

Photoinduced condensation of sol-gel hybrid glass films doped with benzildimethylketal

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Sol-gel hybrid glass films doped with benzildimethylketal (BDK) were prepared from [(methacryloxy)propyl]trimethoxysilane, methacrylic acid, and zirconium *n*-propoxide. Polymerization of methacryl groups and polycondensation of alkoxides by UV illumination and baking were observed using Fourier-transformed infrared spectroscopy. Polymerization kinetics and refractive index increase depend on UV illumination time. The refractive index increase is sensitive to BDK concentration and agrees well with photodecomposition of BDK. Thus, it is found that the refractive index increase is made by incorporation of the radicals produced by photodecomposition of BDK in the network as well as polymerization of methacryl groups.

I. INTRODUCTION

The sol-gel process with low processing temperature allows the incorporation of an organic polymer network into an inorganic glass network leading to formation of the so-called organic-inorganic hybrid materials.¹⁻⁶ Among many kinds of hybrid materials, siloxane-based hybrid materials using organo-alkoxysilane precursors are useful for the design of hybrid materials for photonic applications because of their homogeneity and versatile functionality. Therefore, many siloxane-based hybrid materials, called sol-gel hybrid glass (SGHG), have been developed for photonic applications in recent years.⁴⁻⁶

Recently, the photosensitive sol-gel hybrid glass composed of methacryl and silicate networks has been used for planar optical waveguides replacing existing silica and polymer materials.⁷⁻¹⁰ [(Methacryloxy)propyl]trimethoxysilane (MPTS) and methacrylic acid (MAA) with photoinitiator were used as photopolymerizable components in the SGHG. The refractive index of the UV-exposed region increases by polymerization but that of unexposed region does not increase, so it is not necessary to remove the unexposed region by soaking of the films in a solvent. Thus, the channel waveguide can be easily fabricated without etching process. The increase in refractive index of the SGHG films is mainly governed by photopolymerization of the organic component and polycondensation of the inorganic component.^{10,11} However, the effect of the photoinitiator which has been usually 1-hydroxycyclohexyl-1-phenylketone (HCPK) sensitive to the light from the UV region on the refractive index change has been ignored since a small quantity of photoinitiator has been used. BDK is a common

photoinitiator sensitive to 350 nm light to be used in a general mask aligner. Also, optical absorption of BDK is lower compared to those of other photoinitiators for the UV exposure to better penetrate a greater depth. In addition to photoinitiating characteristics, BDK has been used in fabrication of polymer waveguides, because it can increase the refractive index by photolocking of the radicals produced by photodecomposition of BDK.^{12,13} Thus, BDK in the SGHG films can act as a refractive index modifier as well as a photoinitiator.

In the present study, BDK-doped SGHG films were prepared and their photoinduced condensation behavior was studied. The structural evolution and the polymerization kinetics of the SGHG were investigated as a function of UV illumination time. Especially, the effects of UV exposure, thermal curing, and BDK concentration on the change in the microstructure and refractive index of the films were examined. Finally, the effect on the refractive index increase by photoinduced condensation, particularly photolocking of BDK in the SGHG, was revealed.

II. EXPERIMENTAL PROCEDURE

A. Preparation of sol-gel hybrid glass films

The SGHG of which composition has been already used in optical waveguides was prepared using [(methacryloxy)propyl]trimethoxysilane [MPTS, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$], 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.⁷⁻¹¹ Zirconium in the composition was used to increase refractive

