

Fabrication of Polarization Gratings on the Sol-gel Film Bearing Silylated Chalcone and Disperse red 1

Dong Hoon Choi* and Young Ha Kwon

Department of Textile Engineering, Materials Center for Information Display, Kyung Hee University,
Yongin, Kyungki 449-701, Korea

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Abstract : We report the diffraction behavior of the functionalized sol-gel film composed of two different silanes. One silane (SGDR1) contains disperse red 1 (DR1) that is composed of an azobenzene unit. The other silane (SGCHC) bears a chalcone derivative that is photocrosslinkable under UV irradiation. Two-beam coupling method was employed for fabricating the diffraction gratings. The dynamics of formation and erasure of the gratings was studied in term of the variation of the diffraction efficiency. The decaying behavior of the polarization efficiency was also observed after turning off the two pump beams. For complete erasure of the diffraction gratings, we irradiated the linearly polarized single beam. During two-beam coupling, we irradiated UV light on the film surface. The effects of the photocrosslink between the double bonds in chalcone units on the value and dynamic properties of diffraction efficiency are mainly studied in this work.

Introduction

In recent years, organic and inorganic hybrid materials prepared through sol-gel process have been attractive as optoelectronic materials and their applications.¹⁻³ Sol-gel process with silicon multialkoxides can form various microstructures as a transparent matrix at low temperature.^{4,5} Silicon alkoxide can be hydrolyzed in the presence of water and a catalytic amount of acid or base. The hydrolysis and condensation of organically functionalized metal alkoxides lead to the preparation of new hybrid organic-inorganic compounds exhibiting unique properties. Silicon trialkoxide derivatives can be designed to bear a functional chromophore in one arm of silicon through a flexible spacer. We introduced the azoaromatic chromophore in the side chain of the sol-gel precursor and fabricated the thin film containing silylated chalcone that is photocrosslinkable.

Materials containing azoaromatic chromophores have drawn much interest in the field of optical

data storage, nonlinear optical, and holographic applications.⁶⁻¹⁰ Optically induced anisotropy in the azobenzene-containing film is a very promising property for optical information storage and erasing. The mechanism of writing information involves photo-induced excitation of the azobenzene group, which undergoes *trans-cis-trans* isomerization. This phenomenon results in photo-induced birefringence through the reorientation of azobenzene molecules. The anisotropic polar molecular distribution gives rise to birefringence and dichroism in the film. Under irradiation of the linearly polarized single beam, we can observe the process of the photo-induced anisotropy in the thin film.

Besides the single beam excitation, two-beam coupling on the film surface drove dramatic change of the optical properties in the localized area of the film. Erasable gratings formed in the films of azobenzene-containing materials have been studied extensively since they were first reported by Todorov *et al.*^{11,12} Recently, surface relief gratings (SRG) have been fabricated in the side chain or the main chain azo-polymer film through repeated photoisomerization upon exposure to the

*e-mail : dhchoi@khu.ac.kr

excitation light with an interference pattern.¹³⁻¹⁵ Photo-anisotropic materials like the azobenzene-containing polymers respond to variations in both the intensity and the polarization state of the total electric field of the coupled light. With the proper combination of the polarizations of the two pump beams, we can achieve the pure polarization gratings in the film without large surface modulation. S- and p-polarized pump beams were employed to induce the polarization grating on the surface of the azobenzene-containing film.¹¹

In principles, polarization gratings can be also produced by isomerization and molecular reorientation of the azobenzene chromophore, induced by coupling of the two coherent beams whose polarizations are orthogonal each other. Periodic patterns with different polarizations are formed upon exposure to the appropriate optical light source by a single-step process. All the organic polymers that show efficient polarization gratings reported to date contains azobenzene chromophores in their side groups. However, there has been quite a few report on the formation of diffraction gratings on the sol-gel film that carries the azobenzene chromophore and no report on variation of the diffraction efficiency under pumped two-beam coupling method.

In this work, we report on the properties of the photosensitive sol-gel film for fabricating the diffraction grating controlled by a coupled linearly polarized (s-, p-) visible light ($\lambda = 488$ nm). Fast induction of the periodic optical anisotropy was investigated using the sol-gel film in detail. The dynamics of the diffraction efficiency was investigated under two-beam coupling experiment. Then, we observed the change of the value of the diffraction efficiency under UV-irradiation during two-beam exposure. The effect of the photocrosslinked structure between the chalcone units on the value of the diffraction efficiency and its dynamic properties of the diffraction gratings were also studied.

