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Synthetic control of molecular weight and microstructure of processible poly(methylsilsesquioxane)s for low-dielectric thin film applications

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Abstract

Processible poly(methylsilsesquioxane)s (PMSSQs) were prepared in refluxing THF solutions under nitrogen atmosphere in the presence of HCl catalyst. It was found that various reaction parameters such as concentration, temperature, reaction time, relative amount of water, and relative amount of acid catalyst could affect the molecular weight, microstructure, and the amount of functional end-groups of synthesized PMSSQs. PMSSQ thin films prepared with high molecular weight PMSSQ samples synthesized in solutions exhibited a much improved crack resistance over commercially available samples, probably due to the effects of different microstructures of polymers. The dielectric constants of the fully cured thin films prepared in this study were found to be ca. 2.7, which is nearly the same as those for commercially available samples. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polysilsesquioxane; Low dielectric; Poly(methylsilsesquioxane)

1. Introduction

As the semiconductor structures become smaller and the device packing densities increase accordingly, the signal delay due to the resistance and capacitance (RC) coupling of the interconnects and the cross-talk between metal interconnects have been identified as one of the most serious problems in developing advanced integrated circuit devices [1,2]. According to the International Technology Roadmap for Semiconductors, when the dimension in integrated circuits shrinks down to 0.10 μm around year 2005, the RC interconnect delay is expected to dominate the overall device cycle time [3]. Therefore, in order to reduce the RC delay, it is necessary not only to switch the interconnect metal from aluminum to more conductive copper, but also to introduce low-dielectric materials as the insulating dielectric of the interconnect structure to replace the conventional SiO_2 insulator with a dielectric constant of ca. 4. For this purpose, many research groups have carried out extensive studies to develop suitable low-dielectric insulators by incorporating nanometer-size pores in polymer matrices [4–8]. Among many candidates for such insulators, the inorganic/organic polymer hybrid system shows most interesting and promising results, employing silicon-based polymers such as poly(methylsilsesquioxane) (PMSSQ) as the matrix and organic polymers (known as porogens) as the dispersed domain to produce nanopores upon thermal decomposition [9–11].

Polysilsesquioxanes with empirical formula of $(RSiO_{3/2})_x$, where R is hydrogen or an organic group, have been studied for many years since the first commercialization of silicon polymers as electrical insulation materials used at high temperatures [12]. Poly(phenylsilsesquioxane) (PPSSQ) was the most widely studied material and many synthetic methods were patented [13–15]. Recently, PMSSQ has become prominent as an excellent dielectric owing to its attractive low-dielectric constant close to 2.7, low moisture absorption, excellent thermal stability up to 500°C, and attractive mechanical hardness [12,16,17]. Synthetic methods for preparing soluble and stable PMSSQ by acid or base catalyzed hydrolytic polymerization of methyltrichlorosilane have been known since the early patent publication by JSR in 1978 (as shown in Scheme 1) [18–21]. However, they are still not understood well enough to enable the control over a wide range of microstructures, molecular weights, and the amount and the nature of remaining

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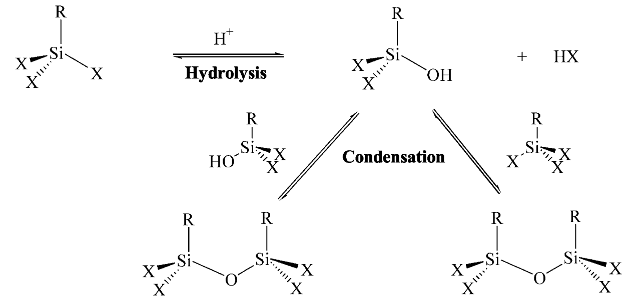

Scheme 1. Acid catalyzed polymerization mechanism of polysilsesquioxane. R = H or alkyl, X = Cl or alkoxy (OR).

functional end-groups, which are important for the mechanical properties of final thin film insulators and the preparation of nanometer-size pores. As a result, the commercially prepared PMSSQ samples tend to be very brittle, exhibiting unacceptably rapid crack propagation in thin films, and their miscibility with porogen polymers becomes problematic.

It is, therefore, the purpose of this work to study the polymerization characteristics and the structure–property relationships of PMSSQ samples prepared under various well-controlled conditions, so as to explore the optimum polymerization conditions and polymer structures to yield the desired electrical and mechanical properties as spin-coated and fully cured thin films.

2. Experimental

Methyltrimethoxysilane (MTMS), purchased from Aldrich, was used without further purification. THF and HCl, purchased from Dae Jung Chemical, Korea, were used for the polymerization. All the polymerization reactions were performed under a nitrogen atmosphere by a standard Schlenk line technique unless otherwise specified. ^{1}H and ^{29}Si NMR spectra were obtained at room temperature with tetramethylsilane (TMS) as an internal standard using Bruker DPX-300 MHz and Bruker DRX-500 MHz, respectively. NMR spectra were obtained in acetone-d$_6$ unless otherwise noted. Gel permeation chromatographic (GPC) analyses were carried out using house-made GPC equipped with a mixed bed Jordi column and Waters 2410 differential refractometer. THF was used as an eluent at a flow rate of 1.0 ml/min and the GPC result was calibrated with polystyrene standards (Polymer Standard Service, USA), which range from 500–1,000,000 in molecular weight.

