



Photobleaching of γ -Glycidoxypropyltrimethoxysilane-Chelated Metal Alkoxide Gel Films

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Abstract. Thick photosensitive inorganic-organic hybrid gel films are fabricated using a silica-PEO(poly(ethylene oxide)) polymeric network and several chelated metal alkoxides: $\text{Ti}(\text{OEt})_4$, $\text{Al}(\text{OBU}^{\text{sec}})_3$, $\text{Zr}(\text{OPr}^t)_4$. The γ -glycidoxypropyltrimethoxysilane (GPTS) and the metal alkoxides stabilized by β -ketoester or β -diketone are used as precursors. The chelated metal complex in the gel films are photodecomposed and forms the oxide network by UV exposure. The photodecomposition of the chelate ring and the photobleaching of the UV absorption bands are investigated as a function of UV exposure time. The photobleaching rates with respect to chelating agents, metal alkoxides and photon energy are compared.

Keywords: inorganic-organic hybrid gel, chelated metal complex, γ -glycidoxypropyltrimethoxysilane, photodecomposition, photobleaching

1. Introduction

γ -glycidoxypropyltrimethoxysilane (GPTS) is a useful precursor for sol-gel preparation of inorganic-organic hybrid materials. The silica network is formed by hydrolysis and condensation of a methoxy radical in the presence of water, and the poly(ethylene oxide) polymeric network is made by the polymerization of the epoxy ring with an addition of polymerization initiator [1]. Crack free thick films of the silica PEO hybrid materials can be prepared due to the flexibility of the polymer in silica network. On the other hand, metal alkoxides are very reactive to hydrolysis and condensation. Thus, the chemical modification of metal alkoxides with organic additives such as β -diketones and β -ketoesters is known to be a very effective method to control the reactivity of metal alkoxides and the final properties of the gels [2]. These chemically modified metal alkoxides present an optical absorption band in the UV-region due to the photoexcited π - π^* transition state of 6-membered chelate ring. A number of photochemical studies involving β -diketonated metal

complexes have shown that a photon dissociates the chelate bond by excitation of π - π^* transition and reduces their solubility in organic solvents or acid aqueous solutions due to the structural changes associated with the photodecomposition of chelate rings [3, 4]. Thus, the direct photoinscription of inorganic sol-gel materials is possible via the photochemical feature of β -diketone in sol-gel matrix [3, 4]. This method has been used to fabricate micropatterning, gratings, and planar waveguides [5]. The chelated metal complex can be incorporated with inorganic-organic hybrid materials to fabricate micropatterning of thick hybrid gel films. In this paper, we investigate the photochemical properties of gel films fabricated using GPTS as a precursor for hybrid materials and the chelated metal alkoxides, $\text{Ti}(\text{OEt})_4$, $\text{Al}(\text{OBU}^{\text{sec}})_3$, $\text{Zr}(\text{OPr}^t)_4$, as a refractive index modifier as well as a photobleaching agent.

2. Experimental Procedure

GPTS was used as a precursor for a silica polymeric network. 1-methylimidazol (MI) was used as a catalyst as well as a polymerization initiator of the epoxy

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group. Homogeneous metal alkoxide solutions were prepared by chelating the metal alkoxides $\text{Ti}(\text{OEt})_4$, $\text{Al}(\text{O}i\text{Bu}^{\text{sec}})_3$, and $\text{Zr}(\text{OPr}^n)_4$ with ethyl acetoacetate (EAcAc) or 1-benzoylacetone (BzAc) in a 1 : 1 molar ratio. Through the careful cohydrolysis of the two systems, a photosensitive sol solution was obtained. Gel films were deposited on various substrates, a Si wafer for FT-IR and a fused silica for UV-spectrophotometer, by spin coating. Film thickness of 6–10 μm varies with spin-coating speed. Depending on the kind of chelating agent, UV absorption band appears in a different wavelength. For UV exposure, we used 1000 W Xenon arc Deep-UV (220–260 nm) lamp (ORIEL 82511 model) and 300 W xenon arc Near-UV (350 nm) lamp. Photobleaching and photodecomposition were examined using UV absorption spectra and FT-IR spectra of the gel, respectively, as a function of UV exposure time.