Experimental

The synthetic procedure of SGDR1 and SGCHC was described in detail in our previous results.¹⁶

Material Processing. For preparing the solution

to fabricate the thin film, SGDR1 (0.5 g, 0.89 mmole) and SGCHC (0.459 g, 0.89 mmole) were dissolved in THF (4 mL). Water and HCl were added into the solution for hydrolysis and condensation. The molar composition of the solution is as follows: SGDR1/SGCHC : H₂O : HCl : THF = 1 : 4 : 0.01 : 2. The viscous solution was stirred at room temperature for 24 hrs. The solution was filtered before spin coating with a 0.2 μ m filter. Films were spun at about 1,000 rpm on the borosilicate glass for the diffraction grating experiments. It is noted that the films were dried under vacuum at 50 °C for 48 hrs.

Formation of the Polarization Grating.

The gratings on the thin sol-gel films were recorded under ambient conditions with the interference pattern produced by a linearly p-polarized argon-ion laser at 488 nm (Lexel 100 mW/cm²). Figure 1 shows the two-beam coupling setup for this experiment. Laser beams with s- and p-polarizations were used to be coupled on the film surface. The angle between the two beams is approximately 6°. Two writing beams with an equal intensity (50 mW/cm²) were crossed in the sample film and produced the interference pattern with the fringe spacing. Under this condition, the resulting grating was in the Raman-Nath grating regime which is known to generate multiple-order diffraction. A linearly polarized He-Ne laser light ($\lambda = 633$ nm) with weak intensity (1 mW) was used as a probe beam, which was incident at normal to the surface of the polymer film. The grating formation was monitored by measuring the intensity of the first-order diffracted beam and that was determined by the ratio of intensities between the incident probe and the diffracted beam. During irradiation of the coupled beam, we focused the UV light on the coupled spot using a high pressure Hg lamp equipped with a liquid optic cable.

Results and Discussion

We prepared the photosensitive triethoxysilane (SGDR1) by reaction between alcohol and isocyanate. The synthetic methods of 4-hydroxychalcone (HC) and 4-(2-hydroxyethoxy)chalcone (HEC) were already known.^{17,18} After synthesizing the HEC, it was reacted with isocyanate to give a silylated

