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Preparation of low density poly(methylsilsesquioxane)s for LSI interlayer dielectrics with low dielectric constant. Fabrication of Ångstrom size pores prepared by baking trifluoropropylsilyl copolymers

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We report a method to fabricate Ångstrom size pores in poly(methylsilsesquioxane) films in order to decrease the density and the dielectric constant of the film. Copolymers bearing methyl(trisiloxysilyl)units and alkyl(trisiloxysilyl) units are spin-coated and baked at 250 °C to provide rigid siloxane matrixes. Films are baked up to 450 or 500 °C to remove thermally labile alkyl groups and holes are left corresponding to the sizes of the substituents. Trifluoropropyl, cyanoethyl, phenethyl and propyl groups are investigated as thermally labile substituents. Only the trifluoropropyl group works well under the limitation of baking temperatures up to 450 or 500 °C, the pores collapsing for films bearing other substituents. A film P5 with a dielectric constant of 2.3 was obtained for trifluoropropyl. The total surface area of this film was 1.34 times that of poly(methylsilsesquioxane) film (P1) prepared by a conventional sol–gel method. The peak of pore distributions is in the region <10 Å. The peculiarity of the trifluoropropyl group is discussed.

Introduction

As feature sizes in integrated circuits approach to <0.15 μm, problems with interconnect resistance–capacitance(RC) delay, power consumption, and cross-talk become more significant.[1] Integration of low dielectric constant materials will partially mitigate these problems. The dielectric constant of SiO_2 which has been so far employed is *ca.* 4.0.

Development of materials with low dielectric constants of <3.0 with stability at >450 °C have been focused on. One approach is to increase the heat resistant properties of organic polymers, a number of which have dielectric constants of <3. However, such organic polymers suffer from potential problems including thermal instability (thermomechanical and heat resistant properties), and low thermal conductivities,[2] and there is often a trade off between low dielectric constants and good thermal properties.[2] Aromatic polyimides and heterocyclic polymers such as poly(phenylquinoxaline)s and poly(quinoline)s are well known polymers with very high heat resistant properties, but (T_g) values of these polymers are <400 °C. In order to improve the heat resistant properties of polyimides, phase-separated inorganic–organic hybrids have been prepared.[3]

The other approach is to decrease dielectric constants of SiO_2 or SiO_2 derivatives which are known to have adequate heat resistant properties. The dielectric constant (ε) is related to molar polarization (P_m) and molar volume (V_m) by $(\varepsilon-1)(\varepsilon+2)=P_m/V_m$. Therefore, dielectric constants increase with decrease in molar volume, *i.e.* density. Densities can be decreased by (1) introduction of structures leading to steric hindrance[4] and (2) fabrications of small pores in films.[5–13]

Films having methyl groups or hydrogen groups on Si atoms belong to the first category and poly(methylsilsesquioxane)s and poly(hydrogen silsesquioxane)s have dielectric constants of 2.7–3.0.[4]

Several materials in the second category have also been reported. Pore sizes and distributions are controlled by adjusting assembling processes of small particles (method A) solvent evaporation processes on sol–gel methods (method B),[5] or calcination of polymer films containing thermally labile and heat resistant segments (method C).

Inorganic spin-on glass materials composed of circular hydrogen silica sols whose surfaces are covered with poly(hydrogen silsesquioxane)s have been prepared by method A.[6] Circular hydrogen silica sols make small spaces between the neighboring sols, and poly(hydrogen silsesquioxane)s on these sols act as the adhesive forces in silica sols.

By employing method B, nanoporous silicas known as low density aerogels or xerogels, can be fabricated. In this process, the density is fixed by the solvent concentration at the gel point.[5]

Porous silica gels have been prepared by baking precursor polymers, organic polymer–silica gel hybrids [*e.g.* poly(2-methyl-2-oxazoline)/$Si(OEt)_4$ hybrids at 600 °C (method C)].[7,8] Because of hydrogen bonds between poly(oxazoline)s and SiOH groups of silicone polymers, these two polymers have been reported to be uniformly organized in the polymer film, which makes it possible to fabricate uniform pores of 10–20 Å diameter after thermally labile poly(oxazoline)s are removed by baking processes.[7] Polystyrenes,[9] ionic surfactants,[10–13] and non-ionic polyethylene oxide(PPO) surfactants[14] have all been employed as thermally labile materials.

Low dielectric constants (<2.0) have been achieved with low density aerogels or xerogels fabricated by method B.[15] However, absorption of moisture is assumed to be large owing to the structural similarity with silica gels. Because low moisture absorption is one of the required properties for interlayer dielectrics, poly(methylsilsesquioxane) matrices [trisiloxysilyl(T) matrices] should be superior to silica-gel matrices[tetrasiloxysilyl(Q) matrices] and thus such matrices were employed here.

Poly(methylsilsesquioxane)s are considered to be organic polymers in which the inorganic components are molecularly organized. Phase separated poly(phenylquinoxaline) (PPQ)–poly(propylene oxide)(PPO) copolymer films have been reported to give films with nanosize pores after the thermally labile PPO segments were removed by baking.[16,17] These pores are fabricated by phase separations or entanglements of more than two polymer segments. Therefore, they have a peak of pore distributions at >20 Å which corresponds to the volume of the polymer segments [Fig. 1(a)].[7–9,16,17]

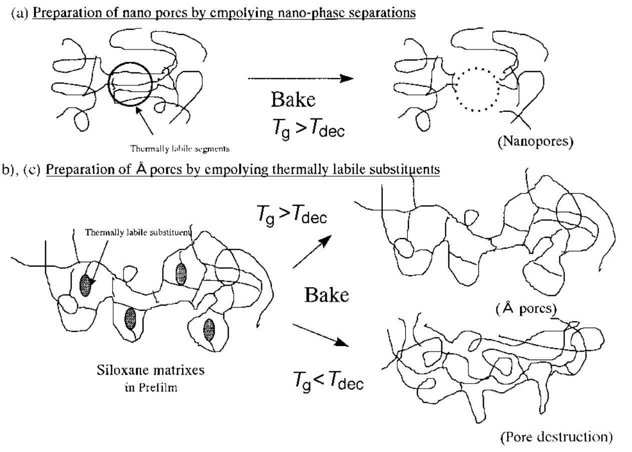


Fig. 1 Differences in methods to fabricate low density films, and relation between T_g and pore characteristics.

