

OPTICAL CHARACTERISTICS OF SILICA-POLY(ETHYLENE OXIDE) HYBRID THIN FILMS

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ABSTRACT

Silica-PEO hybrid materials which have both silica network and polymer network are synthesized from hydrolysis, condensation and polymerization of γ -glycidoxypropyltrimethoxysilane(GPTS). Polymerization of the epoxy groups to poly(ethylene oxide) units is achieved by using mixed triarylsulfonium hexafluorophosphate salt as a UV curing agent. The structural change of the hybrid solution is investigated by using NMR spectroscopy. The microstructure of silica hybrid film can be changed according to the degree of polymerization controlled by the UV curing conditions. The epoxide polymerization is confirmed by using FT-IR. The hybrid material is densified due to the epoxide polymerization as well as silica condensation with UV curing. The optical properties such as optical absorbance and refractive index of the silica hybrid thin films are measured as functions of curing conditions. These optical properties are then correlated to the epoxide polymerization.

INTRODUCTION

The hybrid materials have an oxide backbone and an additional organic component as a network modifier or former. Starting from hydrolyzable molecular compounds, such as alkoxy compounds of silicon for instance $R'Si(OR)_3$, hydrolysis and condensation, i.e. formation of inorganic polymeric network, are induced by addition of water. Whereas non-reactive organic groups R' such as alkyl or phenyl groups act as network modifiers, the use of reactive epoxy, methacryl or vinyl groups permits formation of the additional organic network by means of thermally or UV-induced polymerization reactions [1-2].

The silica-polymer hybrid materials can be made from organo-alkoxysilane, which increase the homogeneity on a molecular level based on the silica network and a high degree of organic crosslinking. Thus, the silica-polymer hybrid materials have been extensively studied for application of the optical coatings because of their excellent optical properties, low cost and easy process[3-4]. The representative silica-polymer hybrid

material is silica-poly (ethylene oxide) (PEO) hybrid material prepared by using γ -glycidoxypropyl-trimethoxysilane (GPTS) as a precursor. The silica network is formed through hydrolysis and condensation in the presence of water, and PEO polymeric network is made by epoxide polymerization with addition of polymerization initiator. However, in the presence of water and catalyst, the epoxy group could react with water to form glycol by opening epoxy rings to terminate the polymerization [1].

In the previous work[5], we prepared silica-PEO hybrid materials by thermal curing and examined their optical properties. However, the UV curing is more desirable for the application of integrated technology. Thus, in the present study, the silica-PEO hybrid material is prepared by sol-gel reaction of GPTS, followed by epoxide polymerization by UV curing using UV polymerization initiator. The structural evolution by UV curing is examined and the epoxide polymerization is confirmed. Concurrently, the variation in the optical properties of the silica-PEO hybrid thin films is investigated.

EXPERIMENT

Synthesis of the Silica-PEO Hybrid Solution

The silica-PEO hybrid solutions were prepared by using γ -glycidoxypropyl-trimethoxysilane (GPTS, Aldrich) as the starting precursor. The water for hydrolysis was added to the GPTS solution, and the solution was stirred for 16 hours. The molar ratio of water to GPTS was 1.5:1 and the pH of the solution was adjusted at 5.5 by bubbling CO₂ through it (prehydrolyzed GPTS). The prehydrolyzed GPTS was refluxed at 80 °C for 12 hours to form the silica network because the cationic polymerization initiator could not work in base contamination. Mixed triarylsulfonium hexafluorophosphate salt(UVI-6990, Union Carbide) was used as a cationic polymerization initiator. The prepared solution was mixed with UVI-6990 before the coating process. Then the solution was deposited on Si(100) wafers and fused silica substrates by the spin-coating method.

Structure Analysis and Optical Characterization

The structural evolution with the hydrolysis and condensation of the solution was examined by using ¹H & ¹³C nuclear magnetic resonance (NMR) spectroscopy (Bruker AM 300). The epoxide polymerization of silica-PEO hybrid materials was examined through the changes of epoxy groups as UV doses. The change of epoxy group was investigated by Fourier-transformed infrared spectroscopy (FT-IR, Bruker EQUINOX55). The optical absorbance was examined using a UV/VIS/NIR spectrophotometer (Shimadzu UV-

3101PC). Also, the refractive index of the films deposited on fused silica was measured by using prism coupling method.