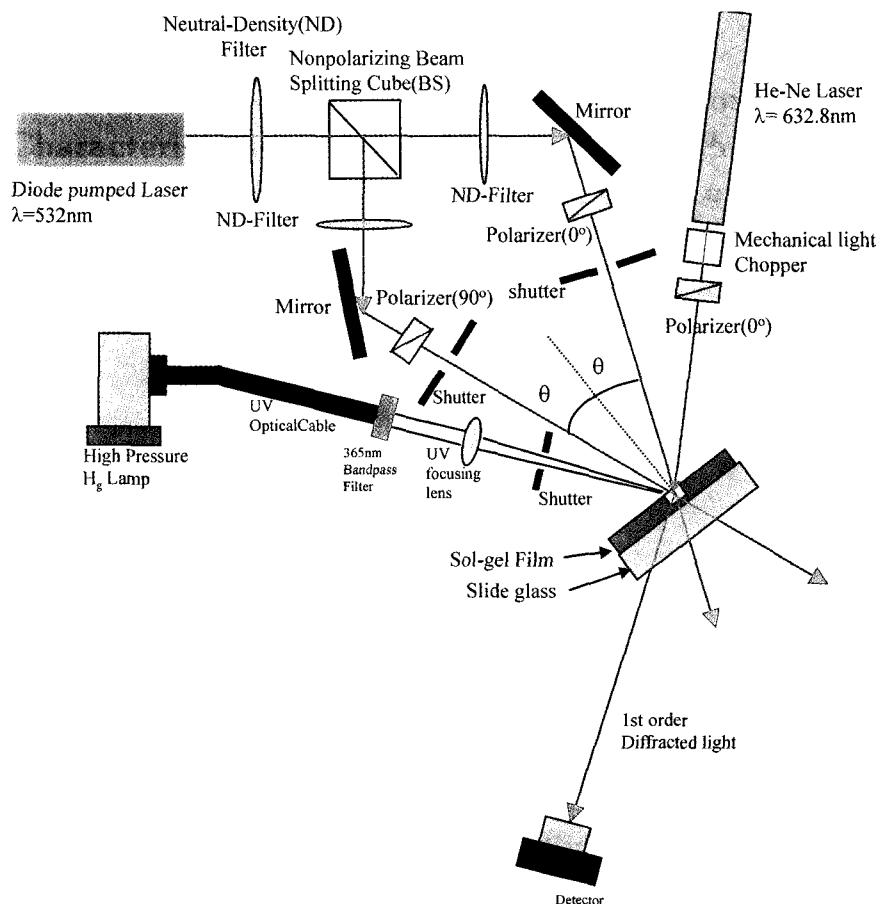


Figure 1. Optic setup for measuring the intensity of the first order diffracted light. The UV light source was involved in this setup for two-beam coupling with UV curing.

chalcone (SGCHC). NMR and IR spectroscopy characterized the structures of all compounds used herein. Synthesis and the structures of compounds are illustrated in Figure 2. SGDR1 and SGCHC are well soluble in THF, acetone, dimethylformamide, pyridine etc. After hydrolysis and condensation, we could fabricate quite transparent films using the sol.

Photochemical Reaction of the SGCHC Films. The UV-induced $2\pi + 2\pi$ cycloaddition reaction of SGCHC that bears the chalcone in the side group was investigated by the UV irradiation with a high pressure Hg lamp. Chalcone is well known compound that can be dimerized under UV ($\lambda = 300\text{-}365\text{ nm}$) exposure. Cycloaddition reaction can be performed to form a cyclobutane

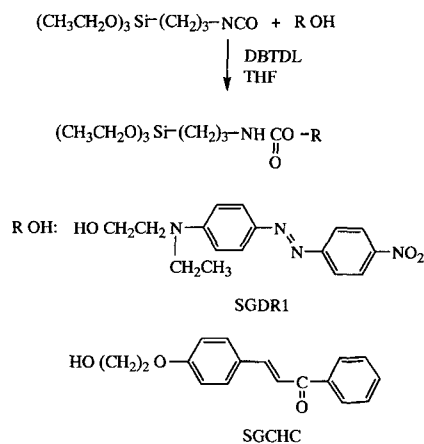


Figure 2. Synthesis and structures of SGDR1 and SGCHC.

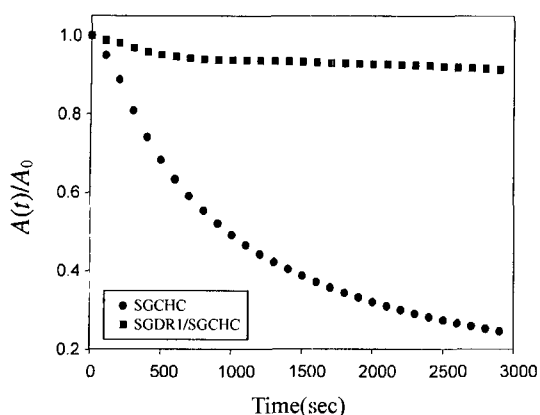


Figure 3. Change of the absorbance at 336 nm under UV irradiation. *Sample: SGCHC and SGDR1/SGCHC film

between two chalcone molecules. The chalcone compound possesses very high absorption coefficient, ϵ around 300-365 nm. The rate of reaction is relatively faster than that of cinnamoyl derivative under the light from a high pressure Hg lamp.

Photosensitivity of the SGCHC and SGDR1/SGCHC film was investigated under UV exposure (365 nm, intensity 0.5 mW/cm²). UV-VIS absorption spectra of SGCHC were recorded to observe the absorbance at λ_{max} . The samples were not dried at high temperature ($\sim 200^\circ\text{C}$) so that the glass transition temperature of the matrix is expected very low due to the low degree of polymerization.

Immediately apparent is the decrease of the absorbance at 336 nm. Using the change of the absorbance at 336 nm, we could consider the rate of cycloaddition reaction (See Figure 3). The decaying behavior of absorbance at 336 nm can be analyzed by a stretched exponential function (equation (1)).

$$A(t)/A_0 = \exp(-(t/\tau)^\beta) + R \quad (1)$$

where $A(t)$ is the absorbance at 336 nm after UV exposure for time t and A_0 is the absorbance at 336 nm before UV exposure. β is the stretching parameter and R is the residual fraction of the absorbance at 336 nm.