Attempts to eliminate small side chains and make smaller pores than those obtained *via* polymer segments have been made. For example, polyimide precursor films bearing carbonate groups in the side chain have been prepared. These thermally labile carbonate groups are eliminated by baking, leading to porous materials.[18] The pore size was, however, very large, because gases were released near T_g of the polyimide. This should be the simplest way to fabricate small pores with molecular dimensions. There are many publications on methods of creating nanoscale pores in silica matrixes (Q matrixes), however, as far as we are aware, there are no reports on low density poly(methylsilsesquioxane) films prepared by this method, probably because T matrices are more flexible than Q matrices[19] and pores prepared by loss of substituents would be collapsed.

Our goal is to propose a method to lower the density of poly(methylsilsesquioxane) films (film P1) which already have a lower density than SiO_2 owing to steric hindrance of methyl groups. Such poly(methylsilsesquioxane) films (P1) prepared by conventional sol–gel methods have been reported to have excellent thermal stability and low dielectric constants of *ca.* 2.8.[2] The size of pores aimed at corresponded to those fabricated in P1 films, *i.e.* pore sizes resulting from steric hindrance *i.e.* <10 Å. In other words, our purpose is to increase surface areas of poly(methylsilsesquioxane) films without changing the distribution peak of pore sizes. Fig. 1 summarizes our aim and differences from the phase-separation method.

Experimental

Materials

Monomers employed and their abbreviations are summarized in Fig. 2.

All silyl monomers are commercially available and purchased from Shin-etsu Kagaku Corporation and were purified by distillation before use.

Preparation of sol solutions

15 g of alkoxysilane or alkoxysilane mixture, 15 g of isopropyl alcohol, 5 g of *n*-butanol, 5 g of distilled water, and 0.1 g of oxalic acid were mixed together and the mixture was refluxed for 6 h (in the case of P5) to polymerize the alkoxysilanes (Scheme 1). Then the reaction mixture was cooled and spin-coated on a substrate. The reaction time was varied, depending on the alkoxysilane structure. The polymer (sol) compositions and their abbreviations are summarized in Table 1.

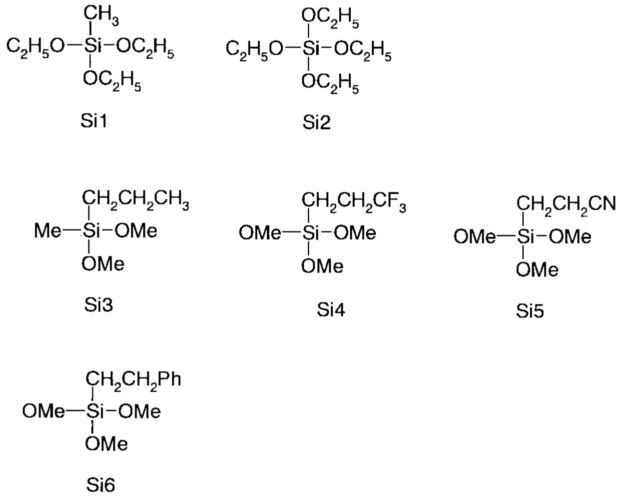
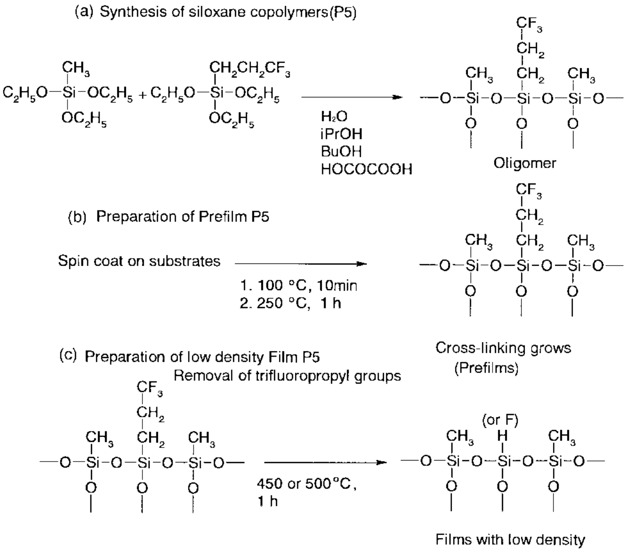


Fig. 2 Monomer structures and their abbreviations.



Scheme 1 Syntheses and preparation of copolymers, prefilms and films with low density.

Table 1 Abbreviations of copolymers, prefilms, films and their compositions

Copolymer abbreviation	Prefilm[a]	Film[b]	Monomers					
			Si1	Si2	Si3	Si4	Si5	Si6
P1	P1	P1	100					
P2	P2	P2		100				
P3	P3	P3	90			10		
P4	P4	P4	80			20		
P5	P5	P5	70			30		
P6	P6	P6	50			50		
P7	P7	P7		90		10		
P8	P8	P8		80		20		
P9	P9	P9		70		30		
P10	P10	P10	90		10			
P11	P11	P11	80		20			
P12	P12	P12	70		30			
P13	P13	P13	90				10	
P14	P14	P14	80				20	
P15	P15	P15	70				30	
P16	P16	P16	90					10
P17	P17	P17	80					20
P18	P18	P18	70					30

[a] Prefilm prepared by prebaking copolymer X below 250 °C. [b] Film prepared by baking prefilm X above 250 °C to remove substituents.

