

Synthesis and Characterization of Photopatternable Epoxy Hybrid Materials for the Fabrication of Thick and Thermally Stable Microstructures with a High Aspect Ratio

Kyung Ho Jung, Byeong-Soo Bae

Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

Received 7 November 2007; accepted 26 December 2007

DOI 10.1002/app.27966

Published online 29 February 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Photosensitive cycloaliphatic-epoxy oligosiloxane was synthesized using a nonhydrolytic sol-gel reaction for the fabrication of thick and thermally stable microstructures with high aspect ratios. Its formation was confirmed by ^{29}Si and ^1H nuclear magnetic resonance spectroscopy, small-angle neutron scattering, and Fourier transform infrared spectroscopy. Photocuring of cycloaliphatic-epoxy oligosiloxane resin resulted in a thermally stable epoxy hybrid material (epoxy hybrimer). Micropat-

terns with a high aspect ratio (>5), an excellent sidewall shape, and low shrinkage were fabricated directly from these materials using a simple photolithographic process. The fabricated micropattern sustained temperatures of up to 250°C . © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3169–3176, 2008

Key words: lithography; nanocomposites; oligomers; photopolymerization; polysiloxanes

INTRODUCTION

The fabrication of microstructures using photopatternable materials by simple photolithography without using post dry etching processes has attracted much attention. This is due to their widespread and numerous applications such as fabrication materials for diffractive optical elements,¹ waveguides,² data storage, and electronic devices,^{3,4} as well as their use as conventional photoresists.⁵ Recently, these materials have also been used in devices as dielectric materials in contrast to photoresists that are removed after microstructure fabrication. Thus, the development of cheap and easy to use photopatternable materials with desirable electrical, thermal, or optical characteristics is required. Because of the demand for the high-density integration of components in many of these applications, high aspect ratio lithography (thickness/resolution) capabilities using

thick photocurable films ($>100\ \mu\text{m}$) and high photosensitivity are required to provide excellent dimensional control and well-defined sidewalls. This is especially true for recent advanced applications in RF and microwave devices, multimode optical waveguides, and microelectromechanical system (MEMS) devices. Also, the microstructures need to be thermally stable to be resistant to subsequent processing.

The most common photopatternable materials are photopolymers. These include photoresists in which selective etching is achieved by an increase in molecular weight via photopolymerization⁶ or the formation of new insoluble products via the photochemical rearrangement of organics.⁷ Many types of high-photosensitive photoresists have been developed and commercialized for use in semiconductor and display manufacturing processes. However, a high thermal stability and the capacity to adjust the electrical and optical characteristics are limited in devices with thick microstructures with a high aspect ratio. To overcome these problems, photosensitive organic-inorganic hybrid materials (known as hybrimers) have been introduced in recent times for the photopatterning of microstructures.^{8–16} It has been reported that hybrimers containing the photopolymerizable methacryl group can be used to make thick photopatterned and thermally stable films with unique characteristics.¹⁷ The acryl or methacryl groups usually employ UV-curable materials based on free radical polymerization because of their excel-

This article contains supplementary material available via the Internet at <http://www.interscience.wiley.com/jpages/0021-8995/suppmat>.

Correspondence to: B.-S. Bae (bsbae@kaist.ac.kr).

Contract grant sponsor: Korean Government (MOST) (Korea Science and Engineering Foundation (KOSEF)); contract grant number: SRC/ERC: R11-2007-045-03002-0.

Contract grant sponsor: Korea Basic Science Institute (KBSI).

Journal of Applied Polymer Science, Vol. 108, 3169–3176 (2008)
© 2008 Wiley Periodicals, Inc.