3. Results and Discussion

A nucleophilic reaction between β -diketones and metal alkoxides results in the transfer of an acidic γ -hydrogen from the β -diketones to an alkoxy ligands, so the 6-membered chelate ring is formed [6, 7]. The photoexcited π - π^* transition state is generated at the 6-membered chelate ring when it is exposed to UV light. The photoexcited antibonding Lignad Field (LF) state (π - π^*) descends rapidly upon metal-chelate bond lengthening and crosses with non-dissociated lower states [8]. This is the general mechanism of metal-carbonyl dissociation. Using the photodissociation features of the metal-chelate complex, the gel structure can be controlled; that is, the leaving of the chelate agent leads to a further hetero- or homo-condensation of metal alkoxides as follows:

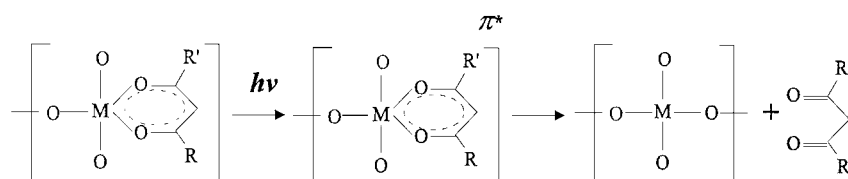


Figure 1(a) shows the FT-IR spectral change of the GPTS/Zr/BzAc film coated on a Si wafer as a function of UV light exposure time. The peaks at 1597 cm^{-1} (A) and 1520 cm^{-1} (C) are assigned to the delocalized C=O and C=C bonds of the BzAc chelate ring, respectively. The peaks at 1566 cm^{-1} (B) and 1489 cm^{-1} (D) are due to the phenyl group of the BzAc. It is assumed that the peak at 1380 cm^{-1} (E) is attributed to the formation of

the chelate ring. With increasing UV exposure time, the intensity of these peaks decrease gradually. On the other hand, the peak at 1716 cm^{-1} relating to the C=O stretching mode of the free BzAc appears. This means that the photoexcited π - π^* transition of the chelate ring is generated by UV light and leads to the photodissociation of the chelate ring. Figure 1(b) shows FT-IR spectral change of the GPTS/Al/EAcAc films.

The peaks related to delocalized C=O bond and C=C bond appear at 1610 cm^{-1} (A) and 1529 cm^{-1} (B), respectively. These peaks also represent the formation of the EAcAc chelate ring. The peak at 1307 cm^{-1} (C) is assigned to the chelate ring. Thus, the C=O bond and the C=C bond related to the delocalized bonding in the 6-membered chelate ring are diminished with increasing UV exposure time due to the photodissociation of the chelate ring.

Decrease of the UV absorption bands with increasing UV exposure time is shown in Fig. 2. The UV-absorption band which is accompanied by the photoexcited π - π^* transition state of the chelated metal complex appears at 284 nm in the GPTS/Zr/EAcAc system (Fig. 2(a)) and 356 nm in the GPTS/Ti/BzAc system (Fig. 2(b)) [3, 4]. In Fig. 2(b), the absorption band at 261 nm is due to the π - π^* transition of phenyl group in BzAc [3, 4, 9]. These absorption bands are photobleached by the photodecomposition of chelate ring around metals leading to the hetero- or homo-condensation in the hybrid gel films.

Both the photodissociation and photobleaching are also observed in all the systems using various chelate agents as well as metal alkoxides. Figure 3 shows the reduction of the absorption band intensity as a function of UV exposure time. Line (A) is the variation curve for the GPTS/Ti/BzAc system, line (B) for

the GPTS/Zr/BzAc system, line (C) for the GPTS/Al/EAcAc system and line (D) for the GPTS/Zr/EAcAc system. The slopes of the lines can represent the photobleaching rate. The slope γ_1 in the GPTS/Ti/BzAc system is slower than the slope γ_2 in the GPTS/Zr/BzAc system. This result indicates that the influence of a photon flux is a major effect on the photobleaching rate. Because the line (A) is obtained by using a 1000 W