index as well as to improve mechanical properties of the films. First, MPTMS was hydrolyzed with 0.75 equiv of H_2O in the presence of 0.01 M HCl as a catalyst. ZPO was reacted with MAA in a molar ratio of 1:1 to avoid undesired precipitation of ZrO_2 particles by chelating complex formation. After that, the chelated ZPO solution was added to the prehydrolyzed MPTMS solution and stirred for 1 h to advance hydrolysis and condensation. The mixed solution was reacted with additional water for 20 h to complete the hydrolysis and condensation. The total amount of water was equal to the 1.5 equiv of total alkoxides in the solution. Benzildimethylketal [BDK, $\text{C}_6\text{H}_5\text{COC}(\text{OCH}_3)_2\text{C}_6\text{H}_5$] used as a photoinitiator was introduced to polymerize the vinyl substituents in the composition before the coating process. The concentration of BDK was 5 and 10 mol% over total polymerizable methacryl groups in the MPTMS and MAA. All the chemicals were used as received without any purification. The prepared solution was then deposited on Si(100) wafers and fused silica substrates by the spin-coating method. A single coating yields approximately 4–5 μm thickness of the films. The films were illuminated by the UV lamp (300-W Xe) filtered at 350 nm wavelength for 0–60 min. The UV-illuminated films were dried at 70 °C for 30 min. Finally, the films were baked at 180 °C for 1 h. A schematic fabrication process is described in Fig. 1.

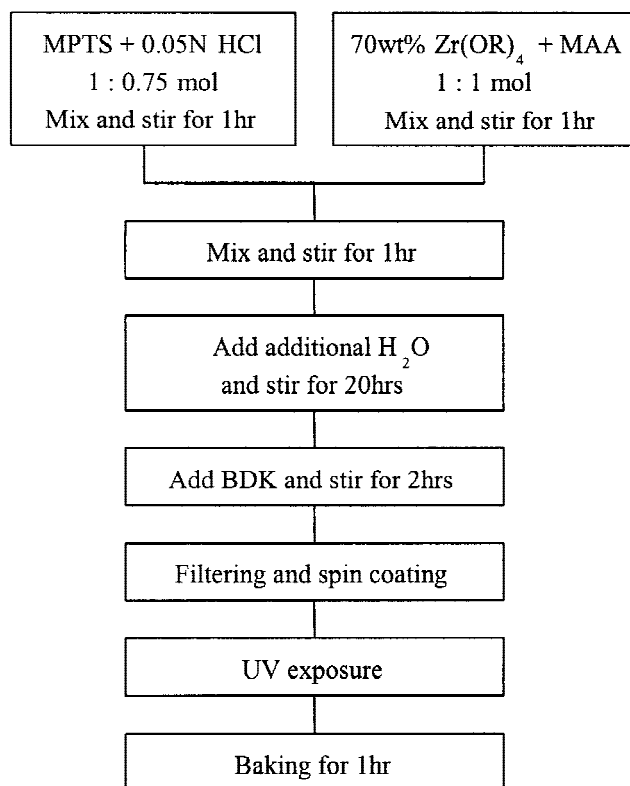


FIG. 1. Schematic flow chart for the preparation of sol-gel hybrid glass film doped with BDK.

B. Structural analysis and optical characterization

The structural evolution of the films on Si wafer was examined by Fourier-transformed infrared (FTIR, Bruker EQUINOX55, Billerica, MA) spectroscopy. All the measurements were performed in the 4000–400 cm^{-1} range with a resolution of 4 cm^{-1} . An UV/vis/NIR spectrophotometer (Shimadzu UV-3101PC, Kyoto, Japan) was used to examine the dissociation of BDK in the films on fused silica substrate.

The refractive index of the films was determined using a prism coupling method. The prism coupler was composed of a HeNe laser and semiconductor laser diode to obtain the refractive index at wavelengths of 632.8 and 1550 nm, respectively.