The relaxation times, τ of the SGCHC and SGDR1/SGCHC sample were obtained to be 940 and 1,160 sec respectively after fitting the data of

normalized absorbance to a single exponential function. We can compare the rate of photocrosslink in the mixed film of SGDR1/SGCHC and only SGCHC film with the change of composition. The rate of disappearance of the $\pi-\pi^*$ absorption band in C=C bonds indicates that the photoreactivities of the sol-gel films are highly affected by the concentration of SGCHC. After 3,000 sec irradiation, 90% of the initial absorbance remained in the SHDR1/SGCHC film, which is much larger than that in SGCHC film. Compared with the decaying rate in the homogeneous SGCHC film, it is much slower due to the low concentration of SGCHC and geometrical hindrance of chalcone unit in the mixed film. The mechanism of the reaction is similar to that of cinnamic acids and its derivatives in which cyclobutane structure was formed.

In order to investigate the effect of photocrosslink on the diffraction efficiency, we have to irradiate the UV light on the film surface for longer than 3,000 sec under the same intensity used herein.

Infrared Spectra of SGCHC Film before and after UV Exposure. We could observe the evidence of the photocrosslinking reaction through the change of the IR spectrum before and after UV irradiation. The IR spectra of the SGCHC films with chalcone derivative showed strong absorption at $\nu_{\text{C=O(s)}} = 1661$ and $\nu_{\text{C=C(s)}} = 1605$ cm⁻¹ before irradiation, which can be assigned to the carbonyl stretching vibration in unsaturated ketone and the ethylenic double bond stretching vibration in the chalcone unit (See Figure 4). Additionally, another absorption band of the carbonyl stretching vibration appeared around 1690 cm⁻¹ in the carbamate, which is mostly hydrogen bonded with the proton in the secondary amine. First, the absorbance of the ethylenic double bond stretching vibration at 1605 cm⁻¹ decreased after UV irradiation ($t = 60$ min, $I = 5$ mW/cm²). At the same time, the absorption band at 1661 cm⁻¹ disappeared and the new band around 1675-1680 cm⁻¹ appeared. During UV exposure, the two unsaturated double bonds formed the cyclobutane ring so that the saturated carbonyl stretching band appeared at the higher wavenumbers. However, the new absorption band at the higher

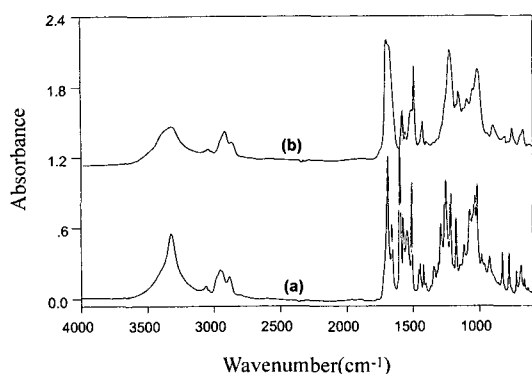


Figure 4. Infrared spectra of SGCHC film before and after UV irradiation. (a) Before irradiation; (b) After irradiation.

wavenumber was not clearly isolated because it overlapped with the stretching band of the hydrogen bonded carbonyl group in the carbamate. The absorption intensity at 1691 cm^{-1} decreased and the intensity at 1721 cm^{-1} increased after UV irradiation. Appearance of the new isolated carbonyl stretching band around 1721 cm^{-1} is mainly attributed to the geometrical hindrance for hydrogen bond formation between the carbonyl group and the secondary amine in the carbamate. The absorption band around 3331 cm^{-1} can be assigned to the stretching vibration of the secondary amine. The absorption band at 3430 cm^{-1} is due to the stretching vibration of the isolated secondary amine group and its intensity increased after UV irradiation. Resulting from the above infrared spectral analysis, we could confirm the formation of the cyclobutane between the two chalcone units arising from cycloaddition.

Polarization Grating on the Sol-Gel Film.

