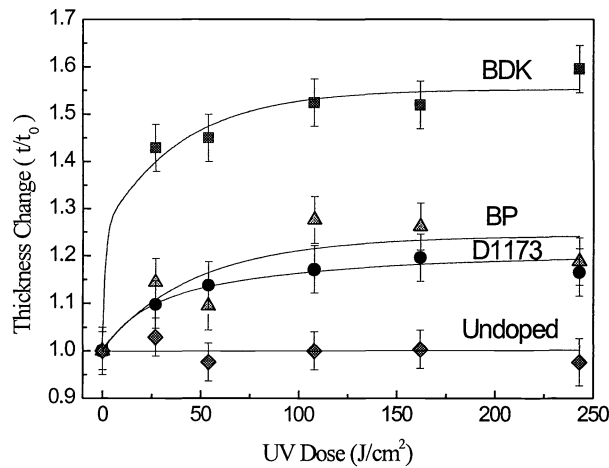


Fig. 4 Normalized film thickness change of undoped and doped films over unexposed film thickness (30mol% BDK, 20mol% BP, and 30mol% Darocur1173 are doped)

films along the film thickness depending on UV exposure. The change in refractive index as well as film thickness upon UV exposure can be found. For the undoped SGHG film, the refractive index is unvaried but the film thickness decreases due to photoinduced densification. However, for the doped SGHG films, the refractive index increases but the film thickness is reduced upon UV exposure as expected. The refractive index variation of the films along the film thickness is very uniform except for the BP-doped films. As already described above, the photochemical reaction of BP is not reactive upon UV exposure so that induce the lower refractive index inside the film.

### 3.3 Channel waveguide fabrication by photochemical self-developing

Fig. 6 presents SEM photographs of cross section and surface morphology of the BDK-doped SGHG films. It is shown the deposited film is uniform and homogeneous in thickness and morphology to be applicable to waveguide application. In order to make channel waveguide, the film on the thermally oxidized silicon substrate ( $12\mu\text{m}$  oxide thickness) was exposed to UV through a photolithography mask with  $5\mu\text{m}$  width openings. Fig. 7 shows a top-view optical microscope photograph of the channel waveguides fabricated by photochemical self-developing. The real width of the fabricated waveguide is