III. RESULTS

A. Photoinduced polymerization

Figure 2 shows FTIR spectra of the SGHG films containing 10 mol% BDK as a function of UV illumination time. The films were not dried, and it is assumed that the spectra show the effect of UV illumination without thermal curing. Band assignments of the FTIR spectra in the SGHG were already made in previous reports.^{11,14} The bands at 1720 and 1638 cm^{-1} in Fig. 2(a) represent the carbonyl group C=O stretching mode and the vinyl group C=C stretching mode, respectively. As the UV exposure time increases, the C=C stretching mode disappears, indicating that polymerization proceeds. As the polymerization proceeds, the C=O band shifts to higher wavenumber, showing that the carboxyl group does not conjugate with carbon double bond any more. Figure 2(b) also shows the formation of silicate network by further hydrolysis and polycondensation upon UV illumination. The Si–O–Si mode band at 1063 cm^{-1} becomes distinct as the other bands at 1168 cm^{-1} (–CH₃ rock of Si–OCH₃), 1012 cm^{-1} (CH wag of =CH₂), 980 cm^{-1} (CH₂ wag of =CH₂), 944 cm^{-1} (Si–OH), and 816 cm^{-1} (Si–O–C) diminish. Thus, the UV illumination may reduce both silanol and methoxy groups by enhancing alkoxide polycondensation. Similar results were found in the FTIR spectra of the SGHG films doped with photoinitiator, 1-hydroxycyclohexyl-1-phenylketone (HCPK), illuminated by deep UV light.¹¹ Figure 3 shows FTIR spectra of the SGHG films containing 10 mol% BDK composition after baking as a function of UV illumination time. After baking of the films, all the C=C bond peaks disappear regardless of UV illumination time as shown in Fig. 3(a). It is explained that the removal of the C=C bond peak is not made by the polymerization but by the thermal dissociation during baking the films. Figure 3(b) represents the distinguished Si–O–Si mode band at 1063 cm^{-1} eliminating other bands in all the films. Thus, it is found that

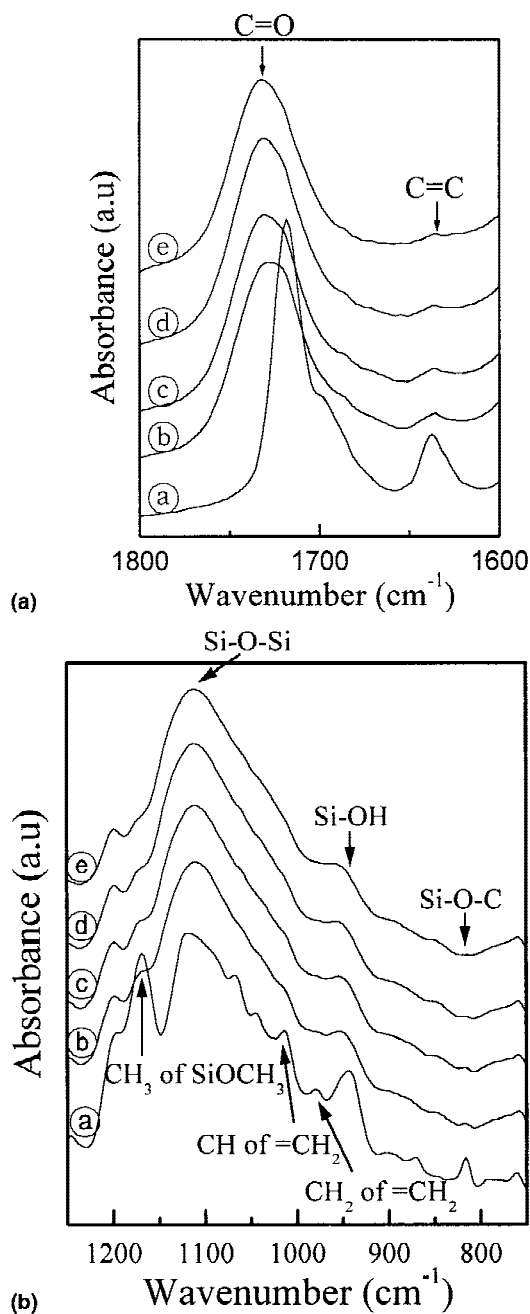


FIG. 2. FTIR spectra of (a) methacryl and (b) silanol, methoxy, and silicate groups in the films with various UV illumination times, (a) 0, (b) 5, (c) 10, (d) 20, and (e) 60 min, respectively. Samples are not dried.

the baking allows further polycondensation of the silicate glass network and densification of the films by removing hydroxy and methoxy groups in the films.