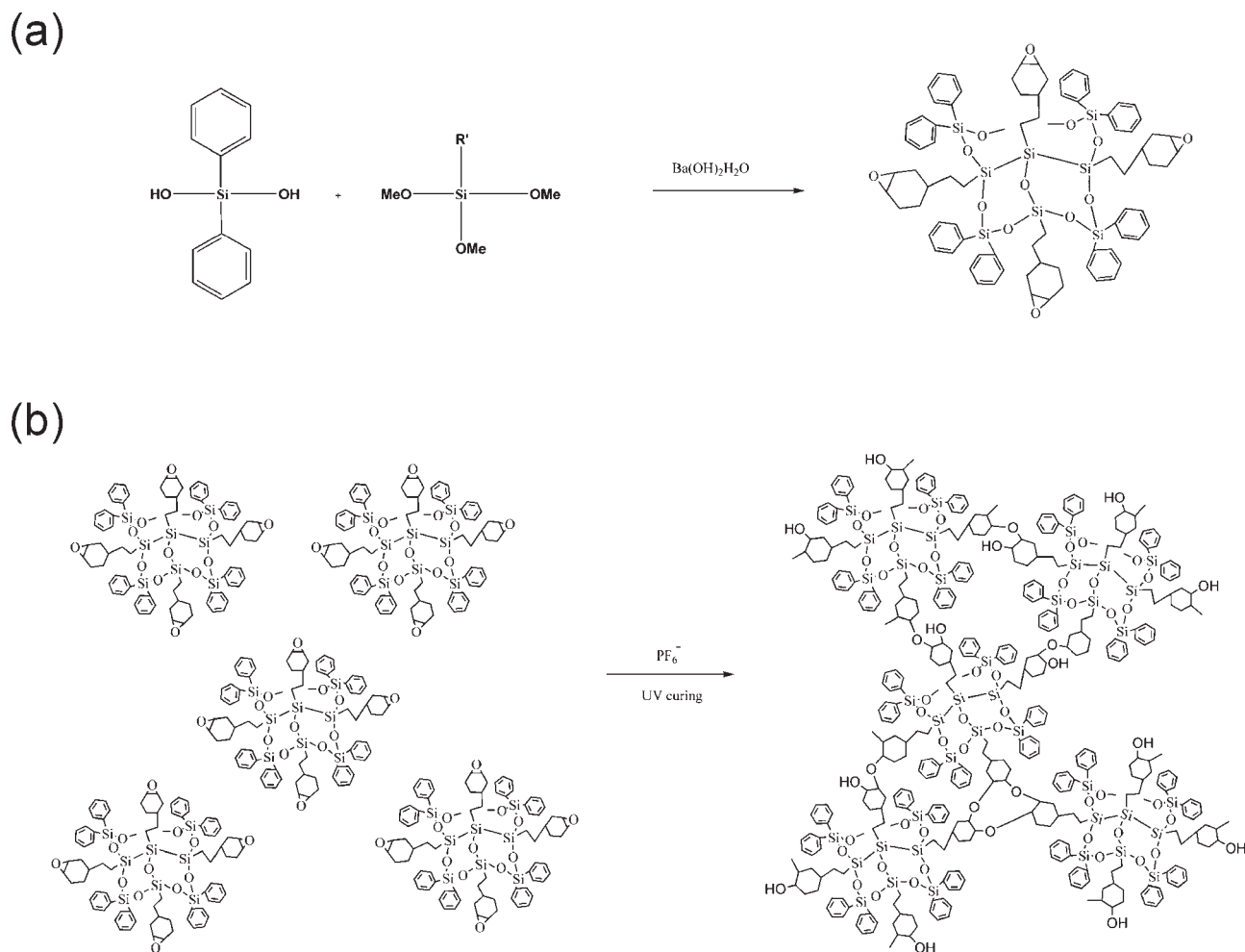


Figure 1 Schematic procedure for (a) synthesis of cycloaliphatic-epoxy oligosiloxane and (b) fabrication of epoxy hybridimer.

lent reactivity. However, these groups are vulnerable to heat and, compared to other polymers, are not adequate for electrical applications. Furthermore, photosensitive materials based on these groups undergo relatively high shrinkage during curing (about 10%) compared with epoxy-functionalized polymers. This not only causes poor dimensional control and unreliable patterns, but also tends to result in detachment from the substrate, especially from substrates made of a low shrinking metal or plastics. The oxygen inhibition of photopolymerization in these groups can also degrade the photosensitivity of the hybridimers.^{18,19}

Epoxy is a common organic thermosetting and thermally stable polymer, has a variety of molecular weights, and is cheap to produce. It has already been reported that hybridimers containing glycidyl epoxide can be synthesized by thermal curing.²⁰ However, polymerization of the glycidyl epoxide is not sensitive to UV light. In this article, we used 2-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane to form oligosiloxanes by nonhydrolytic sol-gel reaction. It is known that cyclo-

aliphatic epoxide can be made from cationic photopolymerization without the use of a vacuum or inert atmosphere and shows the best photosensitivity among all known epoxides.²¹ The cycloaliphatic epoxide film has excellent clarity in the visible and ultra violet region, because the cycloaliphatic epoxide does not have aromatic rings or chloride. Also, the use of cationic polymerization using a ring-opening mechanism can improve chemical and plasma resistance, shrinkage after crosslinking, and adhesion with various substrates, thus allowing reliable patterning.

In this work, the photosensitive cycloaliphatic-epoxy oligosiloxane was synthesized using a simple condensation reaction. Figure 1 shows a schematic of the chemical fabrication route of the cycloaliphatic-epoxy oligosiloxane and epoxy hybridimers. Diphenylsilanediol (DPSD) and alkoxy groups in 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS) can synthesize modified oligosiloxane as shown in Figure 1(a). Figure 1(b) shows the fabrication of the epoxy hybridimers by polymerization of the synthesized cycloaliphatic-epoxy oligosiloxanes using UV light. The size and molecular structure

of the oligosiloxane in the resin can be modulated by altering the composition ratio of the precursors. The variation of the molecular structure directly influences the rheological, electrical, and optical properties of the epoxy hybrid such as the viscosity, refractive index, and dielectric constant. Microstructures with a high thermal stability as well as a thick, high aspect ratio can be achieved using this resin because of the high thermal stability arising from rigid siloxane linkages and chemically bonded epoxy groups.