Preparation of films

After a polymer solution was spin-coated on a substrate, the substrate was baked at 100 °C for 5 min. in order to remove solvents. Then, the substrate was baked at 250 °C for 1 h and 450 or 500 °C for 1 h. It took 1 h to raise the temperature from r.t. to 250 °C and from 250 to 450 or 500 °C, respectively.

Characterization of polymer films

IR spectra were recorded with a Nippon Bunko model FT-IRWS/IR-8300. Thermal properties of polymers were measured with a Seiko Denshi model TG-DTA220. Film uniformity was monitored with a JEOL model JEM4000FX high resolution transmittance electron microscope(HRTEM). The polymer solution was spin-coated on an Si wafer and the wafer was baked at 450 °C in the method described above to fabricate 0.2 µm thickness films. Thin films for HRTEM observations were fabricated by an ion mealing method (etching by Ar ions). Dielectric constants were monitored with a HP model 4194 LCR meter. Refractivity was measured with a SOPRA model ES-4G elipsometer. A polymer film of 0.5 µm thickness on an Si wafer with 6 in diameter was employed for the measurement of film densities. Film densities were calculated from the thickness and the weight of the polymer film. Thermally decomposed products were analyzed by a GC–MS–IR apparatus equipped with a GC(HP5890)/MS(HP5972A) MS selective detector/IR(HP5965B) FT-IR detector. Films were subjected to nitrogen sorption porosimetry studies. Surface areas of the films were obtained by the Langmuir method from their isotherm curves.[20,21] Dispersities of pore volumes of films were calculated by the Barrett–Joyner–Halenda (BJH) method from absorption isotherm curves obtained by nitrogen absorption porosimetry of the films.[20,22] The presence of micropores was estimated by a t-plot method, where the thickness of N_2 adsorptions, t, was calculated by a Harkins–Jura(HJ) equation.[23,24] The amount of fluoride left in films was determined with a Dionex model 100 ion chromatograph column.

Results

The processing of films was as follows. Note the term ‘prefilm’ is used for films before removal of substituents.

(1) Spin-coating a solution of precursor polymers, (methylsilsesquioxane)copolymers, on a Si wafer.

(2) Baking the wafer at 250 °C for 1 h in order to obtain well developed network structures of Si–O–Si bonds which lead to a high T_g for the prefilm and durability towards collapse at higher temperatures after the subsequent baking process. At 250 °C, even thermally labile substituents should be retained in the structure [Scheme 1(b)].

(3) Baking the wafer at 450 or 500 °C in order to remove thermally labile substituents on the siloxane backbones and leave holes corresponding to where the substituents were present [Scheme 1(c) and Fig. 1(b)]. Pore collapse occurs when matrices do not have high thermal stability [Fig. 1(c)]. The upper limit of the baking temperature is determined by the temperature at which other parts of LSI devices are not damaged thermally.

In this process, relative thermal stabilities between siloxane back-bones and thermally labile substituents should be considered.

Thermal degradation of polysiloxanes have been investigated by many researchers.[25–39] It has been reported that below 400 °C, no charring *via* breakage of Si–C or C–H bonds occurs, rather, cyclic silicones are the primary products of thermal degradations of (–$OSiR_2$–) polymers through Si–O bond scission and rearrangement.[27,38,39] Lin has reported that thermal stabilities of polysiloxanes measured by thermogravimetric analyses on air varied as follows: polydimethylsiloxane > poly(methylvinylsiloxane) > poly(dimethyl-co-diphenylsiloxane) > poly(dimethyl-co-diphenyl-co-methylvinylsiloxane).[37] He explained this phenomena by the fact that for polydimethylsiloxanes, cyclic oligomers, once formed, rearrange to form non-volatile compositions, but for poly(dimethyl-co-diphenyl-co-methylvinylsiloxane), the presence of diphenylsilyl units makes such rearrangement unfavorable.[37]

Polysiloxanes bearing methyl or phenyl groups degrade thermally to generate methane or benzene as well as cyclic siloxane oligomers.[26–36] The half-lives of phenyl and methyl groups at 250 °C in air are more than 100 000 times longer than those of ethyl, propyl and butyl groups.[25] When cyanoethyl and trifluoroethyl groups are decomposed by a pyrolyzer at 600 °C, β-elimination products such as acrylonitrile and trifluoropropene are formed as well as the cyclic products.[26] Knight and Wright have reported that weight losses of poly(MeRSi–O–) increase in the order of methyl = vinyl < phenyl < trifluoropropyl[38] when these polymers are isothermally held in air or N_2. These reports suggest that both silicone chain reorganizations and losses of substituents may occur during a cure process from 250 to 450 or 500 °C and the balance between siloxane reactivities and substituent reactivities varies with the properties of substituents. Silicone chain reorganization may not be favorable for the fabrication of low density materials.

In our study we selected four substituents shown in Fig. 2, namely, propyl, trifluoropropyl, cyanoethyl and phenethyl groups. Thermally induced β-eliminations were expected for trifluoropropyl, cyanoethyl and phenethyl groups.

Thermal analyses

Fig. 3 shows a representative weight loss curve for prefilm P5 when the prefilm was baked up to 500 °C at a rate of 5 °C min^{-1}. The prefilm was precured at 100 °C for 5 min to evaporate solvents. The weight loss seen at (A) in Fig. 3 corresponds to loss of EtOH and H_2O formed by condensation of SiOH or SiOEt groups to form Si–O–Si linkages (note step A was not observed for the prefilm P5 precured at 250 °C for 1 h). The weight loss seen at (B) corresponds to loss of trifluoropropyl groups. Methyl groups on Si–O main chains have been reported to be very stable up to 500 °C.[40] This was also confirmed by our results as will be discussed later.