B. Photoinduced refractive index change

Figure 4 shows the change in refractive index of the films containing 5 and 10 mol% BDK, respectively, after baking process. As the UV illumination time increases from 0 to 60 min, the refractive index of all the films

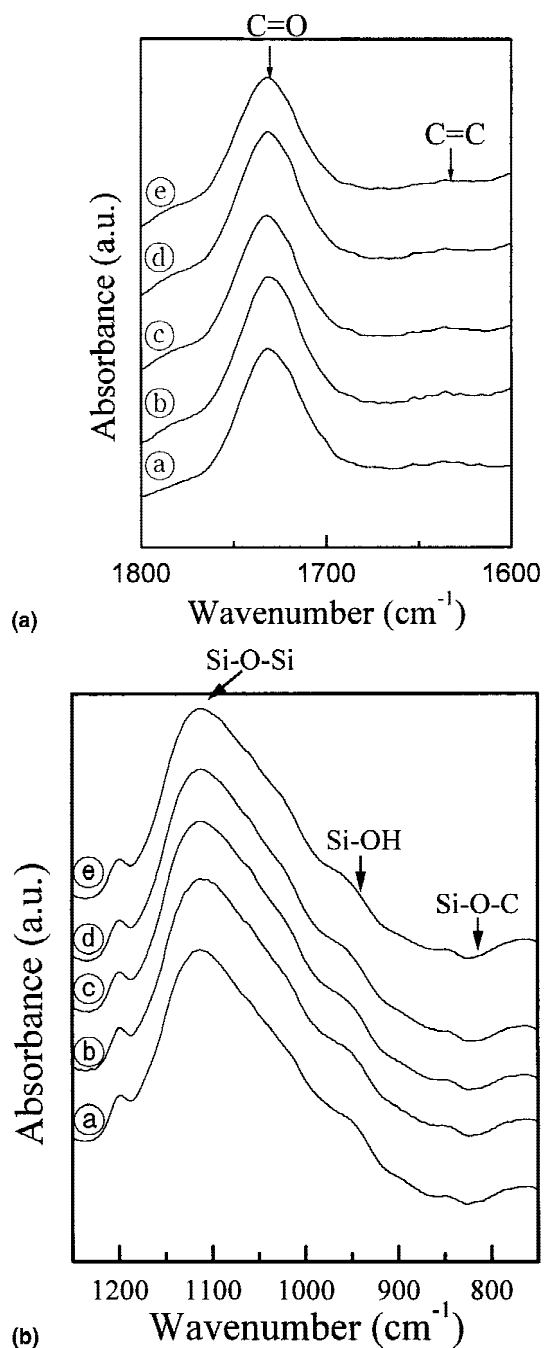


FIG. 3. FTIR spectra of (a) methacryl and (b) silanol, methoxy, and silicate groups in the films with various UV illumination times, (a) 0, (b) 5, (c) 10, (d) 20, and (e) 60 min, respectively. All the samples are baked at 180 °C for 1 h.

increases and then is saturated. Thus, the refractive index change during the UV exposure is found in all the films as already shown in other studies.^{8,10} The refractive indices of the 5 mol% BDK films at 633 and 1550 nm increases from 1.523 and 1.506 to 1.529 and 1.513, respectively. Thus, the refractive index increase is 0.006 and 0.007 at 633 and 1550 nm, respectively. For the 10 mol% BDK films, the refractive indices at 633