EXPERIMENTAL

Preparation of cycloaliphatic-epoxy oligosiloxane

The cycloaliphatic-epoxy oligosiloxane was synthesized by a condensation reaction between ECTS (Fluka, USA) and DPSD (TCI, Tokyo, Japan), in various molar ratios without further purification; barium hydroxide monohydrate (BH, Aldrich, USA) was added as a catalyst to promote the reaction between the two. The total amount of BH contained 0.2 mol % equivalents of the ECTS in the solution. The composition and notation used to denote each sample of the epoxy hybrid are presented in Table I. For the homogeneous condensation reaction between the two precursors, DPSD in its solid state was continuously added to the liquid state of ECTS in a flask while stirring the solution with a magnetic stirrer at 80°C for 2 h. The resulting solution was then mixed for an additional 2 h to complete the condensation reaction. Methanol, a by-product of the condensation was removed by vacuum heating, and BH was removed by a 0.45- μm pore-sized Teflon filter. Finally, a clear solution of photosensitive cycloaliphatic-epoxy oligosiloxane resin was obtained. Subsequently, arylsulfonium hexafluorophosphate salt (CYRACURE UVi-6992, Dow Chem, Michigan, USA) was added as a cationic initiator for the photoreaction of cycloaliphatic-epoxy via UV light exposure. The typical amount of photoinitiator was 2 wt % of the total weight percent of epoxy-functional groups in the oligosiloxane resin.

Fabrication of high aspect ratio microstructures

To fabricate the high aspect ratio microstructures, a *p*-type Si (100) substrate was first cleaned then exposed to an O₂ plasma for 5 min to remove any organic compounds on its surface. The viscosity of the epoxy hybrid can be controlled from 300 to 15,000 cps with DPSD contents. Subsequently, a single spin-coating of the epoxy hybrids (ED41 composition) at 300 rpm for 30 s was used to produce a 120- μm thick layer. The coated films were selectively exposed for 10 s with a mercury UV lamp ($\lambda = 350\text{--}390\text{ nm}$, optical power density = 85 mW/cm²) using a patterned photomask and mask aligner. After UV exposure, the samples were developed for 30 s in an

TABLE I
Composition of Chemical Precursors for Synthesis of Cycloaliphatic-Epoxy Oligosiloxane

Notation	ECTS (g)	DPSD (g)	Ba(OH) ₂ H ₂ O (g)
ED33	16.51 (0.067 mol)	7.14 (0.033 mol)	0.025
ED41	14.54 (0.059 mol)	8.87 (0.041 mol)	0.022
ED50	12.32 (0.05 mol)	10.82 (0.050 mol)	0.019

n-propylacetate/isopropyl alcohol mixture (volume ratio 3 : 7). There was no need to carry out the pre-bake, postbake, PR deposition and elimination, and etching step, as well as the multicoating step for these microstructures.

Characterization

²⁹Si and ¹H nuclear magnetic resonance (NMR) spectra of the resin in chloroform-*d* were recorded using a Bruker FT 500 MHz instrument. Chromium(III) acetylacetonate was added as a silicon relaxation agent at a concentration of 30 mg/L. The sample temperature was 300 K and the pulse delays were set to 30 s. The spectrum of tetramethylsilane (TMS) was used as a reference. Raman Spectra were measured with a 488 nm Ar-Kr ion laser (Coherent Innova 70 series, Laser Innovations, Moorpark, CA) and double-grating monochromator (U-1000, Jovin Yvon, Edison, NJ). Small-angle neutron scattering (SANS) experiments were performed on the HANARO Reactor at the Korea Atomic Energy Research Institute (KAERI). A wavelength of 5.08 Å with a spread (FWHM) of 12%, and detector-sample distance of 3 m was used for all SANS measurements. The scattering vector ranged between 0.04 and 0.25 Å⁻¹. The resins were diluted to a 10 wt % concentration in acetone-*d*₆ to obtain a good contrast between the resins and the solvent. Fourier transform infrared (FTIR) spectra of the epoxy hybrid materials were obtained with a JASCO FTIR 460plus with a resolution of 4 cm⁻¹ in the wavenumber range 400–4000 cm⁻¹. Thermal measurements using thermogravimetric analysis (TGA) and dilatometer were performed using bulk epoxy hybrid samples. The bulk sample was prepared by casting of the cycloaliphatic-epoxy oligosiloxane resin followed by UV exposure. The TGA and dilatometer experiments were carried out under nitrogen atmosphere at a heating rate of 10 and 5°C/min, respectively. The micropatterns were also examined using scanning electron microscopy (Philips, XL30SFE).

