Available online at www.sciencedirect.com
SCIENCE DIRECT®
European Polymer Journal 40 (2004) 2505–2512
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Effect of the linear siloxane chain in cyclic silsesquioxane (CSSQ) on the mechanical/electrical property of the thin films

Yi-Yeol Lyu [a], Jin-Heong Yim [a,*], Younghun Byun [a], Sang-Yun Lee [a], In-Sun Jung [b], Lyong Sun Pu [a]

[a] *Electronic Materials Lab., Samsung Advanced Institute of Technology (SAIT), P.O. Box 111, San 14-1, Nongseo-ri, Kiheung-eup, Yongin-shi, Kyungki-do 449-712, Korea*
[b] *AE Center, Samsung Advanced Institute of Technology (SAIT), San 14-1, Nongseo-ri, Kiheung-eup, Yongin-shi, Kyungki-do 449-712, Korea*

Received 20 January 2004; received in revised form 14 June 2004; accepted 21 June 2004
Available online 26 August 2004

Abstract

Several kinds of cyclic silsesquioxane (CSSQ) precursors containing linear siloxane chain were prepared to improve both the mechanical properties of their thin films and the compatibility with heptakis (2,3,6-tri-*O*-methyl)-β-cyclodextrin (tCD) as a porogen. The precursors were synthesized using a hydrolysis/condensation reaction with 2,4,6,8-tetramethyl-2,4,6,8-tetra (trimethoxysilylethyl) cyclotetrasiloxane (cyclic monomer) and three kinds of linear siloxane monomers. As the linear siloxane chain length increases in the CSSQ precursors, the compatibility between the CSSQ precursor and tCD molecules improved due to the chain flexibility of the precursor. Moreover, the mechanical strength of the CSSQ precursor (4ST37) containing linear tetrasiloxane was the best among the prepared precursors. The enhancement of mechanical property might also be attributed to the content of Si–OH groups as well as the chain flexibility, which could help the crosslinking reaction of Si–OH groups in the film curing process.

Keywords: Cyclic silsesquioxane (CSSQ); Thin films; Dielectric properties; Spin coating; Polycondensation; Porogen

1. Introduction

The polysilsesquioxanes (PSSQ) have been extensively researched due to their excellent thermal, mechanical, and electrical properties. Various applications of PSSQ have been reported in the field of ceramics, additives, low-k (low dielectric constant) materials and high performance engineering plastics [1–5]. Especially, promising candidates of low-k applications are inorganic spin-on polymers such as hydrogensilsesquioxane (HSQ; $k = 3.1$), methylsilsesquioxane (MSQ; $k = 2.7$), hybrid organic silsesquioxane polymer (HOSP; $k = 2.5$), since the spin-on polymers have excellent thermal stability up to 500 °C as well as inherent low dielectric constant [6]. However, the existence of Si–R (H or CH_3) bonds

* Corresponding author. Tel.: +82 312 806 732; fax: +82 312 806 725.
E-mail address: ch20889@sait.samsung.co.kr (J.-H. Yim).

0014-3057/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2004.06.018

in these inorganic polymer films leads to their potential lack of mechanical stability for various semiconductor fabrication steps such as chemical mechanical polishing (CMP). Therefore, high mechanical strength as well as toughness is needed for inorganic thin films to be used for the chip integration [7]. Several studies on the organic-inorganic hybrid materials have been performed to improve mechanical properties [8–13]. Recently, we demonstrated the thin film using cyclic silsesquioxane (CSSQ), which was polymerized with cyclic silane monomer (monomer I in Scheme 1) [14,15]. The mechanical and electrical properties of the CSSQ thin films showed fairly good performance compared to the previous spin on glass (SOG) type low-k materials.