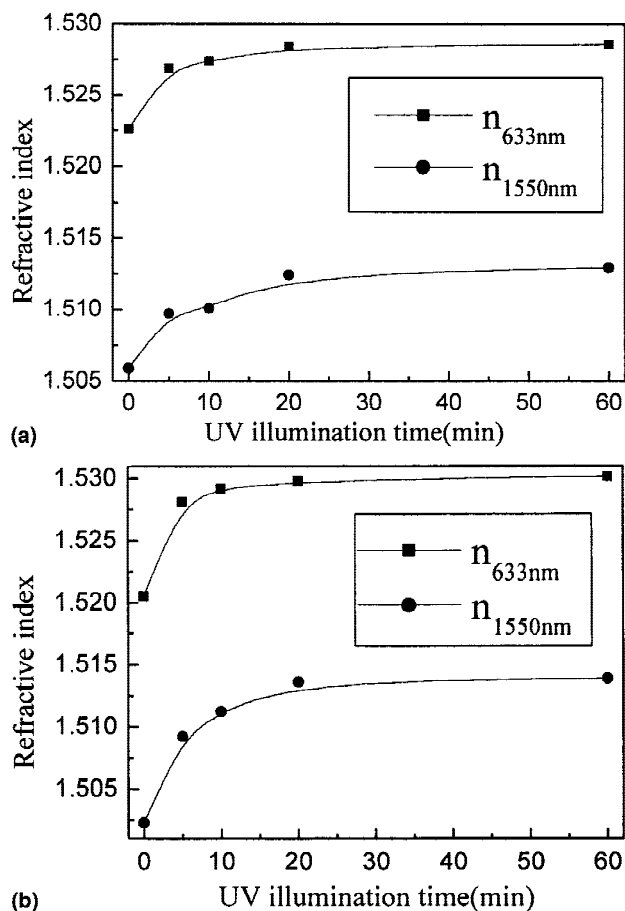


FIG. 4. Refractive index change in the films doped with (a) 5 mol% BDK and (b) 10 mol% BDK concentrations as a function of UV illumination time. All the samples were baked at 180 °C for 1 h.

and 1550 nm increase from 1.521 and 1.502 to 1.530 and 1.514, respectively. Thus, the refractive index increase is 0.009 and 0.012, respectively. The refractive index of the unexposed films is almost the same regardless of BDK concentration. Because BDK in the unexposed film is not photodecomposed, BDK can be removed during baking, which was already found in previous studies.^{12,13} Thus, the unexposed film with higher BDK concentration may be less dense than that with lower BDK resulting in reduction of the refractive index. However, the higher refractive index is obtained for the UV illuminated film, as BDK concentration is larger. Also, the refractive index increase is larger for the higher BDK concentration film. Thus, it is found that the photosensitivity of the SGHG film is closely related to BDK concentration.

IV. DISCUSSION

Discussion will be made on polymerization kinetics, because it is related to the change of the refractive index of the films. In the early stage of UV illumination, the C=C bonds are rapidly consumed by the photodecomposition of BDK and initiation of polymerization of

methacryl group in MPTMS and MAA. Then, the consumption of the C=C bonds slows down because the propagation step requires diffusion of monomeric species. The formation and destruction of radicals occur at the same rate shortly after the reaction begins, which implies a steady state. For most free radical polymerizations, the polymerization kinetics at steady state can be expressed by the following equation:¹⁵

$$-\frac{d[M]}{dt} = k_p[M] \sqrt{\frac{fk_d[I]}{k_t}}$$

where $[M]$ is the total concentration of all chain radicals, $[I]$ is the concentration of initiator, and f is the fraction of initiator radicals that actually start a polymer chain and are not consumed by side reactions. k_p , k_t , and k_d represent the rate constants for propagation, termination, and dissociation of initiator, respectively. Since $[I]$, k_d , k_t , and f are independent of $[M]$, the concentration of monomer should be reduced logarithmically as the reaction proceeds. The C=C stretching mode band areas at 1638 cm^{-1} in Fig. 2 are integrated and represented depending on the UV illumination time in Fig. 5. Since the band area is proportional to methacryl monomer concentration, the reduction of the band area can represent