Fig. 4 shows the relation between weight loss of prefilms and temperature when the temperature was raised at 2 °C min^{-1} from room temperature to 580 °C. Because these prefilms were prebaked at 250 °C for 1 h weight-loss assigned to losses of ethoxy groups were not observed. All substituents we tried started to decrease in weight at *ca.* 450–460 °C.

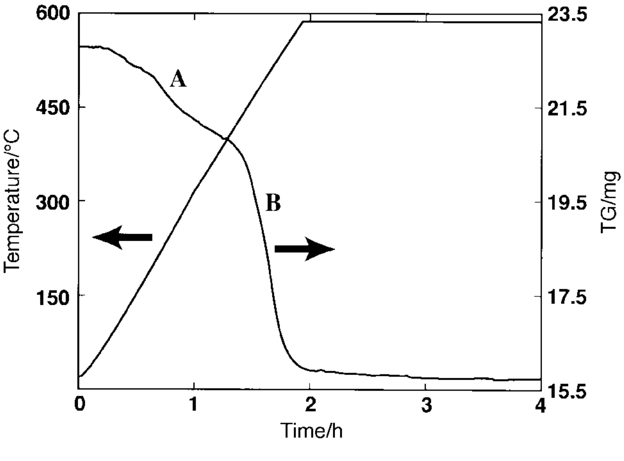


Fig. 3 Weight loss curve for prefilm P5. The sample employed was baked at 100 °C for 5 min to remove any solvent. A is associated with loss of alcohols and water to fabricate matrices and B is associated with loss of trifluoropropyl groups.

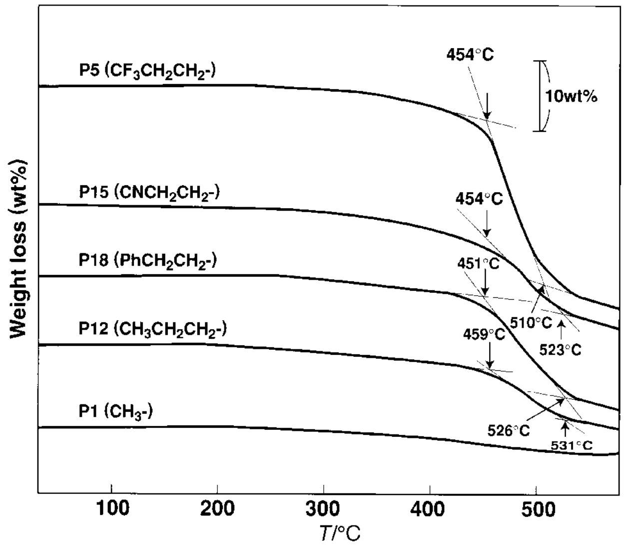


Fig. 4 Weight loss curves of various prefilms. The temperature was raised at a rate of 2 °C min^{-1} and prefilms were baked at 250 °C for 1 h before measurement.

However, temperatures at which losses level off increased in the following order: trifluoropropyl < cyanoethyl ≈ phenethyl < propyl. The loss of trifluoropropyl groups seems to occur most readily.

Similar behavior was observed when prefilms were baked isothermally at 300, 400, 450 and 500 °C, respectively, for 3 h during which weight losses level off. Fig. 5 shows the relation between weight losses and baking temperatures for prefilm P5 and P15. Weight losses for prefilm P5 were completed at lower temperature than for prefilm P15. These results suggest that the trifluoropropyl group is a good candidate as a thermally labile substituent. Inserts in Fig. 5 show the isothermal weight loss curves. Table 2 summarizes ideal weight losses when all of substituents are lost, and the weight losses actually observed at 580 °C (Fig. 4) where these weight losses level off. Substituents were retained to some degree in film P12, P15 and P18 and the complete weight loss of prefilm P5 contrasted with those of other prefilms. Only small weight loss was observed in prefilm P1.

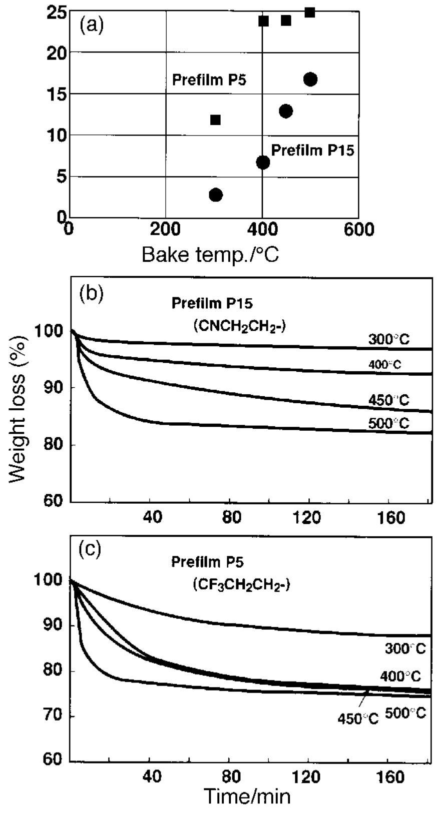


Fig. 5 (a) Relation between weight losses and bake temperatures; prefilms were prepared by baking at 250 °C for 1 h. (b), (c) Relation between weight loss and time at each bake temperature for prefilm P15(b) and P5(c).