Two-Beam Coupling: The polarization holographic recording was accomplished by two plane waves with mutually orthogonal polarizations (s- & p-) at 488 nm wavelength. In this type of writing, the resulting light electric field is not modulated by intensity but only by pure polarization. The induced optical anisotropy (dichroism or birefringence) is spatially modulated in accordance with the polarization modulation of the electric field of the pump light. A photoanisotropic material can be used to record this periodic polarization modulation as a spatially varying redistribution of the orientation-

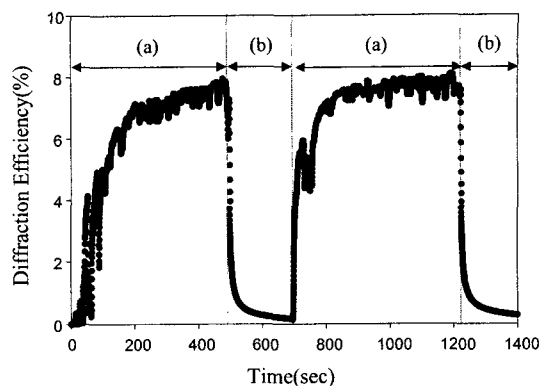


Figure 5. Diffraction efficiency of SGDR1/SGCHC(1:1) film as a function of exposure time. (a) Two beam exposure; (b) Single beam exposure. *Probe beam: He-Ne laser $\lambda = 632\text{ nm}$, 1 mW/cm^2 .

ally dependent probability that the dye molecules are in the *cis* or the *trans* state.

The periodic distribution of the anisotropy depends on the intensity of the pump beam, dye concentration, and the unique properties of the investigated polymers. The experimental results from two-beam coupling in the SGDR1/SGCHC sample is shown in Figure 5.

We observed that the stable diffraction gratings could be fabricated on the film at room temperature. We could also observe the variation of diffraction efficiency under optical writing and erasing process. Under the polarizations (s-, & p-) of the coupled beams we used herein, the interference patterns only have pure polarization variation. It was relatively easy to remove the diffraction gratings under a single beam irradiation compared to those inscribed by intensity and polarization variation within the grating period. When the polarization hologram is erased by thermal or optical method, it can be recorded again and the same value of diffraction efficiency can be achieved after multiple use.

As shown in Figure 5, the experimental curve exhibits an initial rapid growth of the diffraction efficiency up to $\eta = 8\%$ corresponding to the formation of the reversible polarization gratings. During irradiation of the single beam, a fast relaxation of the diffraction efficiency occurs. It is known that the birefringence grating of azo polymer films, which

was formed due to photo-induced alignment of the azo chromophore is photoerasable by single laser beam exposure easily. Under the single beam irradiation, the periodicity of the grating diminished gradually and the reorientation of all azo molecules occurs to the specific direction. We can observe two regimes of diffraction efficiency in the writing and optical erasing process. The fast process in recording is due to the pump condition and quantum yield of photoisomerization according to the angular hole burning model.¹⁹ The mechanism of the formation of the diffraction gratings is based on the selective photochemical excitation of *trans* chromophore having a component of their dipole in the same direction as the laser polarization. The *trans* chromophore will undergo *trans-cis-trans* photoisomerization cycles, accompanied by a change of orientation of the chromophores toward the perpendicular direction with respect to the polarized light. This uniaxial angular reorientation induces a strong modification of the optical properties. The induction and removal of the periodic birefringence of the sol-gel film are remarkably fast. Irradiation of the coupled pump beam on the sol-gel film results in a very fast periodic redistribution of the chromophore. In this case, no residual diffraction efficiency after optical erasing process was observed. The fast decay can be attributed to the fast randomization of the periodic dipole reorientation. Shortly, the sol-gel film has some advantages to control the degree of polymerization and to control the glass transition temperature easily. Then, at ambient conditions, the diffraction grating can be highly resolved and the erasure process can be also performed very fast without any residual trace.

Two-beam Coupling with UV Curing: We performed the different experiment using the same sample used above. First of all, we irradiated the coupled beam on the film surface. When the first order diffracted intensity was saturated, we start to irradiate the random polarized UV light isolated with 365 nm band pass filter. The periodic regularity of the grating was well defined before UV irradiation. However, under UV irradiation, the diffraction efficiency gradually decreased to almost half of the initial signal for 5,000 sec. This implies that the highly resolved periodic distri-

bution of the chromophore was interrupted by the formation of the cyclobutane between the double bonds in the chalcone unit. The cycloaddition reaction proceeded slowly to disrupt the orientation of the azobenzene chromophores as the UV exposure time elapsed.