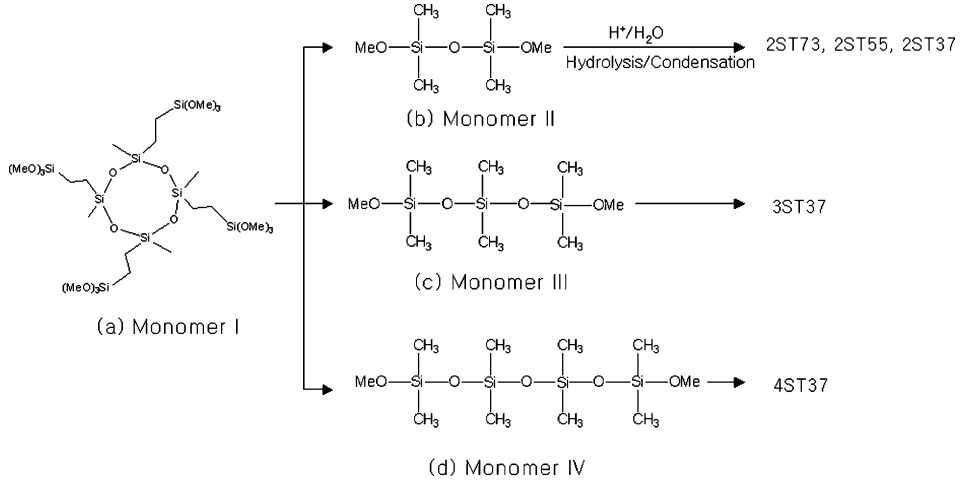
It is inevitable to incorporate nano void into the matrix film to obtain ultra low-k thin film ($k < 2.2$). One approach to generating nanoporous structures in thin films is to formulate a thermally stable low-k precursor with a pore generator (porogen) that can be decomposed and volatilized at a high temperature to leave pores in the film [16–23]. The pore structure can be controlled by using different types of pore generators (porogen). Recently, we have introduced the potential of porous low-k thin films with cyclodextrin (CD) as a porogen [24,25]. The CDs are cyclic oligosaccharides consisting of at least six glucopyranose units which are joined together by α $(1 \rightarrow 4)$ linkages. The CD compounds have a three-dimensional structure with a maximum diameter varying from 13.7 to 16.9 Å. These CDs could be molecularly dispersed in the film, acting like a single nanoparticle in the matrix precursor, and making *isolated* nanopore via their decomposition.

In this study, we made several kinds of CSSQ precursors having different siloxane chain lengths to know the effect of linear siloxane chain on the thin film's properties. And, we prepared the CSSQ thin films made porous using heptakis (2,3,6-tri-*O*-methyl)-β-cyclodextrin (tCD) as a porogen in order to achieve ultra low-k film with a dielectric constant below 2.2. The electrical and mechanical properties of the thin films were monitored and the values of each film were compared to investigate the effects of the molecular structure of the CSSQ precursors.

2. Experimental section

2.1. Materials

Silicon based compounds such as trichlorosilane (Tokyo Chemical Industry Co.), 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (Aldrich Chemical Co.), dichloro dimethylsilane (Aldrich Chemical Co.), 1,5-dichloro hexamethyl trisiloxane (Aldrich Chemical Co.), 1,7-dichloro octamethyl tetrasiloxane (Aldrich Chemical Co.) were used as they were received. Catalysts such as hydrochloric acid (Samchun Pure Chemical Co., LTD), platinum (O)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (Aldrich Chemical Co.) also were used as they were received. Heptakis (2,3,6-tri-*O*-methyl)-β-cyclodextrin (CYCLO LAB. Co.), triethylamine (Aldrich Chemical Co.), anhydrous sodium sulfate (Samchun Pure Chemical Co., LTD), methyl alcohol (Aldrich Chemical Co.), and acetone (J.T. Baker) were used as they were received without further purification. Solvents such as tetrahydrofuran (J.T. Baker), and diethyl ether (J.T. Baker) were purified by distillation in the presence of sodium under a N_2 atmosphere.



Scheme 1. Systematic design, abbreviations of various CSSQ precursors and the structures of monomers: (a) monomer I: 2,4,6,8-tetramethyl-2,4,6,8-tetra (trimethoxysilylethyl) cyclotetrasiloxane; (b) monomer II: 1,3-dimethoxydimethylsilane; (c) monomer III: 1,5-dimethoxyhexamethyltrisiloxane and (d) monomer IV: 1,7-dimethoxyoctamethyltetrasiloxane.

Table 1
Summary of monomer compositions for hydrolysis/condensation[a]

Precursor	Monomer I		Monomer II		Monomer III		Monomer IV	
	(mmol)	(g)	(mmol)	(g)	(mmol)	(g)	(mmol)	(g)
2ST73	6.62	5.52	15.45	3.00	–	–	–	–
2ST55	15.45	12.88	15.45	3.00	–	–	–	–
2ST37	12.00	10.00	5.14	1.00	–	–	–	–
3ST37	12.00	10.00	–	–	5.14	1.38	–	–
4ST37	12.00	10.00	–	–	–	–	5.14	1.76

[a] Reaction condition: r_1 (HCl/Si–OMe)=0.001, r_2 (H_2O/Si–OMe)=3.333, reaction temperature=70 °C, polymerization time=20 h, THF=150 cc.

2.2. Monomer synthesis

2,4,6,8-tetramethyl-2,4,6,8-tetra (trimethoxysilylethyl) cyclotetrasiloxane (monomer I in Scheme 1) was synthesized according to our previous work [5]. 1,3-dimethoxytetramethyldisiloxane(monomer II in Scheme 1) was synthesized as follows. A flask was introduced 10.0 g (49.208 mmol) of 1,3-dichlorotetramethyldisiloxane, and this was diluted with 500 ml of tetrahydrofuran. Next, the flask was cooled to −78 °C, 10.95 g (108.212 mmol) of triethylamine and 3.46 g (107.90 mmol)of methyl alcohol were added, and the reaction mixture was slowly warmed to room temperature. The reaction was continued at room temperature for 15 h; the reaction mixture was filtered through celite for the removal of triethylamine hydrochloride, and then volatile materials were removed from the filtrate under a reduced pressure of about 0.1 Torr. The remaining mixture was added 100 ml of hexane; the mixture was stirred for 1 h and then was filtered through celite to provide a clear, colorless solution. The hexane was evaporated from the solution under a reduced pressure of about 0.1 Torr to afford a colorless liquid. ^{1}H-NMR of monomer II ($CDCl_3$) $\delta = 0.068$ (s, 12H, $4 \times CH_3$), 3.45 (s, 6H, $2 \times OCH_3$).