IR analyses

Fig. 6 shows IR changes for prefilm P5 during baking. When P5 was baked at 100 °C for 10 min, IR absorptions assigned to C–F and OH stretchings at 1230 and 3400 cm^{-1} were still observed. Upon baking at 250 °C for 1 h, the absorption assigned to –SiOH stretching decreased, but that assigned to C–F stretching was unchanged. Upon baking at 450 °C for 1 h, the absorption assigned to C–F stretching started to decrease and almost disappeared at 500 °C. These IR spectra suggest upon baking at 250 °C for 1 h that cross-linkage of Si–O–Si backbones occurred prior to removal of trifluoropropyl groups which were lost at 450–500 °C.

Elemental analyses

The amount of fluoride released was estimated quantitatively by ion chromatography and results are summarized in Table 3. For example, for P5, the amount of fluoride contained in the prefilm baked at 250 °C was 14.5 wt% which decreased to 1.61 wt% when prefilm P5 was baked at 450 °C for 1 h. Because the calculated value of fluoride in prefilm P5 should be 15.3 wt%, almost all trifluoropropyl groups are released at 450 °C. This also supports the explanation of weight loss curves shown in Fig. 3. The amount of fluoride remaining in the film after baking at 450 °C increased with an increase in the copolymerization ratio of trifluoropropyl groups from prefilm P3 to P5. The amount of fluoride remaining in the film increased when the siloxane matrix was changed from methyl(trisiloxy)silyl (T) units (P3, P4, P5) to (tetrasiloxy)silyl (Q) units (P7, P8, P9). Matrix structures as well as substituent structures affect how readily substituents are removed.

Analyses of gases released by baking

Released gases were analyzed by a GC–MS–IR apparatus. When Prefilm P5 was heated to 450 °C, mixtures containing $CH_3CH_2{=}CF_2$ and cyclic siloxanes containing methyl groups were observed with characteristic absorptions assigned in Fig. 7. It has been reported that poly(methyltrifluoropropyl)-siloxanes decompose thermally to form $CH_2{=}CHCF_3$ [Scheme 2(b)] and $CH_3CH_2{=}CF_2$ [Scheme 2(a)] as well as siloxanes containing Si–F linkages. Our results were consistent with those reported by Pavlova *et al.*[41]

Comparison of densities, refractive indices and dielectric constants

Table 4 summarizes film properties when these films were prepared by baking up to 450 °C. In order to evaluate film densities either direct measurements or measurements of refractive indices were performed. Densities or refractive indices decreased with an increase in copolymerization ratios of trifluoropropyl group from prefilm P3 to P5. However, for films prepared from prefilms bearing phenethyl and cyanoethyl groups, densities or refractive indexes were lowest when these substituents were copolymerized at 20 wt% (film P17 and P14), and increased again at 30 wt% (film P18 and P15).

Fig. 8 shows the relation between copolymerization ratios of trifluoropropyl groups in prefilm P5 and properties of baked films, namely, densities, refractive indices and dielectric constants. When prefilms were baked at 250 °C for 1 h in order

Table 2 Ideal and measured weight losses (%) after baking[a]

	Prefilm P5 $-CH_2CH_2CF_3$	Prefilm P12 $-CH_2CH_2CH_3$	Prefilm P15 $-CH_2CH_2CN$	Prefilm P18 $-CH_2CH_2Ph$	Prefilm P1(ref.) $-CH_3$
Decrease in weight (ideal)	26	18	22	29	0
Decrease in weight at 580 °C	30	12	18	18	3

[a] Prefilms prepared by baking at 100 °C for 5 min and 250 °C for 1 h. Weight losses were obtained from results in Fig. 4.

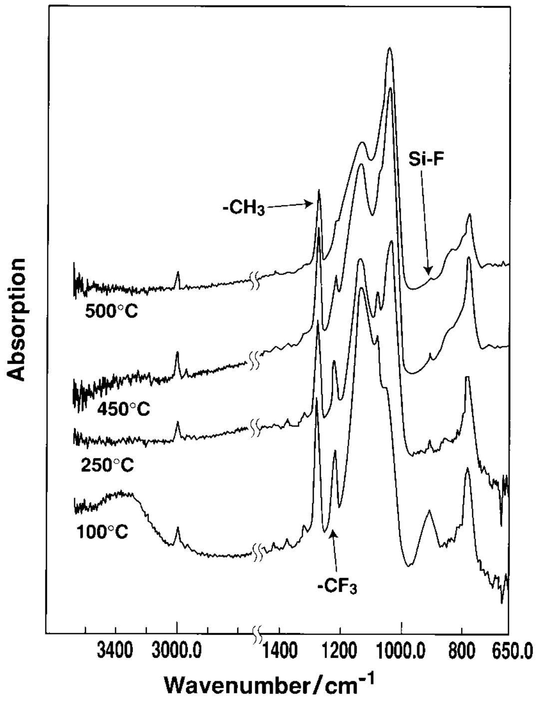


Fig. 6 IR spectral changes for prefilm 5.

Table 3 Amount of F remaining in baked films

Copolymer	Ideal	Detected 250 °C[a]	 450 °C[b]
P3	6.9	4.2	0.9
P4	12	9.5	1.1
P5	15.3	14.5	1.6
P7	8.3	4.1	2.5
P8	14.1	7.8	4.5
P9	19	13.1	5.9

[a] Baking process: 100 °C for 5 min, 250 °C for 1 h. [b] Baking process: 100 °C for 5 min, 250 °C for 1 h, 450 °C for 1 h.

to lead to Si–O–Si cross-links, trifluoropropyl groups are retained in the prefilms. Therefore, decreases in densities and dielectric constants were not observed when the ratio of trifluoropropyl groups in prefilms increased. When these prefilms were baked at 500 °C, densities and dielectric constants decreased with an increase in copolymerization ratios. The dielectric constant of film P5 was 2.3. These results also support the reaction mechanisms shown in Scheme 1 and Fig. 1.