RESULTS AND DISCUSSION

Preparation of Silica-PEO Hybrid Materials

GPTS was hydrolyzed with water by bubbling CO_2 through it, and then the solution was refluxed at 80°C for 12 hours (refluxed GPTS solution). The structural changes with refluxing to the prehydrolyzed GPTS solution was investigated. Fig. 1 shows ^1H NMR spectra of the prehydrolyzed GPTS and the refluxed GPTS solutions. There are two peaks at the chemical shifts, ~ 2.5 and 2.7 ppm corresponding to the two protons in β positioned carbon of the epoxy ring, (a) in the structural model. When the epoxy group undergoes hydrolytic ring opening or epoxide polymerization, the epoxy peak area should decrease. Therefore, the change of the epoxy content can be estimated by comparing the sum of epoxy peak area with the standard one (b), $\delta = \sim 1.6$ ppm). The ratio of the epoxy peak area to the standard peak does not change after refluxing, which implies that epoxy content is unvaried, within the error of the measurement. However, the silanol peaks (c), $\delta = \sim 2.4$ and 2.8 ppm) disappear after refluxing. It is found that the siloxane bonds are formed through the silica condensation.

^{13}C NMR spectra of the prehydrolyzed GPTS and refluxed GPTS solutions are shown in Fig. 2. It is known that the glycol peaks, which are formed by hydrolytic ring opening reaction, are located at 59 and 69 ppm [5]. As shown in Fig. 2, there are no glycol peaks after refluxing at 80°C . In particular, the peak of carbon adjacent to silicon near 10 ppm (A) is split into broad and sharp peaks. It could be concluded that the carbons adjacent to silicon have two different chemical shifts around 10 ppm as the environment of the silicon is changed by silica condensation. This indicates that monomeric and polymeric species coexist

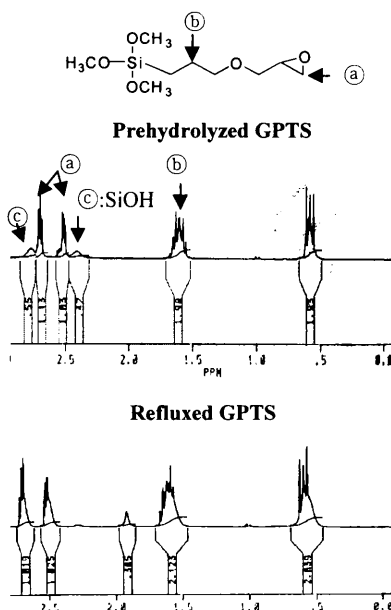


Fig. 1 ^1H NMR spectra of prehydrolyzed GPTS and refluxed GPTS solutions. Structural model is shown for assignments of the peak position.

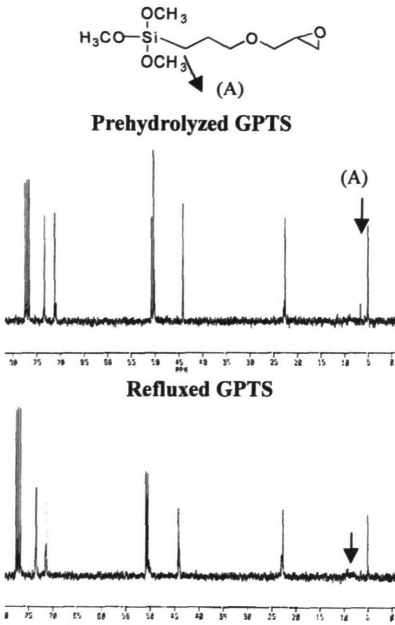


Fig. 2 ^{13}C NMR spectra of prehydrolyzed GPTS and refluxed GPTS solutions. Structural model is shown for assignments of the peak position.

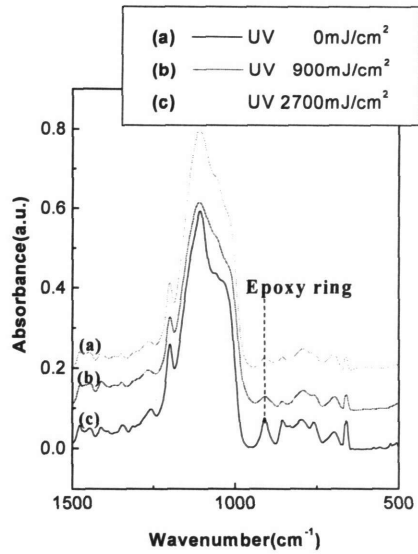


Fig. 3. FT-IR spectra of refluxed GPTS/UVI coating films with the irradiation dose of the 254nm light. The dashed line indicates the epoxy asymmetric stretching mode.

in the solution. Thus, it is found that the silica network is formed with maintenance of epoxy group.