RESULTS AND DISCUSSION

Synthesis of cycloaliphatic-epoxy oligosiloxane resin

Cycloaliphatic-epoxy oligosiloxanes resin was prepared using a direct condensation reaction between

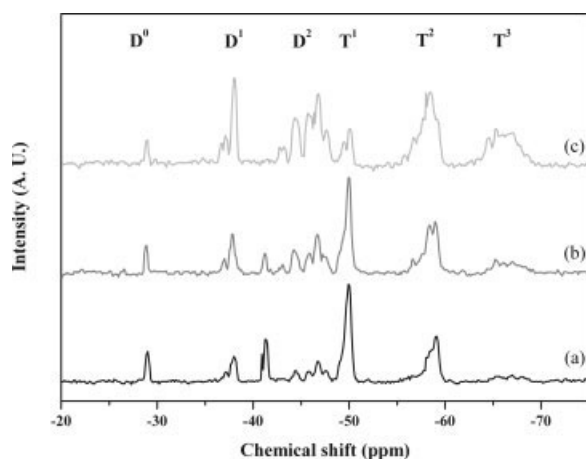


Figure 2 ^{29}Si NMR spectra of cycloaliphatic-epoxy oligosiloxane resin of various compositions (a) ED 33, (b) ED 41, and (c) ED 50.

the methoxy radical of ECTS and the diol radical of DPSD to form siloxanes with a methanol by-product. Usually, the epoxy rings are easily opened in the catalysis environment so that the epoxy is not polymerized.²² Thus, it is difficult to maintain polymerizable epoxy rings during conventional sol-gel reactions using aqueous HCl forming cycloaliphatic-epoxy polysiloxanes. To solve this problem, the basic catalysis, BH, was used to promote the condensation reaction and prevent the self-condensation of the DPSD in the absence of water. Since BH is insoluble in water and any alcohol, it may remain in the resin but can be removed by filtration. The synthesized resin presents good shelf stability because of the absence of solvents such as water and alcohol, and unreacted diol groups.

Oligosiloxane formation was confirmed by the creation of Si—O bonds using ^{29}Si NMR spectroscopy. Figure 2 shows the ^{29}Si NMR spectra of the cycloaliphatic-epoxy oligosiloxanes samples listed in Table I with different DPSD contents. In NMR notation, D^n and T^n represents Si from DPSD and ECTS, respectively. The superscript “ n ” denotes the number of bridging oxygen atoms to a Si atom. Depending on the composition of the reactants, different siloxane bonds are formed. It can be seen in Figure 2 that the D^2 , T^2 , and T^3 peaks are enhanced as the DPSD content in the reactants is increased.^{17,23} Also, small amounts of unreacted Si species (D^0 : -29 and -34 ppm) which are not desirable are found in all the spectra. The D^0 peak at -29 ppm is found in the form of diphenylmethoxysilanol or diphenyldimethoxysilane, which is a product of the reaction between DPSD and methanol. However, the D^0 peak at -34 ppm representing DPSD is rarely found. This means that the condensation reaction between ECTS and DPSD proceeded well, and that the epoxy-

grafted oligosiloxanes were successfully synthesized. Theoretically, T^3 species are not formed in the condensation reaction due to the diol radical in the reactants. However, the T^3 peak is present and especially apparent in the ED50 composition sample. This might be due to a re-esterification reaction of the methoxy group in the ECTS. Water, which is a by-product of the condensation reaction between diol and methanol, produces T^2 -OH by hydrolysis of the methoxy group in ECTS. Thus, the self-condensation reaction of T^2 -OH species can form T^3 species. Consequently, the degree of condensation (DOC) depending on the DPSD content in the reactants can be calculated using the following equation²⁴:

$$\text{DOC} = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100 \quad (1)$$

It is found that the DOC increases from about 60 to 80% with a change in the DSD content from 33 to 50%.

^1H NMR spectroscopy was employed to confirm whether the cleavage of the epoxy ring occurred during the condensation reaction. ^1H NMR spectra of the cycloaliphatic-epoxy oligosiloxanes with various compositions are shown in Figure 3. The chemical shifts of the H atoms at C atom that directly bonded to the Si atom and epoxy ring are 0.5 and 3 ppm, respectively. The cleavage of the epoxy ring can be verified by comparison with the area under the two peaks, as the same number of H atoms is involved in the two cases. No difference in the areas of the peaks is found for any of the compositions. This implies that the cycloaliphatic-epoxy oligosiloxanes were successfully synthesized without opening the epoxy rings.

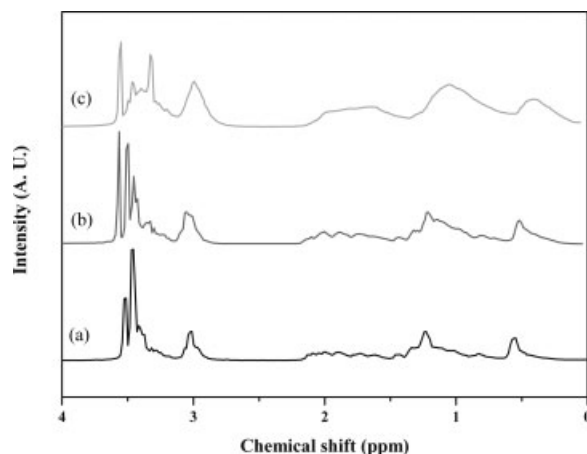


Figure 3 ^1H NMR spectra of the cycloaliphatic-epoxy oligosiloxane resins with various compositions (a) ED 33, (b) ED 41, and (c) ED 50.