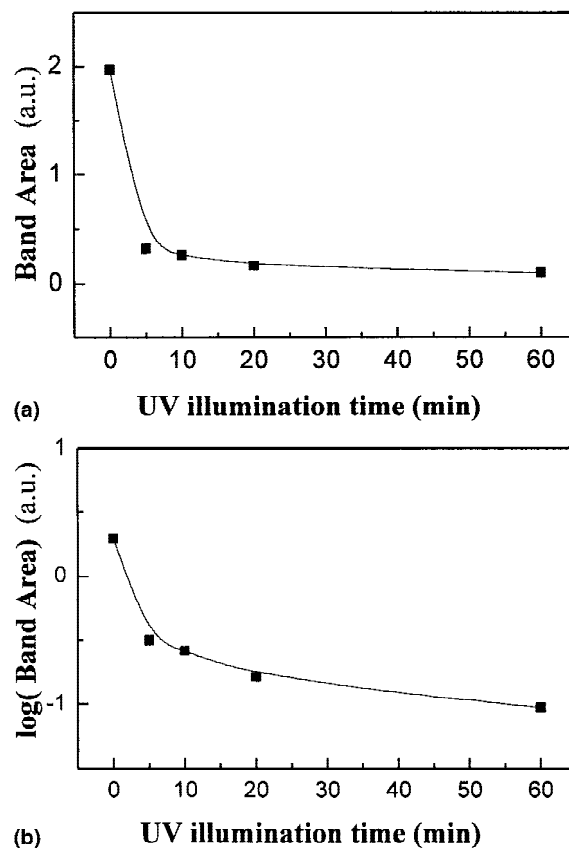


FIG. 5. (a) Normal and (b) logarithm plot of the C=C stretching mode band area at 1638 cm^{-1} as a function of UV illumination time. Samples are not dried.

degree of polymerization. The band area is reduced suddenly in initial UV illumination but slowly decreases after 5 min of UV illumination as expected. Thus, a linear relationship is found between $\log [M]$ (band area) and reaction time (UV illumination time) after reaching steady state, as shown in Fig. 5(b). This behavior agrees well with general polymerization kinetics.

In a comparison of the refractive index change and the polymerization kinetics as shown in Figs. 4 and 5, respectively, their dependence on the UV illumination time is different. The refractive index change is slower than the polymerization kinetics although they should be identical if it is assumed to be made by the polymerization. It was found that the UV illumination also enhances the alkoxide polycondensation reaction. Thus, the photoinduced condensation of inorganic groups contributes to the refractive index change depending on the UV illumination time. However, since the polycondensation of inorganic groups is mainly made by thermal energy from the result of Fig. 3, the effect of thermal energy on the refractive index change is assumed to be the same in the baked films. Therefore, another factor to increase the refractive index can be the incorporation of photodecomposed radicals in the SGHG network since the refractive index change is sensitive to BDK concentration. Actually, it was found that the radicals produced by photodecomposition of BDK are locked or fixed in polymers to increase the refractive index while BDK is very mobile

to diffuse out during baking of the polymers.^{12,13} To monitor the photodecomposition of BDK, the UV absorptions of the films were examined depending on the UV illumination time. When BDK is irradiated by UV light, it is activated by an $n(sp) \rightarrow M^*$ transition within the molecular orbits of the $>C=O$ group. This transition is followed by an α -splitting.¹³ If BDK is photodecomposed to two radicals, they can initiate polymerization or make a new molecule by the coupling of two benzoyl radicals.¹² Detailed schemes of BDK photochemical reactions are represented in Fig. 6. The absorption peak of BDK around 350 nm decreases as the photodecomposition proceeds. Figure 7 presents the decrease in the area of the absorption peak at 350 nm with increasing UV illumination time. The curve-fitting technique was employed to obtain the component absorption band area. When BDK is decomposed to the radicals, the initiating radicals may rapidly react with polymerizable methacryl groups as shown in Fig. 6. Also, the radicals produced by the photodecomposition of BDK can undergo coupling of two benzoyl radicals to make a benzil molecule as shown in Fig. 6. In the present study, there was no absorption peak at 380 nm that would be caused by the benzil molecule.¹³ The benzil molecule is also photosensitive and undergoes further photochemical reaction during UV illumination. Therefore, the coupling effect of the benzoyl radicals may be neglected in BDK-doped SGHG. Anyway, the radicals produced by photodecomposition of BDK may be incorporated into the SGHG network, which are then not mobile and volatile remaining after baking. This phenomena was already found and called "photolocking" in BDK-doped poly(methyl methacrylate) (PMMA).¹⁶

The radicals produced by photodecomposition of BDK have high electronic polarizability due to the phenyl group in the radicals. Thus, the incorporation of the radicals in the SGHG can increase the refractive index of the films. The BDK absorption band area may be considered