The refluxed GPTS solution was mixed with UVI-6990 before the coating process (refluxed GPTS/UVI). The refluxed GPTS/UVI solution was coated on Si(100) wafers by spin coating and dried at 80°C for 10 minutes. After that, the coated films were irradiated by UV lamp at a wavelength of 254nm. Then the films were thermally cured at 180°C for 30mins to enhance silica condensation and freeze the structure. The FT-IR spectra of the coated films as a function of UV dose are shown in Fig. 3. The peaks at 910 , 1030 and 1080cm^{-1} are attributed to $\nu_{\text{as}}(\text{C-O-C ring})$, $\nu_{\text{as}}(\text{Si-O-Si})$ and $\nu_{\text{as}}(\text{Si-O-C})$, respectively. Apparently, the epoxy asymmetric stretching mode at 910cm^{-1} disappears as UV energy increases. Thus, it is found that the epoxy group is polymerized to poly(ethylene oxide) with increasing UV energy.

Optical Characteristics of Silica-PEO Hybrid Thin Films

From the above discussion, it was found that the structure of silica-PEO hybrid thin films

was changed by UV curing. In order to investigate the optical absorbance, the silica-PEO hybrid solution was coated on fused silica substrates by spin coating. Fused silica substrate was selected because of its excellent transparency in the UV region. As shown in Fig. 4, there are an absorption peak of not reacted UVI-6990 at 240nm with no UV dose. But UVI-6990 undergoes the homolytic or heterolytic cleavage with UV irradiation. Therefore, when

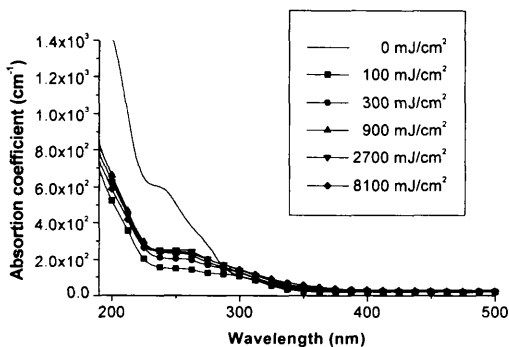


Fig. 4. FT-IR spectra of refluxed GPTS/UVI coating films with various irradiation dose of the 254nm light. The dashed line indicates the epoxy asymmetric stretching mode.

the hybrid films are irradiated by UV the peak at 240nm disappears abruptly and the new peak at 256nm appears. Also, as the UV dose increases, the absorption near 250nm increases. This could be understood as follows. The UVI-6990 is dissociated into intermediate compounds with UV irradiation. As the UV dose increases, the intermediate compounds are dissociated again and then superacid($H^+PF_6^-$) is generated to initiate the cationic epoxide polymerization. Also, the intensity of new peak at 256nm increases because the amount of diarylsulfonium increases as a result of the superacid generation.

Prism coupling method was used to determine refractive index of the hybrid thin film. TE_0 mode could be observed in all of the hybrid films illuminated with different UV energy. Thus, the thickness of the film was measured using the profilermeter. The refractive index was calculated using effective index and thickness of the film. The incident angle of TE_0 mode, effective index and refractive index of the films are represented in Table I. The refractive index increases from 1.501 to 1.507 as the UV dose increases from $0mJ/cm^2$ to $8100mJ/cm^2$, respectively. Therefore, it could be concluded that the epoxide polymerization raised the refractive index with larger UV curing.

Table I. Incident angle of TE₀, effective index and refractive index of refluxed GPTS/UVI films with various UV irradiation dose measured by prism coupler.

UV dose(mJ/cm ²)	Incident angle of TE ₀	Effective index	Refractive index
0	21.231	1.4875	1.5011
100	22.456	1.4984	1.5044
900	22.645	1.5001	1.5063
8100	22.890	1.5023	1.5071

CONCLUSIONS

Silica-PEO hybrid materials were prepared from γ -glycidoxypropyltrimethoxysilane (GPTS) and mixed triarylsulfonium hexafluorophosphate salts(UVI-6990). The silica network is formed by refluxing at 80 °C for 12 hours. As the UV dose increases, the area of the peak related to epoxy group in FT-IR spectra decreases due to the epoxide polymerization. Thus, the silica-PEO hybrid materials which have both silica and poly(ethylene oxide) network was fabricated successfully.

Homogeneous and crack free silica-PEO hybrid films are obtained by spin coating. When the hybrid films are irradiated by UV lamp, the superacid is generated from the dissociation of UVI-6990. The absorption peak at 240nm disappears and the new peak at 256nm in UV spectra increases because of the formation of diarylsulfonium resulted from the superacid generation. Superacid(H⁺PF₆⁻) plays an important role to initiate the cationic epoxide polymerization. The refractive index increases from 1.501 to 1.507 as the UV dose increases from 0mJ/cm² to 8100mJ/cm², respectively. This increase of refractive index through UV curing is due to epoxide polymerization and thermal densification.

ACKNOWLEDGEMENTS

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