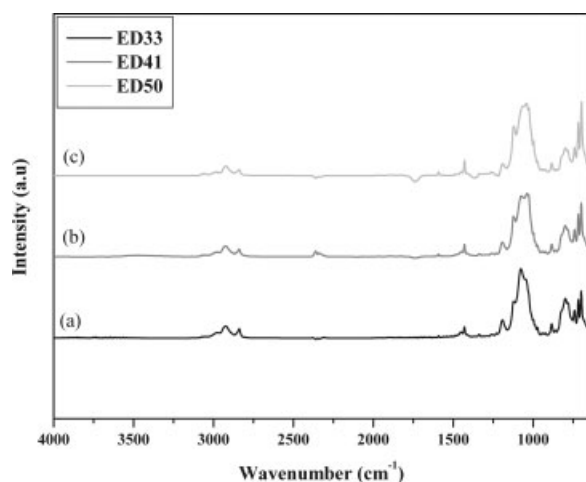


Figure 4 FTIR spectra of the cycloaliphatic-epoxy oligosiloxane resin with various compositions (a) ED 33, (b) ED 41, and (c) ED 50.

In addition, FTIR spectra of these resins support the results of the NMR spectra. No FTIR bands associated with $-\text{OH}$ and $\text{Si}-\text{OH}$ bonds ($3200\text{--}3600\text{ cm}^{-1}$) are observed in any of the spectra shown in Figure 4. The characteristic absorption band of the siloxane bonds in the epoxy hybrimer was observed at 1100 cm^{-1} . Bands due to the vibration of the epoxy groups are observed at 880 cm^{-1} . This indicates that the direct condensation reaction between DPSD and ECTS was achieved. Also, the existence of silanol groups and unreacted precursors was small, thereby preventing further self-condensation of the resin.

Size of the cycloaliphatic-epoxy oligosiloxanes

The size of the synthesized cycloaliphatic-epoxy oligosiloxane was determined by SANS measurements. Guinier plots of the SANS data for each precursor composition are shown in Figure 5. The radius of gyration (R_g) was estimated from a linear plot of $\ln(I(Q))$ versus Q^2 in the Guinier region ($0.1 < R_g < 1$) according to the Guinier Law.²⁵ The R_g values of the various compositions are listed in Table II. From these values, the sizes of the oligosiloxanes were calculated using the following equations:

$$R_g = \sqrt{\frac{3}{5}} R_s \quad (2)$$

$$R_g = \frac{3}{\sqrt{12}} R_r \quad (3)$$

where R_s is the radius of the oligosiloxane assuming a spherical shape, and R_r denotes their length assuming they have a rod-like shape. Assumed the oligosiloxanes is spherical shape, the size is the smallest. Thus, it could be deduced that the molecular size of the oligosiloxanes was around 2 nm in the

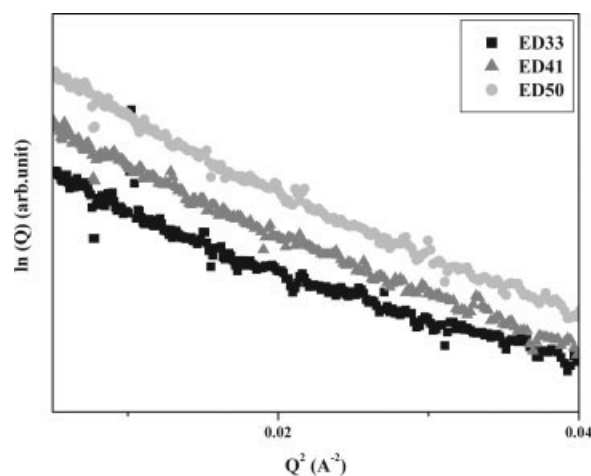


Figure 5 Guinier plots of the SANS data of the cycloaliphatic-epoxy oligosiloxane resins.

range between $2R_s$ and R_r , regardless of the precursor composition, as presented in Table II. The nanosized epoxy hybrimer can be formed as uniform film on the substrate and expected high resolution of the micropatterns.

Photopolymerization of cycloaliphatic-epoxy oligosiloxane

Photopolymerization of the synthesized cycloaliphatic-epoxy oligosiloxanes was examined using FTIR spectroscopy. The peak at 880 cm^{-1} is associated with the epoxy group stretching mode, and the peak at 1590 cm^{-1} indicates the phenyl group stretching mode. The decrease in intensity of the epoxy group peak indicates epoxy polymerization by the opening of epoxy rings as the UV exposure is increased. On the other hand, the intensity of the phenyl group peak remains constant irrespective of the UV exposure. The conversion degree of the epoxy ring-opening can be expressed in terms of the decrease of the epoxy group peak relative to the phenyl group peak as,

$$\text{Conversion degree (\%)} = \left[1 - \frac{\left(\frac{A_{\text{epoxy}}}{A_{\text{phenyl}}} \right)_{\text{aftercuring}}}{\left(\frac{A_{\text{epoxy}}}{A_{\text{phenyl}}} \right)_{\text{resin}}} \right] \times 100 \quad (4)$$