Using the same conditions as 1,5-dimethoxyhexamethyltrisiloxane (monomer III in Scheme 1) and 1,7-dimethoxyoctamethyltetrasiloxane (monomer IV in Scheme 1), except that 1,3-dichlorotetramethyldisiloxane was replaced with 1,5-dichlorohexamethyltrisiloxane and 1,7-dichlorooctamethyltetrasiloxane respectively. ^{1}H-NMR of monomer III, ($CDCl_3$) $\delta = 0.068$ (s, 12H, $4 \times CH_3$), 0.077 (s, 6H, $-CH_3$), 3.44 (s, 6H, $2 \times OCH_3$), ^{1}H-NMR of monomer IV, ($CDCl_3$) $\delta = 0.068$ (s, 24H, $8 \times CH_3$), 3.45 (s, 6H, $2 \times OCH_3$).

2.3. Preparation of CSSQ based precursors

An adequate amount of 2,4,6,8-tetramethyl-2,4,6,8-tetra (trimethoxysilylethyl) cyclotetrasiloxane (monomer I) and linear siloxane monomer (monomer II or III or IV) was added to the flask then diluted with 150 ml tetrahydrofuran. Next, the diluted HCl solution (1.10 mM hydrochloride) prepared by dilution of conc. HCl (35 wt% hydrochloride) with deionized (D.I.) water was slowly added thereto at −78 °C, followed by the addition of more D.I. water, so that the total amount of water including the inherent water in the above added diluted HCl solution. Thereafter, the flask was slowly warmed to 70 °C, and allowed to react for 20 h. Then, the reaction mixture was transferred to a separatory funnel, 180 ml diethylether was added thereto, and then rinsed three times with 50 ml D.I. water. Subsequently, 5 g anhydrous sodium sulfate was added thereto and stirred at room temperature for 5 h to remove all traces of water, and then filtered out to provide a clear colorless solution. Any volatile materials were evaporated from this solution under reduced pressure of about 0.1 Torr to afford the crude precursor as white powder. After dissolving the produced white power in the 5 ml of acetone, residual particles were eliminated by using a membrane filter (0.2 μm). The acetone was evaporated from the solution under a reduced pressure of about 0.1 Torr. The detail monomer compositions for the polymerization are summarized in Table 1.

2.4. Characterization of precursors

The monomer and precursor samples were dissolved in deuterated acetone. Microstructures of monomer and precursors were analyzed by means of ^{1}H, (Bruker AM 300 MHz) and ^{29}Si NMR (Varian DMX 400 MHz). Chemical shifts are recorded as δ unit (ppm) relative to tetramethylsilane. Molecular weight and molecular weight distribution of precursors were measured by means of gel permeation chromatography (Waters 2690).

2.5. Preparation and characterization of thin films

The precursor solutions were prepared by mixing the siloxane-silsesquioxane hybrid polymer and propylene glycol monomethylether acetate (PM-acetate) in accordance with an adequate ratio. These compositions were applied to spin-coating at 3000 rpm for 13 s onto p-type silicon wafers doped with boron. The coated substrates

were subjected to a series of soft baking on a hot plate for 1 min at 150 °C and another minute at 250 °C, so that the organic solvent might be sufficiently removed. The substrates prepared as above were cured in a cylindrical furnace (Linberg type 55642) at 420 °C for 60 min under vacuum condition. The refractive index and thickness of thin films were measured by using a prism coupler (Metricon Co., Prism coupler 2010). Hardness (H) and elastic modulus (E) of hybrid polymer films were measured using the continuous stiffness measurement (CSM) nanoindentation method [26]. In this technique, not only the force required as a function of indentation depth is recorded while a three sided Berkovich diamond indenter is pushed into the sample and then withdrawn, but also contact stiffness for all depths are measured by superimposing a small oscillation to the force signal at a relatively high frequency. The amplitude and frequency employed for this experiment were 1 nm and 45 Hz, respectively. Multiple points (typically, 6 points) on each sample were indented and the results: hardness, and elastic modulus, were averaged to assure their reliability. The hardness, H, is calculated from its normal definition:

$$H = \frac{F_{\max}}{A} \tag{1}$$

where $F_{\max}$ is the peak indentation load and A is the projected area of the hardness impression. For the elastic modulus calculation of Sneddon's solution [27] was adapted:

$$E_r = \frac{1}{\beta}\frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}} \tag{2}$$

where S is the stiffness, A is the contact area, and β is a shape correction factor for the indenter shape ($\beta = 1.034$ for a Berkovich tip, used in this study). To account for the elastic response of the indenter, the modulus in Eq. (2) is assumed to be a reduced modulus E_r defined by

$$\frac{1}{E_r} = -\frac{1-v_{\text{indenter}}^2}{E_{\text{indenter}}} + \frac{-v_{\text{film}}^2}{E} \tag{3}$$

where E and v_{film} are Young's modulus and Poisson's ratio for the film, and E_{indenter} and v_{indenter} are Young's modulus and Poisson's ratio for the indenter.

The dielectric constant of each film with MIM (metal–insulator–metal) structure was measured by LCR meter (HP 4284) instrument at a frequency of 100 kHz. In the MIM structures, for top electrode with a diameter of 1 mm, Al metal was deposited by using the electron beam evaporation method.

3. Results and discussion

3.1. Synthesis and characterization of various CSSQ precursors

Low dielectric thin film using the CSSQ precursor prepared with hydrolysis/condensation of 2,4,6,8-tetramethyl-2,4,6,8-tetra (trimethoxysilylethyl) cyclotetrasiloxane (cyclic monomer; monomer I in Scheme 1) has been reported in our previous work [14,15]. The primary interest of this study was the synthesis of modified CSSQ precursor containing linear siloxane chain. The linear siloxane chain should be more flexible as compared with the rigid silsesquioxane structure. Therefore, the crosslinking reaction of residual Si–OH groups in the CSSQ precursor could be more favorable for the film curing process, due to the molecular flexibility of the precursor. Under this design concept, three kinds of siloxane monomer having different chain length were used as a comonomer (see Scheme 1).

The microstructure of a silicone based polymer have been classified by using the number of Si–O moiety such as M; triorganosiloxy ($R_3Si_{1/2}$) unit, D; diorganosiloxane ($R_2SiO_{2/2}$) unit, T; organosilsesquioxane ($RSiO_{3/2}$), Q; silicate ($SiO_{4/2}$) unit [5]. Table 2 shows the contents of cyclic and linear siloxane units and the ratio of D and T structures in the prepared precursors. Linear siloxane monomer was effectively incorporated into the the CSSQ precursors as controlling the monomer composition in the hydrolysis/condensation reaction regardless of its chain length. It means that the reactivity of cyclic monomer and siloxane monomer is almost similar toward co-condensation. The area ratio of D and T structure in the CSSQ precursors decreased as the amount of cyclic silane increased as shown in Table 2.

Table 2
The content of monomer and ratio of D/T structure in the prepared various precursors

Precursor	Monomer I[a] (mol%)	Monomer II[a] (mol%)	Monomer III [a] (mol%)	Monomer IV[a] (mol%)	D/T ratio[b]
2ST73	31.3	68.7	–	–	1.96
2ST55	51.0	49.0	–	–	1.37
2ST37	67.3	32.7	–	–	1.02
3ST37	73.7	–	26.3	–	1.08
4ST37	73.7	–	–	26.3	1.16

[a] Measured by ^{1}H-NMR.
[b] Measured by ^{29}Si NMR.

In the comparison of microstructures for the 2ST37, 3ST37, and 4ST37 precursors, the area ratio of D and T structure slightly increased with the length of linear siloxane monomer as expected. Fig. 1 shows ^{29}Si–NMR spectra of the CSSQ precursors with different linear disiloxane (2ST37, 2ST55, and 2ST73). The NMR signals of the precursors were observed at −13, −19, −49, −58 and −66 ppm due to D^1, D^2, T^1, T^2 and T^3 structures, respectively. It is interesting to note that T^1 peak of 2ST37 precursor was major among the T structure peaks. The high content of the T^1 structure might be attributed to the relatively large amount of uncondensed Si–OH groups in the precursors.

The contents of the Si–OH groups were measured by ^{1}H-NMR from the various prepared precursors. As summarized in Table 3, the amount of Si–OH drastically increased with increasing the content of cyclic monomer in the 2ST series precursors. There are twelve hydrolyzable groups in the cyclic monomer (monomer I), while there are only two those of disiloxane monomers (Monomer II). Therefore, it is clear that the content of residual Si–OH groups in the 2ST series precursors get larger with the content of cyclic monomer. This result is consistent with ^{29}Si–NMR analysis. The 2ST series precursors have an almost similar molecular weight regardless of precursor composition. In the case of CSSQ based precursors having different siloxane chain length (2ST37, 3ST37, and 4ST37), the content of Si–OH groups was almost the same and the molecular weight slightly increased with the increasing of the siloxane chain length.