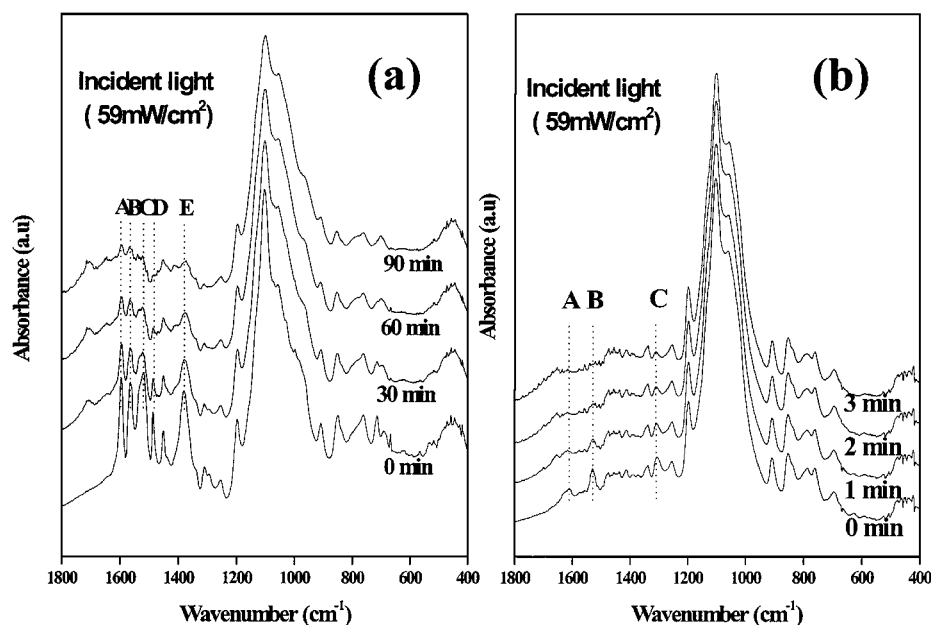


Figure 1. The variation of FT-IR spectra of GPTS/Zr/BzAc (a) and GPTS/Al/EAcAc (b) as a function of UV-light exposure time. UV source is (220–260 nm) Xenon lamp. Incident light intensity is 59 mW/cm².

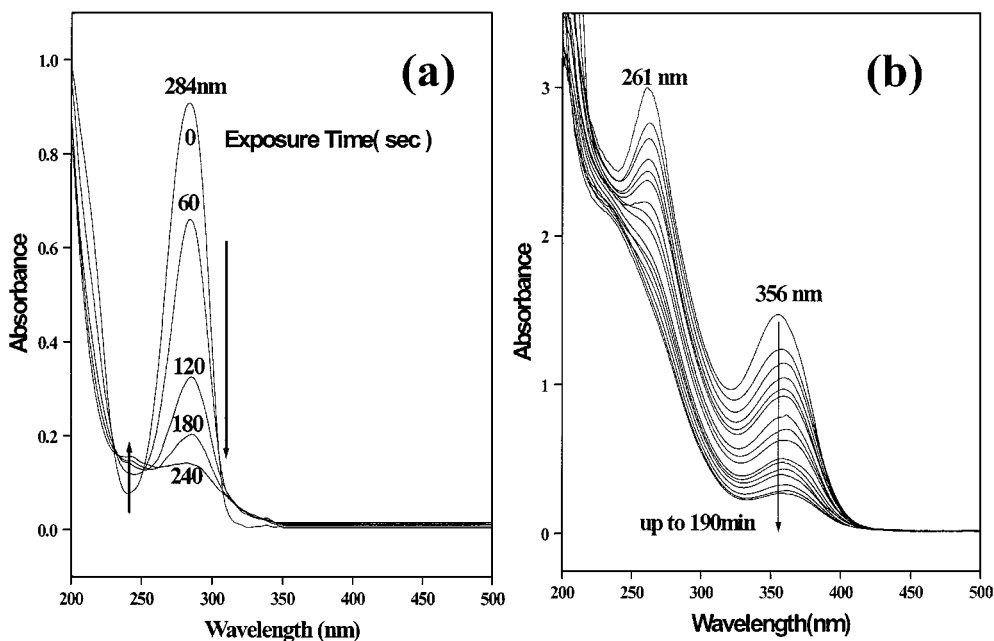


Figure 2. The variation of UV-absorption spectra of GPTS/Zr/EAcAc (a) and GPTS/Ti/BzAc (b) as a function of UV-light exposure time. (220–260 nm) Xenon lamp is used for UV-source in (a) and (350–480 nm) Xenon lamp with 350 nm band pass filter is used in (b).