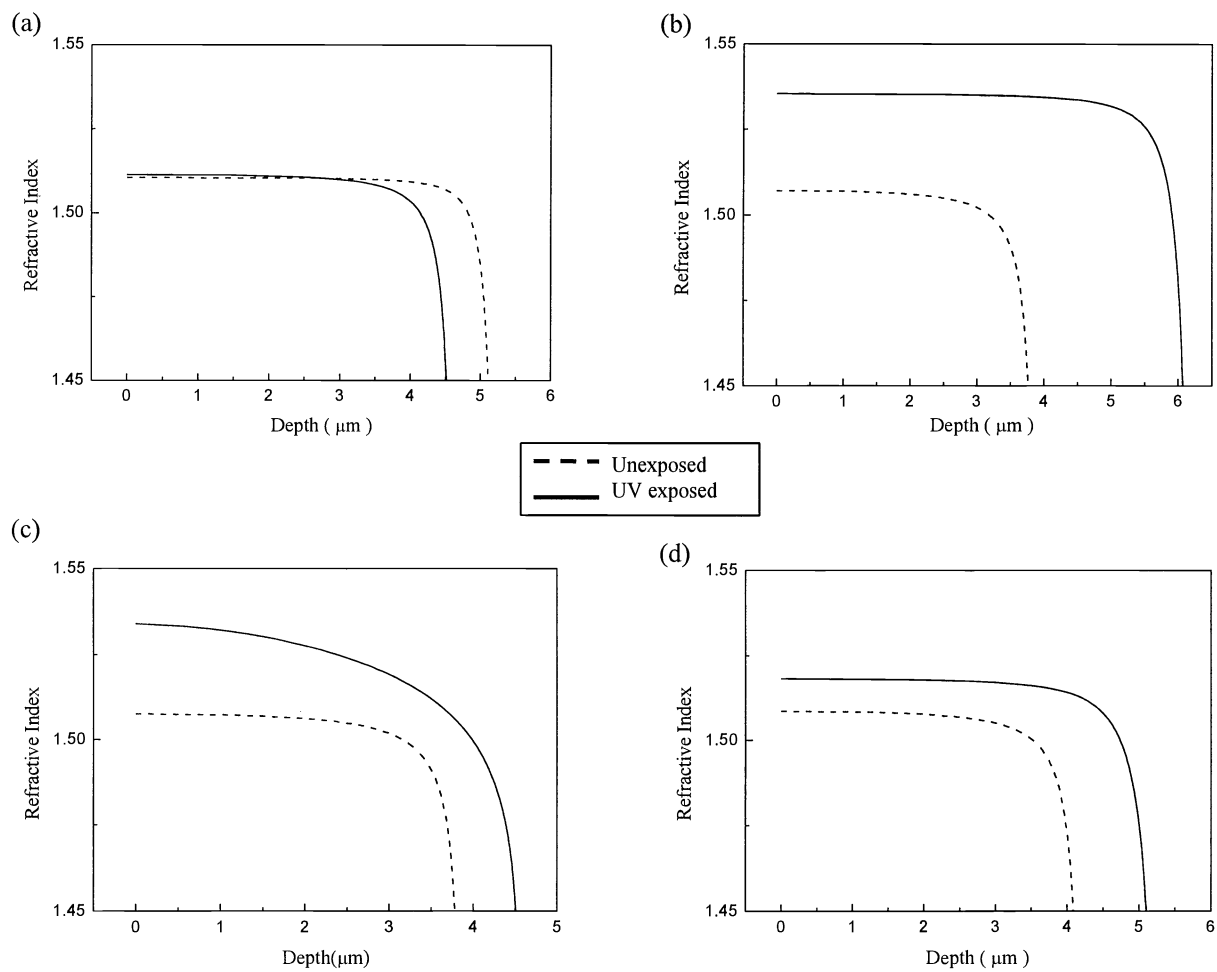


Fig. 5 Refractive index profiles at 1550nm of (a) undoped, (b) BDK(30mol%)-doped, (c) BP(20mol%)-doped, (d) Darocur1173(30mol%)-doped films

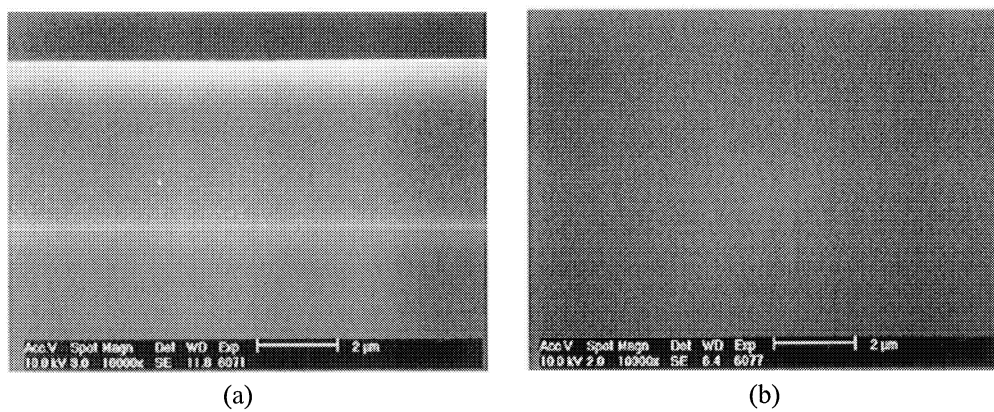


Fig. 6 SEM photographs of (a) cross section and (b) surface morphology of BDK-doped films

broadened due to diffusiveness of the photoinitiators. Fig. 8 shows a near field picture of the output of the waveguides at 1550nm wavelength. It is found a symmetrical and intense single mode profile is obtained

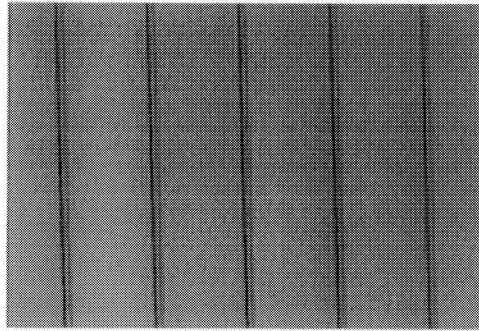


Fig. 7 Optical microscope photograph of channel waveguide fabricated by photochemical self-developing

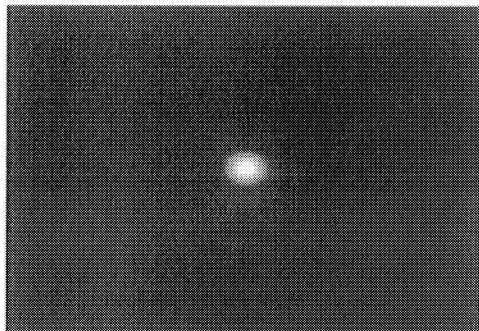


Fig. 8 Near field photograph of output of channel waveguides at 1550nm wavelength

#### 4. CONCLUSIONS

The SGHG films doped with various photoinitiators were prepared and their photoinduced change in refractive index and film thickness was investigated. It was found BDK is most effective to increase refractive index and film thickness by photolocking upon UV exposure. It was demonstrated single mode channel waveguide at 1550nm in the BDK-doped SGHG film was fabricated by photochemical self-developing.

#### ACKNOWLEDGMENTS

This work has been financially supported by Ministry of Information and Communication, and Korea Science and Engineering Foundation (KOSEF) in Korea.

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