TABLE II
Calculated Molecular Sizes of Cycloaliphatic-Epoxy Oligosiloxanes from the Slope of Guinier Plots

Composition	R_g (nm)	Size of the spherical shape (nm)	Size of the rod-like shape (nm)
ED33	0.72	1.86	2.5
ED41	0.76	1.96	2.63
ED50	0.79	2.04	2.74

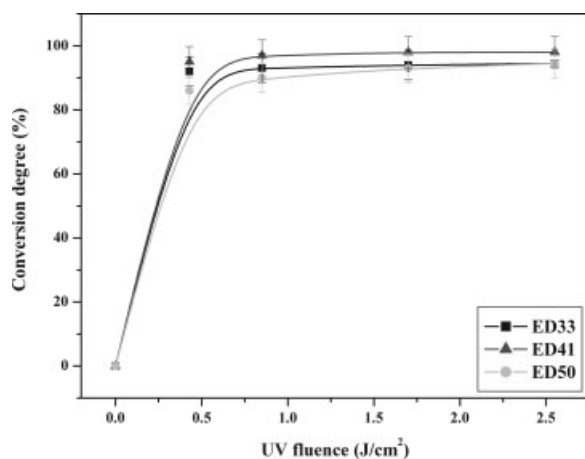


Figure 6 Conversion degree of epoxy ring-opening for various compositions as a function of UV fluence.

where A_{epoxy} and A_{phenyl} represent the area under the peak of the epoxy and phenyl groups, respectively. The conversion degree of the oligosiloxanes resin with different precursor compositions is plotted as a function of UV fluence in Figure 6. All the compositions achieve a conversion degree of up to 90% with a UV fluence of 600 mJ/cm². This implies that the synthesized oligosiloxane is photopolymerizable in the fabrication of epoxy hybriders. However, as the DPSD content is increased, the conversion degree is lowered due to the steric hindrance of the reaction and strong UV absorption by the phenyl groups. The strong UV absorption competes with absorption of the photoinitiator.

Thermal stability of photopatternable epoxy hybriders

A high thermal stability is the most promising hybridier characteristic compared to the polymers and is due to the existence of siloxane bonds in the crosslinked network. Since general polymers have low thermal decomposition temperatures and softening temperatures, their practical application is limited. The enhanced thermal stability enables the hybriders to replace the polymers in practical applications. For example, the representative commercially available polymer, polymethylmethacrylate (PMMA), has a thermal decomposition temperature of about 130°C and a softening temperature of about 105°C.

TGA of the photocured epoxy hybriders are shown in Figure 7. The thermal decomposition temperature (5 wt % loss temperature) of the hybriders is about 410°C regardless of the precursor composition. A rapid weight loss at the decomposition temperature may be due to decomposition of the remaining alkoxy groups as well as epoxy chemical bonds. Thermal expansion, the most sensitive char-

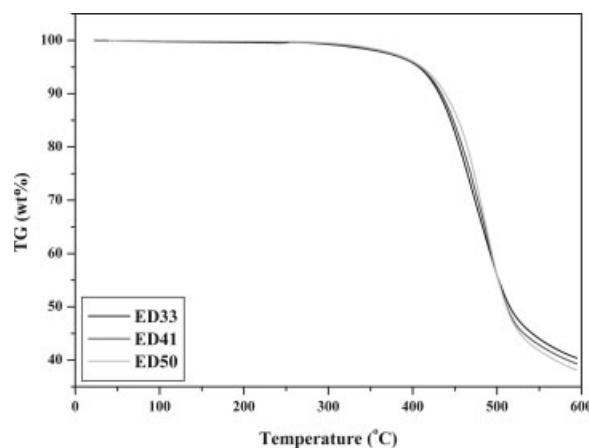


Figure 7 TGA curves of the epoxy hybridier bulk with various compositions at a heating rate of 5°C/min under a nitrogen atmosphere.

acteristic of the hybriders, was measured using a dilatometer. As shown in Figure 8, all the samples have an almost linear thermal expansion up to 250°C. The coefficient of thermal expansion (CTE) was obtained from the slopes of these plots. CTE values of the epoxy hybriders were 230, 180, and 150 ppm/K for the ED33, ED41, and ED50 samples, respectively. The CTE decreases with an increase in DPSD content. This might be due to the formation of larger oligosiloxanes in the samples with a higher DPSD content because of a more active condensation reaction.

The dilatometer results in Figure 8 are astonishing, since a softening temperature in the room temperature to 250°C range is not present. Generally, polymers show a remarkable change in thermal expansion at a softening temperature below 200°C. The abrupt change in this thermal expansion results in the development of stress during the heating cycle. This restricts the reliable use of these materials at ele-

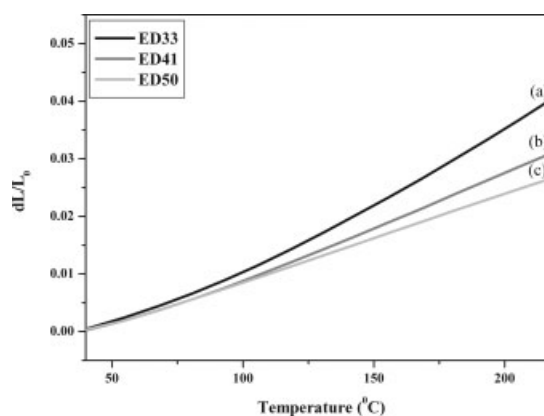


Figure 8 Dilatometer results of epoxy hybridier with various compositions (a) ED33, (b) ED41, and (c) ED50 as a function of temperature.