Deep-UV light, but the 300 W Near UV light with 350 nm filter for line (B). Comparing lines (B) and (D), the slope γ_4 for the GPTS/Zr/EAcAc system is steeper than the slope γ_2 for the GPTS/Zr/BzAc system. The

chelating agent, EAcAc is more photosensitive than BzAc. Thus, the kind of chelating agent also effects the photobleaching rate. However, the kind of metal alkoxide has little effect on the photobleaching rate.

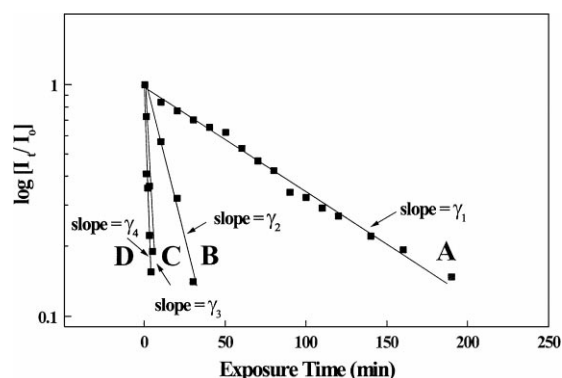


Figure 3. Plot of the variation of absorption band intensity as a function of exposure time. UV light source is Deep-UV (220–260 nm) for (b), (c), (d) and Near-UV (350 nm) for (a). (a) is the GPTS/Ti/BzAc, (b) is the GPTS/ZrBzAc, (c) is the GPTS/Al/EAcAc, (d) is the GPTS/Zr/EAcAc.

The slopes γ_3 and γ_4 for the GPTS/Al/EAcAc system and the GPTS/Zr/EAcAc system, respectively, are similar. More detailed results and discussions will be made in another paper [10].

4. Conclusion

GPTS with various metal- β -diketone (BzAc) or β -ketoester (EAcAc) hybrid gel thick films are prepared. The photobleaching of the hybrid gel films due to the

photodecomposition of the chelate rings around metals are observed depending on the kind of metal alkoxides and chelating agents as well as the photon flux. The photon flux and the kind of chelating agents significantly effect the photobleaching rate. However, the kind of metal alkoxides has little effect on the photobleaching rate. Using the chelated metal hybrid gel thick films, more effective gratings can be fabricated.

References

1. O.H. Park, Y.J. Eo, Y.K. Choi, and B.S. Bae, *J. of Sol-Gel Sci. and Tech.* **16**(3), 235 (1999).
2. C. Sanchez, J. Livage, M. Henry, and F. Babonneau, *J. of Non-Cryst. Solids* **100**, 65 (1988).
3. N. Toghe, K. Shinmou, and T. Minami, *SPIE, Vol. 2288: Sol-Gel Optic III* (1994), p. 589.
4. G. Zhao, N. Tohge, and J. Nishii, *Jap. J. Appl. Phys.* **37**, 1842 (1998).
5. S. Iraj. Najafi, T. Touam, R. Sara, M.P. Andrews, and M.A. Fardad, *J. of Lightwave Technology* **16**, 1640 (1998).
6. J.C. Debsikar, *J. Non-Cryst.* **86**, 231 (1986).
7. C. Sanchez, F. Babonneau, S. Doeuff, and A. Leautic, *Ultrastructure Processing of Ceramic Glasses and Composites* (San Diego, 1987).
8. E.J. Baerends and A. Rosa, *Coordination Chemistry Reviews* **177**, 97 (1998).
9. P.R. Singh and R. Sahai, *Jour. Indian. Chem. Soc.* **46**(10), 945 (1969).
10. H.R. Kim, O.H. Park, and B.S. Bae, in preparation.