We now compared the temporal stability of the diffraction efficiency using the two samples. One is the Sample 1 to which two excitation beams ($\lambda = 488 \text{ nm}$, 50 mW/cm^2) were coupled only. The other one was exposed to the coupled beam and the UV light (Sample 2). When we blocked the two excitation beams, the diffraction efficiency showed relaxation with the elapsed time at room temperature. The decrease in efficiency for phase gratings is easily explained by the angular thermal relaxation process of the chromophores. After the diffraction intensity reached to the maximum, we blocked the two excitation beams to integrate the decaying signal (Sample 1, Figure 6). Afterwards, the two excitation beams were coupled to the film for 800 sec and then UV light was focused on the film in the presence of the coupled beam for 5,000 sec. Then, we blocked the all beams except probe beam ($\lambda = 632 \text{ nm}$, 1 mW/cm^2) (Sample 2, Figure 7). In the case of the Sample 1, the diffracted signal decayed to a half of the signal within 900 sec that is quite fast. The fast decaying behavior was observed in the initial exposure period. However, the efficiency was stabilized to a certain level and

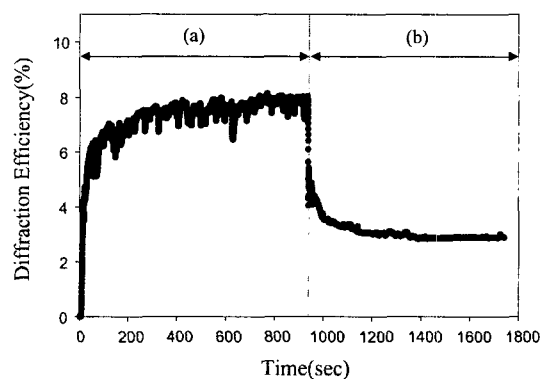


Figure 6. Variation of the diffraction efficiency during two-beam coupling and after blocking them. (a) Two-beam exposure; (b) After blocking the two coupled beams. *Probe beam: He-Ne laser $\lambda = 632 \text{ nm}$, 1 mW/cm^2 .

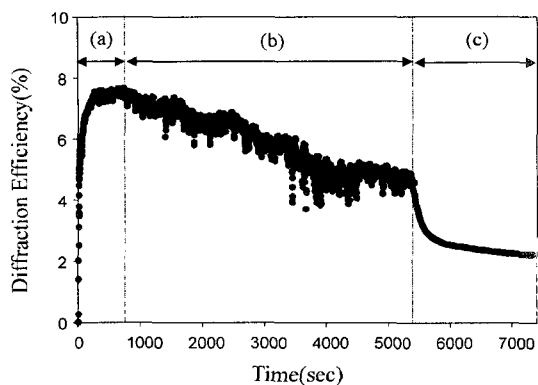


Figure 7. Variation of the diffraction efficiency. (a) Two-beam exposure; (b) Two beam and UV light exposure; (c) After blocking all excitation beams. *Probe beam: He-Ne laser $\lambda = 632$ nm, 1 mW/cm².

then did not vary much. The decrease in efficiency for phase gratings is easily explained by the angular thermal relaxation process of the chromophores. Although the diffraction efficiency was decayed under UV irradiation, the diffracted signal of the Sample 2 decayed relatively slower than that in the Sample 1 after blocking the two excitation beams. When we use the equation (1) to analyze these data, the relaxation time, τ of the Sample 2 is around 230 sec that is quite larger than that of the Sample 1 ($\tau = 32$ sec). This is attributable to the restriction of the molecular rearrangement resulting from the cycloaddition reaction. The density of the matrix was increased higher than that of the Sample I. Due to the geometrical hindrance of the azobenzene chromophore, the rate of decay retarded much smaller than that of the Sample 1.

We are attempting our efforts to induced the photocrosslinking reaction between the side chains bearing the azobenzene chromophore and the effect of them on the dynamic properties of the diffraction gratings.

Conclusion

We prepared the heterogeneous composite film using SGDR1 and SGCHC for studying the dynamics of the polarization gratings. Chalcone group in SGCHC showed photodimerization in the

solid state resulting from 2 + 2 cycloaddition reaction. This gave rise to crosslink formation between the double bonds in the two chalcone groups. Decaying property of the diffraction efficiency in sol-gel neat film was improved using our photoreactive silicon precursor (SGCHC) although the photocrosslinked structure reduced the diffraction efficiency during UV irradiation. Densification of silicon oxide and photo-crosslink in the organic parts have been proved to be effective in improving the temporal stability of the diffraction efficiency.

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