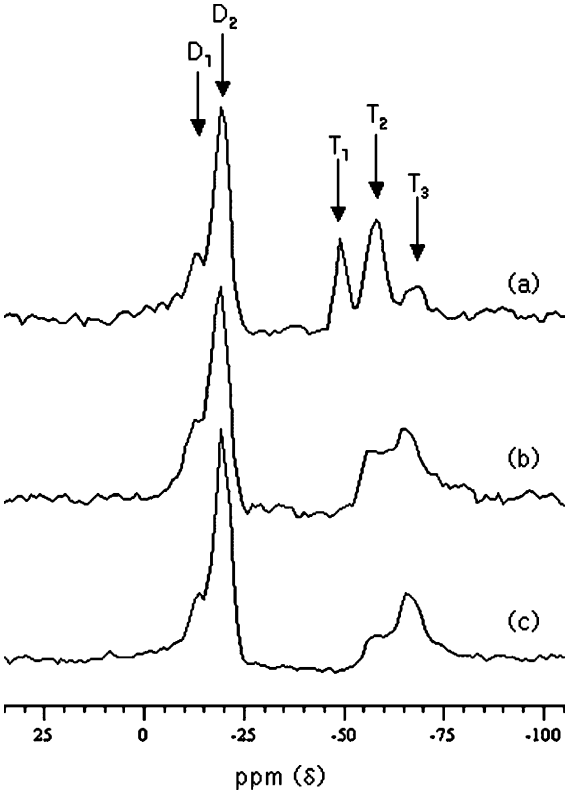


Fig. 1. ^{29}Si spectra of various CSSQ based precursors: (a) 2ST73, (b) 2ST55 and (c) 2ST37.

Table 3
The content of functional groups and molecular weights of various precursors[a]

Precursor	Si–OH[b] (mol%)	Si–OMe[b] (mol%)	Si–CH_3b (mol%)	M_w[c]	MWD[c]
2ST73	6.2	0.3	93.5	16,900	5.52
2ST55	14.3	0.5	85.1	14,400	4.98
2ST37	28.6	0.7	70.7	16,100	5.13
3ST37	30.6	1.0	68.4	25,800	7.91
4ST37	28.1	0.9	71.0	31,800	8.69

[a] Reaction condition: r_1 (HCl/OMe)=0.001, r_2 (H_2O/OMe)=3.333, 70 °C, 20 h.

[b] Measured by ^{1}H-NMR: Si–OH(%)=Area(Si–OH) − [Area (Si–OH) + Area(Si–OCH_3)/3 + Area(Si–CH_3)/3] × 100 Si–OCH_3 (%) = Area(Si–OCH_3)/3 − [Area(Si–OH) + Area(Si–OCH_3)/3 + Area(Si–CH_3)/3] × 100 Si–CH_3(%)=Area(Si–CH_3)/3 − [Area(Si–OH) + Area(Si–OCH_3)/3 + Area(Si–CH_3)/3] × 100.

[c] Measured by GPC.

3.2. Thin films properties of various CSSQ precursors

Various kinds of thin films using CSSQ precursors were prepared with spin a coating and several steps of curing process. Further, we made porous CSSQ films by using coating solution containing tCD porogen (30 wt%) and CSSQ precursor (70 wt%). It is important to understand the relationship between the porosity and the compatibility of porogen with the silsesquioxane (SSQ) precursor. In general, porogens tend to agglomerate each other, when the porogen concentration is high enough (typically porogen loading above 30%) or the compatibility between the matrix precursor and porogen is not good. In such a case, effective porosity could not be obtained as expected due to pore collapse occurring in the porogen decomposition stage. Table 4 shows that the porosity of the CSSQ films made of the 2ST series (with synthesizing disiloxane monomer) increased as the content of cyclic monomer in the precursors increased. It was found that the porosity of thin films prepared with the CSSQ based precursor seem to be strongly related to the content of Si–OH groups in the precursor owing to the compatibility of porogen with the matrix materials. It seems that the interactions between the methoxy groups of tCD and Si–OH groups of the CSSQ precursor becomes much more favorable with the increasing content of Si–OH groups in the precursor. However, in the case of the CSSQ based precursors having different siloxane chain lengths

Table 4
Porosity and dielectric constant of various thin films prepared with various precursors and tCD porogen

Materials	Refractive index[a]	Porosity[b] (%)	Dielectric constant (k)[c]	Dissipation factor[c]
2ST73	1.4056 ± 0.0007	–	2.74	0.003
2ST73/tCD 30 wt%	1.3614 ± 0.0020	9.8	2.45	0.002
2ST55	1.4205 ± 0.0005	–	2.65	0.004
2ST55/tCD 30 wt%	1.3412 ± 0.0005	17.0	2.25	0.003
2ST37	1.4299 ± 0.0004	–	2.65	0.001
2ST37/tCD 30 wt%	1.3298 ± 0.0007	21.1	2.21	0.002
3ST37	1.4355 ± 0.0001	–	2.71	0.002
3ST37/tCD 30 wt%	1.3278 ± 0.0031	22.4	2.19	0.003
4ST37	1.4395 ± 0.0007	–	2.70	0.002
4ST37/tCD 30 wt%	1.3202 ± 0.0017	24.6	2.15	0.001