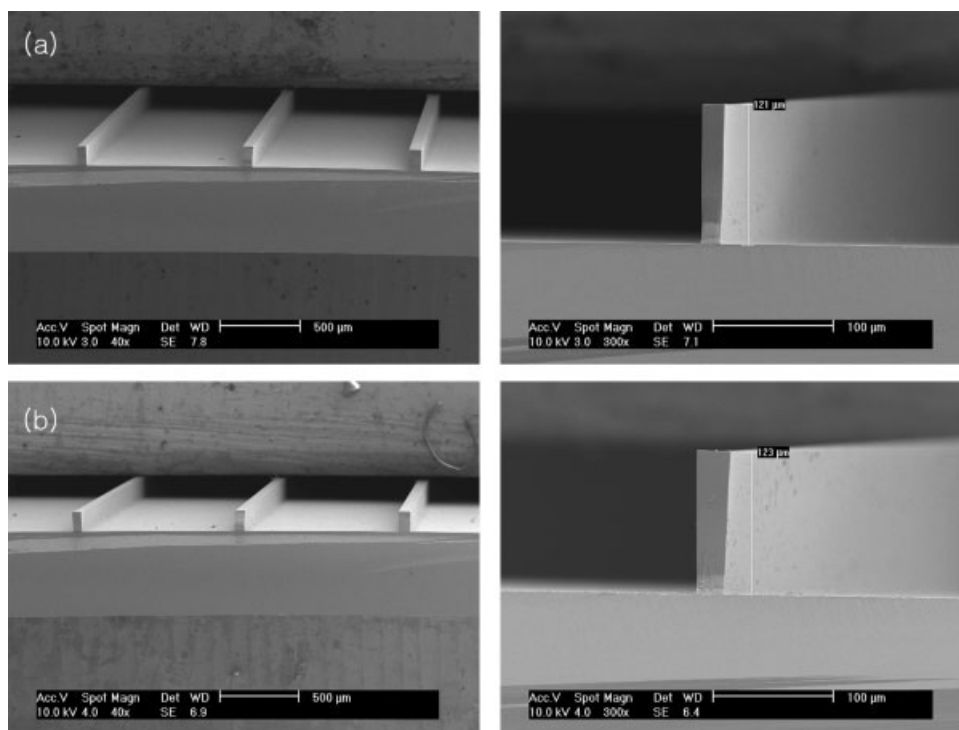


Figure 9 SEM images of the thick photopatterned high aspect ratio microstructure of an epoxy hybrimer film (a) as photopatterning microstructures and (b) after heating at 250°C for an hour.

ated temperatures. However, the epoxy hybridizers do not show any such transition during heating. The rigidity of the high crosslinked structure of organic groups with oligosiloxanes may cause the restriction of chain mobility to be softened.²⁶ Therefore, we have demonstrated that an epoxy hybridizer has been produced to have a high thermal decomposition temperature without a softening temperature. Such a hybridizer can be used in applications at high temperatures.

Photolithography of high aspect ratio microstructures

Microstructures with a width of 20 μm in thick (~120 μm) epoxy hybridizer films on Si wafer substrates were fabricated using a simple photolithographic technique. After UV illumination with a 600 mJ/cm² fluence, the films were developed for 30 s in an *n*-propylacetate/isopropyl alcohol mixture solvent. Figure 9 shows the SEM images of the patterned microstructures with an aspect ratio of over 5 and an excellent sidewall shape. Volume shrinkage of the hybridizer films during photopolymerization may cause the destruction of the microstructures. However, the volume shrinkage estimated from the change in the film thickness before and after heating is less than 3% assuming that the shrinkage is isotropic. This value is much lower than the 10% observed in other photopatternable acrylate poly-

mers. This low volume shrinkage enables the microstructures to be fabricated without demolition. Usually, poor dimensional control by the formation of inclined sidewalls occurs because of the influence of diffraction effects and nonuniform exposure on thick films. Also, the UV absorption in the thick films may reduce the effective dose at some depth within the films. These effects, amplified by developing processes, can form an inclined pattern similar in shape to a mushroom. However, epoxy hybridizers only require low energy consumption for the fabrication of the micropatterns. Thus, precise patterns of a desired shape much like the one shown in Figure 9 can be produced with a very short exposure time. This excellent photopatternability comes from the superior photopolymerization ability of epoxy groups in the epoxy hybrid materials. The fabricated microstructures were heat-treated at 250°C for an hour to confirm their thermal stability. Figure 9(b) shows the photopatterned microstructures after heat treatment. The microstructures on the Si substrate are not deformed or separated from the substrate. The shape of the microstructures is sustained even after many heating cycles up to 250°C. As mentioned earlier, the epoxy hybridizer shows no softening temperature with high decomposition temperatures up to 400°C. This enables the fabricated microstructure to be resistant up to 250°C. Therefore, the optimization of coating and photolithographic processes described earlier allows the thermally stable and

high aspect ratio microstructures to be photopatterned in photosensitive epoxy hybridizers.