Transmission electron microscope analyses

Fig. 9 shows TEM (transmission electron microscope) images of films baked at 450 °C. No texture was observed for film P5 baked at 450 °C. However, some texture was observed for film P6 baked at 450 °C. Nanopores prepared by phase separation methods have been reported to be observed with TEM.[3,16,17]

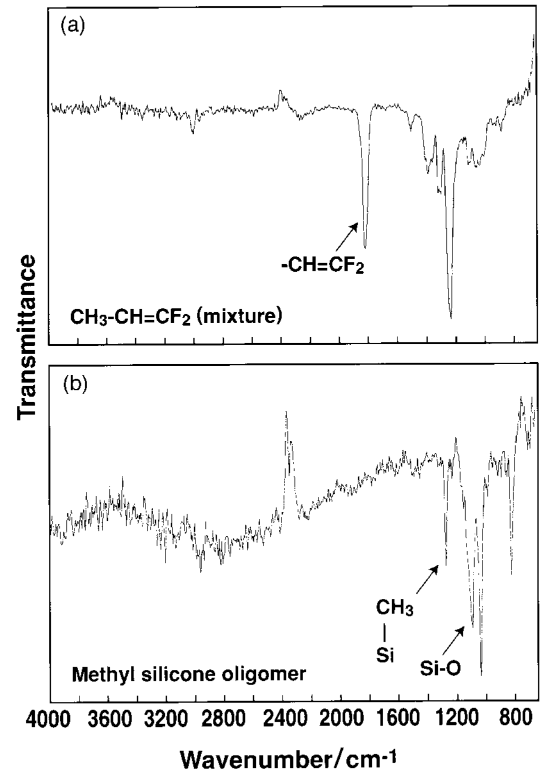
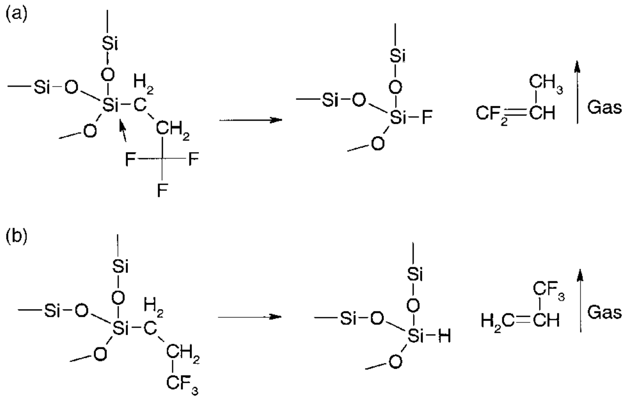


Fig. 7 IR spectra for gases obtained at 450 °C; prefilm P5 was baked at 250 °C for 1 h.



Scheme 2 Expected mechanisms for thermal release of trifluoropropyl groups.

The fact that no texture was observed in film P5 by TEM, despite the decrease in densities, prompted us to determine surface areas and pore size distributions of these films.

Total surface areas and pore distributions

The total surface area of film F5 measured by the Langmuir method was 649 $m^2 g^{-1}$, which was larger than 525 $m^2 g^{-1}$ found for poly(methylsilsesquioxane), film P1.

Fig. 10 shows the relation between pore diameters and pore

Table 4 Properties of films baked at 450 °C[a]

Substituent structures in prefilms	Film	Density/ g cm^{-3}	Refractive index	Dielectric constant
$CH_2CH_2CF_3$	P3	1.3	1.35	2.8
	P4	1.23	1.34	2.6
	P5	1.2	1.26	2.3
$CH_2CH_2CH_3$	P10	1.45		
	P11			
	P12	1.51		
CH_2CH_2Ph	P16	1.36		
	P17	1.2		
	P18	1.28		
CH_2CH_2CN	P13		1.4	
	P14		1.36	
	P15		1.39	
CH_3(ref.)	P1	1.4	1.38	2.9

[a] Baking process: 100 °C for 5 min, 250 °C for 1 h, 450 °C for 1 h.

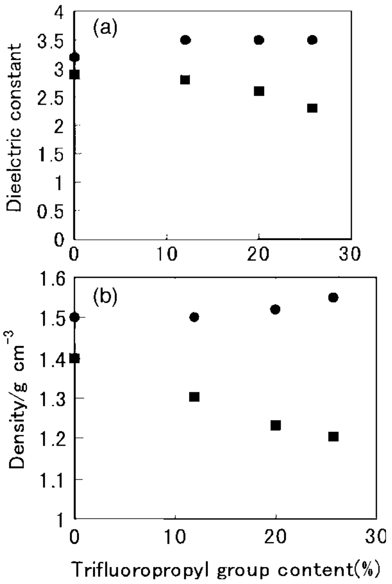


Fig. 8 Relation of dielectric constant and density with trifluoropropyl group content. Prefilms prebaked at 250 °C for 1 h were employed. Baking temperature: 250 °C (●), 450 °C (■).

volumes. This shows that film P5 does not have large pores of >100 Å. The pore volume started to increase at *ca.* 50 Å pore diameter and increased down to 10 Å which is the limit of the N_2 adsorption–desorption isotherm method. Film P1 behaved in a similar way to film P5, but the population at each pore size for film P1 was lower than that for P5. In both cases, no peaks of the pore distribution were observed and are expected to exist in the region <10 Å. Total volumes of pores >10 Å was almost the same as those <10 Å.