[a] Refractive index and thickness measured by a prism coupler.
[b] Porosites were calculated by the Lorentz–Lorentz Eq. (1)

$$\text{Porosity } (\%) = 1 - [(N_p^2 - 1)/(N_p^2 + 2)]/[(N_m^2 - 1)/(N_m^2 + 2)] \quad (1)$$

N_p: refractive index of porous film, N_m: refractive index of matrix film.
[c] Dielectric constant were measured by MIM (metal–insulator–metal).

(2ST37, 3ST37, 4ST37), the porosity slightly increased with the increasing siloxane chain length even though the contents of Si–OH groups were almost in the same range. This may be explained by the flexibility of the CSSQ precursor. As increasing chain length of linear siloxane unit, flexibility of the precursor should be enhanced in the coating solution. Therefore, effective porosity can be increased with the siloxane chain length. For this reason, we can achieve the lowest k value ($k = 2.15$), when 4ST37 precursor with 30-wt% of tCD porogen was used as spin-on coating solution.

Generally, the hardness and modulus of thin film increase as a function of indenting displacement due to the influence of the silicon substrate (elastic modulus ~ 174 GPa, hardness ~ 12.5 GPa), so called "substrate effect" (see Fig. 3). Compared to the hardness, the measured

Table 5
Hardness and elastic modulus of various thin films prepared with various precursors and tCD porogen

Precursor	Thickness (nm)[a]	Hardness (GPa)[b]	Modulus (GPa)[b]
2ST73	965 ± 19	0.28 ± 0.01	2.36 ± 0.03
2ST73/tCD 30 wt%	895 ± 13	0.20 ± 0.01	1.95 ± 0.03
2ST55	1167 ± 20	0.49 ± 0.01	3.41 ± 0.03
2ST55/tCD 30 wt%	928 ± 17	0.32 ± 0.01	2.31 ± 0.04
2ST37	1019 ± 7	0.81 ± 0.01	5.19 ± 0.03
2ST37/tCD 30 wt%	898 ± 9	0.38 ± 0.01	2.63 ± 0.04
3ST37	1113 ± 5	0.95 ± 0.02	5.57 ± 0.09
3ST37/tCD 30 wt%	1008 ± 13	0.42 ± 0.02	2.56 ± 0.04
4ST37	1029 ± 29	1.10 ± 0.02	6.58 ± 0.07
4ST37/tCD 30 wt%	969 ± 17	0.43 ± 0.01	2.71 ± 0.03

[a] Thickness data were measured by means of a Prism Coupler.
[b] Hardness and elastic modulus of all films were collected at the indentation depth of 100 nm.

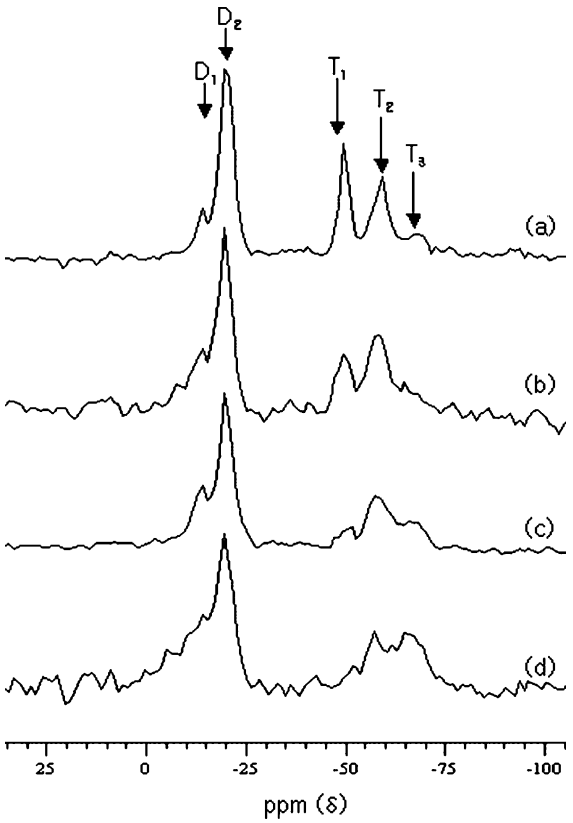


Fig. 2. ^{29}Si spectra of various CSSQ based precursors: (a) 4ST37 (Si–OH=41.2%), (b) 4ST37 (Si–OH=33.3%), (c) 4ST37 (Si–OH=29.9%) and (d) 4ST37 (Si–OH=18.3%).