CONCLUSIONS

In this article, we have developed new UV-patternable and thermally stable epoxy hybridizers for the fabrication of high aspect ratio microstructures based on cationic polymerization. The epoxy hybridizer had good stability because of the low number of unreacted species in the resin and OH groups. The properties of the epoxy hybridizers could also be modulated easily by controlling the composition of the precursors. The nanosized cycloaliphatic-epoxy oligosiloxane resin had excellent photosensitivity to near-UV light without oxygen inhibition. Also, the epoxy hybridizer was thermally stable up to 400°C. The fabricating patterns were shown to be thick (>100 μm), have a high aspect ratio (>5), and good sidewall formation. The microstructures also showed good thermal stability and adhesion behavior. Therefore, the epoxy hybrid materials are suitable for use as photoresists or photopatternable dielectrics in many MEMS and RF microelectronics applications requiring only a simple photolithographic process.

References

1. Yu, W. X.; Yuan, X. -C.; Ngo, N. Q.; Que, W. X.; Cheong, W. C.; Koudriachov, V. *Opt Express* 2002, 10, 443.
2. Uddin, M. A.; Chan, H. P.; Chow, K. C. *Chem Mater* 2004, 16, 4806.
3. Chatzichristid, M.; Raptis, I.; Diakoumakos, C. D.; Glezos, N.; Argitis, P.; Sanopoulon, M. *Microelectron Eng* 2002, 61, 729.
4. Lee, K.; LaBianca, N.; Rishton, S.; Ohlgharnain, S. Z. *J Vac Sci Technol B* 1995, 13, 3012.
5. Wang, C. S.; Shieh, J. Y. *J Appl Polym Sci* 1999, 73, 353.
6. Lorenz, H.; Despont, M.; Fahrni, N.; LaBianca, N.; Renaud, P.; Vettiger, P. *J Micromech Microeng* 1997, 7, 121.
7. Azoplate Corp. U.S. Pat.3,028,239 (1962).
8. Crivello, J. V.; Song, K. Y.; Ghoshal, R. *Chem Mater* 2001, 13, 1932.
9. Cheng, X.; Guo, L. J.; Fu, P.-F. *Adv Mater* 2005, 17, 1419.
10. Blanc, D.; Pelissier, S.; Saravanamuttu, K.; Najafi, S. I.; Andrews, M. P. *Adv Mater* 1999, 11, 1508.
11. Kim, J. K.; Kang, D. J.; Bae, B. S. *Adv Funct Mater* 2005, 15, 1870.
12. Kang, D. J.; Kim, W. S.; Bae, B. S. *Appl Phys Lett* 2005, 87, 221106.
13. Bae, B. S.; Park, O. H.; Charters, R.; Luther-Davies, B.; Atkins, G. R. *J Mater Res* 2002, 16, 3184.
14. Chen, Y.-C.; Yen, C.-T.; Chen, W.-C. *Polymer* 2006, 46, 6959.
15. Brusatin, G.; Giustina, G. D.; Guglielmi, M.; Innocenzi, P. *Prog Solid State Chem* 2006, 34, 223.
16. Crivello, J. V.; Mao, Z. *Chem Mater* 1997, 9, 1554.
17. Eo, Y. J.; Lee, T. H.; Kim, S. Y.; Kang, J. K.; Han, Y. S.; Bae, B. S. *J Polym Sci Part B: Polym Phys* 2005, 43, 827.
18. Decker, C.; Jenkins, A. D. *Macromolecules* 1985, 18, 1241.
19. Lee, T. Y.; Guymon, C. A.; Jonsson, E. S.; Hoyle, C. E. *Polymer* 2004, 45, 6155.
20. Lee, T. H.; Kang, E. S.; Bae, B. S. *J Sol-Gel Sci Technol* 2003, 27, 23.
21. Bulut, U.; Crivello, J. V. *Macromolecules* 2005, 38, 3584.
22. Innocenzi, P.; Brusatin, G.; Guglielmi, M.; Bertani, R. *Chem Mater* 1999, 11, 1672.
23. Lee, T. H.; Kim, J. H.; Bae, B. S. *J Mater Chem* 2006, 1617, 1657.
24. Sepeur, S.; Kunze, N.; Werner, B.; Schmidt, H. *Thin Solid Films* 1999, 351, 216.
25. Roe, R. J. *Methods of X-ray and Neutron Scattering in Polymer Science*; Oxford University Press: Oxford, 2000; p 155.
26. Choi, J.; Yee, A. F.; Laine, R. M. *Macromolecules* 2003, 36, 5666.