Discussion

Relation between substituent structures and film densities

Condensation of ethoxysilanes or silanols occurs at region A in Fig. 3, and loss of substituents occurs at region B. This was confirmed by changes of IR spectra (Fig. 6) and elemental analyses (Table 3). For prefilms having trifluoropropyl groups, film densities after baking decreased as copolymerization ratios of trifluoropropyl groups increased from 10 to 30 wt% (film P3–P5). At 50 wt% (film P6), large pores were observed by TEM (Fig. 9). When the prefilm was baked at 250 °C before baking at 450 °C, no texture was observed. Therefore, the appearance of these large pores is not associated with phase-separations of polymer segments. Unfortunately, T_g values of these films were not able to be observed because these films

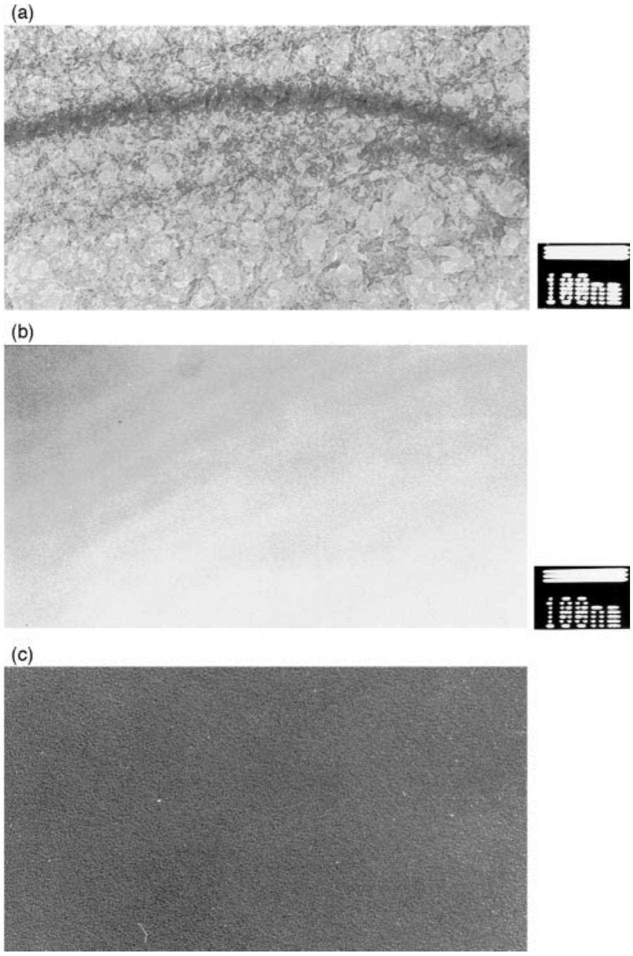


Fig. 9 TEM images for films prepared by baking at 450 °C. (a) Film P6 (×200 000), (b) film P5 (×200 000), (c) film P5 (×500 000).

Table 5 Total surface areas and pore volumes[a]

	Total surface area/m^2 g^{-1}	Pore volume (>10 Å)/cm^3 g^{-1}	Micropore volume (<10 Å)/cm^3 g^{-1}
Film P1	525	0.14	0.17
Film P5	649	0.18	0.22

[a] Baking process 100 °C for 5 min, 100 °C for 5 min, 250 °C for 1 h, 450 °C for 1 h. Micropore volume was calculated by the t-plot method, pore volume >10 Å was calculated by BJH method. [b] Langmuir method.

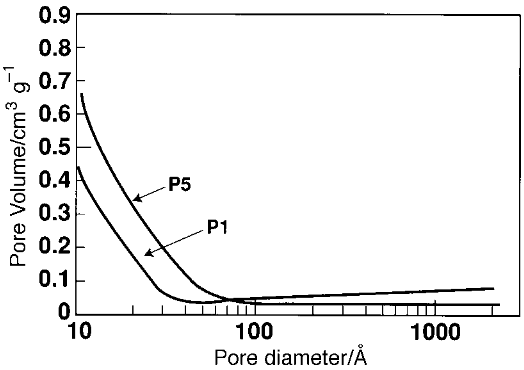


Fig. 10 Relation between pore volume and pore diameter; film P5 baked at 450 °C for 1 h.

are very thin. However, it is reasonable to explain that the incorporation of many trifluoropropyl groups decreased the T_g or modulus of the prefilm or film and rapid eruptions of gases would lead to large holes. It is considered that the decrease in the T_g or the modulus was not so large as to cause destruction of these pores. For prefilms bearing trifluoropropyl groups, the film density decreased without the appearance of large pores up to copolymerization ratio of *ca.* 30%.

The behavior of films prepared from copolymers bearing other substituents differed. Densities or refractive indices of films prepared from copolymers bearing cyanoethyl, propyl or phenethyl groups did not decrease monotonously with increase in the copolymerization ratios. When prefilms prepared at 250 °C from copolymers consisting of 30% substituents (P12, P18 and P15) were baked at 450 °C, the film thicknesses decreased. This was not observed for films prepared from copolymers bearing trifluoropropyl groups. This clearly shows that pore destruction should occur during baking from 250 to 450 °C. Pore destruction should be associated with the rigidity of three dimensional matrices.

Bulkiness of substituents may cause a decrease in the rigidity. The van der Waals' volumes of the substituents were estimated according to eqn. (1),[42,43] and results are summarized in Table 6.

$$\Delta V = 4\pi R^3/3 - \Sigma(1/3)\ \pi h_i^2(3R - h_i) \qquad (1)$$

where ΔV = van der Waals' volume of a molecule, $h_i = R - (R^2 + d_i^2 - r_i^2)/2d_i$, R = van der Waals' radius of an atom A, r_i = van der Waals' radii of an atom A_i bonded to A and d_i = bond length between A_i and A. R and r_i employed are estimated with PM3-MO.