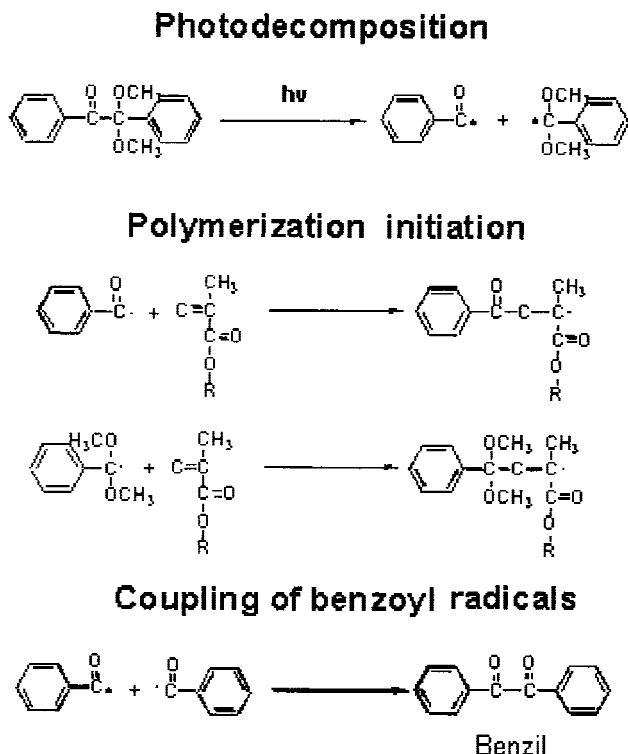


FIG. 6. Schematic diagram for the possible photochemical reactions of BDK.

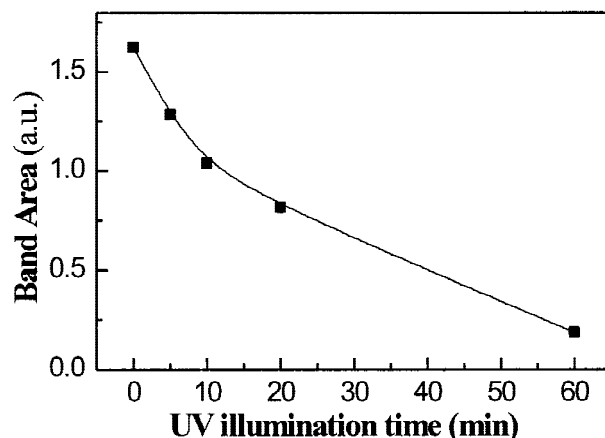


FIG. 7. Change in UV absorption band area at 350 nm as a function of UV illumination time. Samples are not dried.

as the quantity of the incorporated radicals in the methacryl groups. Thus, the reduction of the BDK absorption band area can represent the refractive index increase by the incorporation of the radicals in the SGHG. This indicates that the incorporation of the radicals produced by photodecomposition of BDK in the host may be another factor to increase refractive index of the films upon UV illumination. The decrease in the BDK absorption band area in Fig. 6 is slower than the polymerization kinetics in Fig. 5. Therefore, the photoinduced refractive index change results from the combination of the photodecomposed radical incorporation and the methacryl photopolymerization. Actually, the appropriate combination of the variations of the polymerization kinetics (Fig. 5) and the BDK absorption band area (Fig. 6) can produce the refractive index change (Fig. 4). As a result, BDK can be used as a refractive index modifier as well as a photoinitiator in the SGHG. The higher photosensitivity may be obtained in the higher BDK-doped SGHG.

V. CONCLUSION

BDK-doped SGHG films were prepared by using [(methacryloxy)propyl]trimethoxysilane, zirconium *n*-propoxide, methacrylic acid, and benzildimethylketal. The UV illuminations polymerize the methacryl group initiated by photodecomposition of BDK and enhance the polycondensation of alkoxides in the SGHG. The more cross-linked structure can be obtained when the films are first polymerized by UV irradiation and then baked to complete the condensation and the densification.

The refractive index of the film increases with increase of the UV illumination time. Also, the increase in the refractive index is higher for the higher BDK concentration. BDK is photodecomposed to the radicals that can be incorporated in the SGHG network increasing the refractive index of the film. Thus, the photoinduced refractive index change in the SGHG doped with BDK is made by the incorporation of the radicals produced by photode-

composition of BDK in the host as well as by the photopolymerization of methacryl groups. Therefore, BDK can act as a refractive index modifier as well as a photoinitiator in the SGHG.

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