Table 6
The effect of Si–OH groups in the 4ST37 based precursors on the mechanical properties of thin films

Reaction condition		Analysis of precursor					The properties of thin films			
r_1	r_2	Si–OH (%)[a]	T^{1}[b]	T^{2}[b]	T^{3}[b]	RI[c]	Thickness (nm)[c]	k[d]	Hardness (GPa)[e]	Modulus (GPa)[e]
0.01	3.33	18.3	0.17	0.40	0.43	1.4207	1345.3	2.70	0.68	4.00
0.001	5.55	29.9	0.19	0.52	0.28	1.4358	1047.9	2.66	1.06	6.28
0.0005	3.33	33.3	0.37	0.51	0.12	1.4403	1151.3	2.71	1.18	6.85
0.0003	3.33	41.2	0.40	0.41	0.19	1.4454	1248.5	2.65	1.27	7.15

[a] Si–OH content measured by ^{1}H-NMR.
[b] T^{1}, T^{2}, and T^{3} were measured by ^{29}Si NMR.
[c] Thickness data were measured by means of a Prism Coupler.
[d] Dielectric constant by MIM (metal–insulator–metal).
[e] Hardness and elastic modulus of all films were collected at the indentation depth of 100 nm.

elastic moduli are affected more strongly by the substrate. We made the thick films above 800 nm in order to eliminate the ''substrate effect'' in the nanoindentation. In addition, considering relatively shallow indentation depth of <300 nm compared to the film thickness, we think the plateaus of nanoindentation curve might be good estimates of the true properties of films. Therefore we collected the value of hardness and modulus of all films at the indentation depth of 100 nm. Hardness and modulus of 2ST series thin film increase with the increasing content of cyclic monomer in the precursors as shown in Table 5. The content of Si–OH groups in the CSSQ precursors affects the mechanical property of their thin films such as hardness and modulus. The Si–OH groups in the precursor are reactive groups for crosslinking reaction i.e. polycondensation during the film curing process. It seems to be that a larger amount of Si–OH terminal bond in precursors are able to lead to a higher degree of crosslinking (DC) and result in the improvement of mechanical property. In the case of CSSQ based precursors having different siloxane chain lengths (2ST37, 3ST37, 4ST37), noticeable improvement of mechanical properties were investigated even though the contents of Si–OH groups were almost the same. It is believed that the chain flexibility may also be contributed to the increase of DC at the curing process.

The 4ST37 precursor was selected among the prepared precursors considering its electrical and mechanical properties. The content of Si–OH groups in the 4ST37 precursor could be controlled by varying reaction condition such as the amount of catalyst (r_1) and water (r_2). Various 4ST37 precursors with different contents of Si–OH groups were made in the range from 18 to 42 mol%. Fig. 2 shows ^{29}Si–NMR spectra of various kinds of 4ST37 precursors having different content of Si–OH groups in the precursor. The peak denoted T^{1} structure drastically increased with the content of Si–OH in the 4ST37 precursor as mentioned earlier. The Si–OH groups are thermally reactive toward condensation reaction during the curing process of the thin film as we noted previously. Therefore, DC of the thin film should increase as a function of the Si–OH groups in the CSSQ precursors. For this reason, the content of Si–OH groups in the precursor was very well correlated with

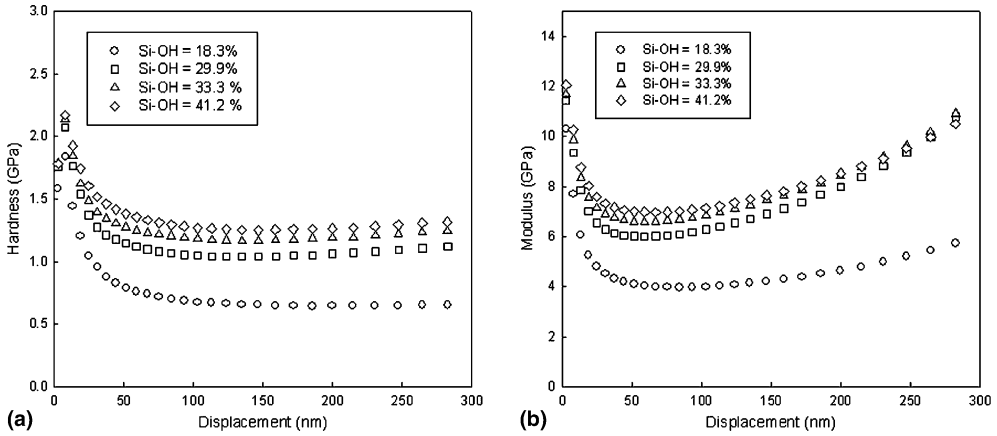


Fig. 3. (a) Hardness and (b) elastic modulus of low dielectric films prepared with various 4ST37 series precursors on silicon substrate plotted as a function of the indentation depth.

mechanical properties such as hardness and modulus as shown in Table 6 and Fig. 3. The residual Si–OH groups in the cured thin film can act as an adsorbing site for moisture in an ambient condition. The existence of residual Si–OH groups in the film results in increasing dielectric constant. The dielectric constants of CSSQ based thin films were not affected with Si–OH groups in the precursor under our experimental conditions. It means that the CSSQ precursors should be almost crosslinked during the vacuum curing process. The CSSQ films may contain a negligible amount of residual Si–OH groups. The dielectric constant of the CSSQ films was not changed in water for 24 h.