Considering molecular repulsions, the molecular volume (V) is obtained as follows: $V = \Delta V/K$ where K is a value associated with the molecular packing; K has been reported to be *ca.* 0.68 for amorphous polyimide films.[43]

The relative bulkiness of the substituents were compared employing the van der Waals' volume instead of the molecular volume. The van der Waals' volume of the trifluoropropyl group is 53 Å^3 which was almost the same as those of cyanoethyl (45 Å^3) and of propyl (44 Å^3). The volume of phenethyl group was twice this at 90 Å^3. Pore destruction observed in film P18 may be partially explained by the large volume of the phenethyl group. However, pore destruction observed in films prepared from other prefilms could not be explained in this way.

Calculated charge densities of each Si did not vary when substituents were changed. This implies that reactivities of Si–O–Et or Si–O–Me cross-linkages were unaffected by inductive effects of these electron withdrawing groups.

It is reasonable to explain the peculiarity of prefilms bearing trifluoropropyl groups as follows. When trifluoropropyl groups decompose thermally, Si–F bonds form partially and some of these react with residual Si–OH or Si–OEt bonds to build up polysiloxane matrices as confirmed by IR spectra shown in Fig. 6. A band at 910 cm^{-1} can be assigned to Si–F and a band at 1230 cm^{-1} can be assigned to C–F of trifluoropropyl groups in the prefilm baked at 250 °C which gradually decreased upon baking at 450 or 500 °C. This implies that a small amount of Si–F bonds already appear at 250 °C before major losses of trifluoropropyl groups occur at 450 °C. These rigid matrices made by the aid of Si–F bonds would prevent molecular size holes from collapsing. Preliminary calculation results suggest that heat of formation for the process in Scheme 2(a) is −15.59 kcal mol^{-1}, which was smaller than that of the process of Scheme 2(b), 45.1 kcal mol^{-1}. It seems likely that intermolecular attack by F shown in Scheme 2(a) is critical and is not expected for other substituents.

Table 6 van der Waals' volumes of substituents

Substituent (R)	Volume of substituent (calc.) Å/cm^3	Mulliken charges[b]			
		Si1	Si2	C1	C2
CF_3	54	1.17	0.85	−0.45	−0.26
CH_3	44	1.14	0.85	−0.42	−0.21
Ph	90	1.15	0.85	−0.42	−0.17
CN	45	1.17	0.86	−0.45	−0.07

[a] van der Waals' radii employed for the calculation: C, 1.54; H, 1.08; F, 1.30; N, 1.48; Si, 2.10 Å (WinMopac V1.0, PM3). [b] $[H_2MeSi(2)O]_3Si(1)C(1)H_2C(2)H_2R$.

Relation between matrix structures and losses of substituents

Matrix structures also affected losses of substituents. As shown in Table 3, the amount of fluoride left in films having tetrasiloxysilyl(Q) matrices was larger than those having methyltrisiloxysilyl(T) matrices. Probably, decomposition products do not escape from rigid Q matrices. The same phenomena were observed in film P18 as shown in Table 2. When prefilm P18 precured at 250 °C was baked at a rate of 2 °C min^{-1} up to 580 °C, the weight loss was only 18 wt% which was only 62% of the ideal weight loss. By contrast, losses in prefilms bearing other substituents were higher than that of prefilm P18. In order to obtain porous materials, Q matrices have been frequently employed, since they are very rigid and do not collapse even if the temperature is raised to >500 °C. Q matrixes were not suitable for our purpose because of the limit of the baking temperature. The only substituents which could achieve our goal were trifluoropropyl groups in poly(methylsilsesquioxane) matrices.

In thermally decomposed gases, oligosiloxanes were observed as shown in Fig. 7. However, as shown in Fig. 4, the weight loss of prefilm P1 was very small at 450 °C. Therefore, we concluded that thermal degradation of main chain siloxanes are negligible, compared to those of the substituents. Contradictions to early reports may be attributed to the backbone structures.[25–39] Early reports employed linear siloxanes and the siloxanes we employed were T matrixes.

Pore structures of P5

In Fig. 10, peaks of pore distributions were not observed and are expected to exist in the region of <10 Å diameter. The pore distribution curve of film P5 was similar to that of film P1 and the population of each pore size in film P5 was larger than that in film P1 implying that pores of film P5 are very small and comparable to those in film P1 whose pores arise from steric hindrance of methyl groups, and increases in surface areas and the population of each pore size are brought about by elimination of trifluoropropyl groups. This is supported by the fact that the intercept of the perpendicular line in the t-plot curve is positive, suggesting that these micropores adsorb single N_2 molecule.[23,24] Our results contrast with those in other papers. Porous films prepared from polymer hybrids such as poly(*N*,*N*-dimethylacrylamide)silica gel, polystyrene/silica gel, and silica gel containing polyethylene oxide surfactants, have been reported to have a maximum peak of pore size distributions at 20–30 Å.[7–9,13,14] The similarity of the pore distribution curve for film P5 to that for P1, increases in the population of each pore size, increase in total surface areas and uniform TEM picture prove that trifluoropropyl groups are removed by baking at 450 or 500 °C and pores are thus created.

Conclusion

Under the limited baking temperatures of 450 or 500 °C, only trifluoropropyl groups in the poly(methylsilsesquioxane) matrix were effectively removed, and pores of the size of substituents were thus formed. The trifluoropropyl groups were not effectively removed in tetrasilyloxysilyl matrices. The peculiarity was explained by build-up of matrices with the aid of Si–F bonds produced partially during thermal decomposition of the trifluoropropyl group. Pores fabricated from the trifluoropropyl groups are very small and comparable to those made in P1 film whose pores result from the steric hindrance of the methyl groups. Films prepared from P5 copolymer have dielectric constants of 2.3. This method would be useful to make uniform low density poly(methylsilsesquoxane) films for low dielectric constant materials of LSI interlayer dielectrics.

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