4. Conclusions

Several kinds of cyclic silsesquioxane (CSSQ) precursors have been successfully synthesized using 2,4,6,8-tetramethyl-2,4,6,8-tetra (trimethoxysilylethyl) cyclotetrasiloxane and linear siloxane monomers with different linear siloxane chain lengths. It was found that the porosity of the CSSQ thin films prepared with tCD porogen affected not only the content of Si–OH groups but also the flexibility of the precursor. The dielectric constant of the porous CSSQ thin film decreased with the increasing Si–OH groups and the flexibility of the precursor even though the same tCD porogen concentration in the coating solution. Moreover, the mechanical property of the CSSQ thin film seems to be related with the content of Si–OH groups as well as linear siloxane chain length in the precursors. The mechanical properties of CSSQ thin films were strongly correlated with the content of Si–OH groups in the precursors.

References

[1] Liou H-J, Pretzer J. Thin Solid Films 1998;335:186.
[2] Albrecht MG, Blanchette C. J Electrochem Soc 1998; 145:4019.
[3] Siew YK, Sarker G, Hu X, Hui J, See J, Chua CT. J Electrochem Soc 2000;147:201.
[4] Heise A, Nguyen C, Malek R, Hedrick JL, Frank CW, Miller RD. Macromolecules 2000;33:2336.
[5] Banley RH, Itoh M, Sakakibara A, Suzuki T. Chem Rev 1995;95:1409.
[6] Hacker NP. MRS Bull 1997;22(10):33.
[7] Cook RF. Mater Res Soc Symp Proc 1999;576:301.
[8] Shea KJ, Loy DA. MRS Bull 2001;26(5):368.
[9] Shea KJ, Loy DA, Webster O. J Am Chem Soc 1992; 114:6700.
[10] Sharp KG, Micalczyk MJ. Mater Res Soc Symp Proc 1996;435:105.
[11] Sharp KG, Micalczyk MJ. J Sol–Gel Sci Technol 1997; 8:541.
[12] Zhang C, Babonneau F, Bonhomme C, Laine RM, Soles CL, Hristov HA, et al. J Am Chem Soc 1998;120: 8380.
[13] Lu Y, Fan H, Doke N, Loy DA, Assink RA, LaVan DA, et al. J Am Chem Soc 2000;122:5258.
[14] Yim J-H, Lyu Y-Y, Jeong H-D, Mah SK, Hyeon-Lee J, Hahn J-H, et al. J Appl Polym Sci 2003;90:626.
[15] Hyeon-Lee J, Lyu Y-Y, Lee M-S, Mah SK, Yim J-H, Kim S-Y. Macromol Mater Engng 2004;289(2):164.
[16] Hedrick JL, Miller RD, Hawker CJ, Carter KR, Volksen W, Yoon DY, et al. Adv Mater 1998;10:1049.
[17] Nguyen CV, Carter KR, Hawker CJ, Hedrick JL, Jaffe RL, Miller RD, et al. Chem Mater 1999;11:3080.
[18] Mikoshiba S, Hayase S. J Mater Chem 1999;9:591.
[19] Kohl AT, Mimna R, Shick R, Rhodes L, Wang ZL, Kohl PA. Electrochem Solid-State Lett 1999;2(2):77.
[20] Aoi N. Jpn J Appl Phys 1997;36:1355.
[21] Yang S, Mirau PA, Pai C, Nalamasu O, Reichmanis E, Pai JC, et al. Chem Mater 2002;14:369.
[22] deTheije FK, Balkenende AR, Verheijen MA, Baklanov MR, Mogilnikov KP, Furukawa Y. J Phys Chem 2003; 107:4280.
[23] Yang S, Mirau PA, Pai C, Nalamasu O, Reichmanis E, Lin EK, et al. Chem Mater: Comm 2001;13(9):2762.
[24] Yim J-H, Lyu Y-Y, Jeong H-D, Song SA, Hwang I-S, Hyeon-Lee J, et al. Adv Funct Mater 2003;13(5):382.
[25] Yim J-H, Seon J-B, Jeong H-D, Pu YS, Baklanov MR, Gidley DW. Adv Funct Mater 2004;14(3):277.
[26] Oliver WC, Pharr GM. J Mater Res 1992;7:1564.
[27] Sneddon IN. Int J Engng Sci 1965;3:47.