All the samples for physical properties measurements in this study were characterized as thin films spin-coated on silicon wafers, cured successively for 1 h at 130, 250, and 430°C, respectively. The refractive index and thickness of thin films were measured with a variable-angle multi-wavelength ellipsometer (Gaertner L2W16C830) with two wavelengths at 633 and 834.5 nm and 49 points wafer scanning set-up. The film thickness was then checked with Tencor Alpha-step profiler 500. The dielectric constants were measured with both metal–insulator–metal (MIM) and metal–insulator–semiconductor (MIS) methods, with evaporated aluminum electrodes, at 1 MHz employing HP4280 CV meter. Crack initiations were made by Akashi MVK-H2 micro-indenter with various loading weights from 10 to 200 g and loading times from 3 to 5 s. After the crack initiation, crack propagations were observed in water by optical microscopy with image analyzer.

Table 1
Average molecular weights of PMSSQ samples prepared in 28% (w/w) THF solutions at 66°C with different R_2s (R_2 = (mole of H_2O)/(mole of methyltrimethoxysilane)) at $R_1 = 0.03$

R_2	M_w [a]	M_n [a]	PDI
1.3	2220	1290	1.7
1.6	3630	1750	2.0
1.9	5470	2170	2.5
2.2	8640	2360	3.7
2.5	4060	1780	2.3
2.7	3490	1710	2.0
3.0	2540	1360	1.8

[a] Determined from GPC with polystyrene standard as a reference.

3. Results and discussion

We have investigated the effects of several synthetic factors on obtaining processible PMSSQs with controlled molecular weights and microstructures, as well as a high content of functional end-groups, which strongly affect the miscibility of the PMSSQ matrix with porogens. The synthetic factors to be considered are solvent, temperature, stirring rate, humidity, molar ratio of catalyst to methyltrialkoxysilane (R_1), and molar ratio of water to methyltrialkoxysilane (R_2). When the method reported in literature [20] was employed to obtain PMSSQs in an open system, where the concentrations of monomer and polymer increase during the reaction process due to the evaporation of solvent and water, it was quite difficult to reproduce polymers with the same molecular weight as mentioned in the literature and to control the amount of functional end-groups.

As a result, in order to generate soluble, reproducible PMSSQs with controlled molecular weights and amounts of functional end-groups, methyltrimethoxysilane (MTMS) was polymerized in refluxing THF solutions of varying concentrations at 66°C under nitrogen in the presence of HCl catalyst. The amount of HCl catalyst affected the polymerization rate through the parameter R_1, and $R_1 = 0.03$ turned out to be the optimum condition to obtain processible solid PMSSQ without encountering the gelation. As reported in the literature [20], the polymerization takes place through the two different reactions and the variation of R_2 value affects the reaction rate and the equilibrium state of each reaction. Consequently, one can expect the

Table 2

NMR analysis results of PMSSQ samples prepared in 28% (w/w) THF solutions at 66°C with different R_2s at $R_1 = 0.03$ (NMR spectra were taken in aceton-d_6 and integration values were used to determine the amount of each functional groups and their refractive indices)

R_2	Si–CH_3[a]	Si–OCH_3[a]	Si–OH[a]	Functional end-group (%)[b]	Si–OH (%)[c]	Refractive index
1.3	8.0	1.0	0.5	15.5	5.0	–
1.6	18.8	1.0	1.3	12.3	6.3	–
1.9	27.9	1.0	1.4	7.6	2.1	1.37
2.2	84.7	1.0	3.8	4.8	4.3	1.37
2.5	70.5	1.0	4.8	7.6	6.2	–
2.7	89.1	1.0	6.5	7.8	6.7	1.37
3.0	69.3	1.0	6.3	9.5	8.2	1.38

[a] Normalized value to the integration value of Si–OCH_3.

[b] Functional end-group (%) = [(Si–OCH_3 + Si–OH)/(Si–CH_3 + Si–OCH_3 + Si–OH)] × 100.

[c] Si–OH (%) = [Si–OH/(Si–CH_3 + Si–OCH_3 + Si–OH)] × 100.

hydrolysis reaction to become more favorable with large R_2 values and the equilibrium of the condensation reaction to shift back to the reactants yielding low molecular weight polymers with a large amount of –OH end-groups. Therefore, R_2 was varied from 1.0 to 15 in order to assess the important influence of the R_2 value on both the molecular weight and the amount of functional end-groups. The resulting polymer products were characterized by ^{1}H, ^{29}Si NMR and GPC. Some representative GPC and ^{1}HNMR results are summarized in Tables 1 and 2 for polymerization in 28%(w/w) THF solutions.

When R_2 is increased, the molecular weight of PMSSQs initially increases until R_2 reaches 2.2 (although the stoichiometric value of R_2 is 1.5), showing a maximum molecular weight, as shown in Table 1. After the maximum point, the molecular weight of PMSSQ quickly decreases upon further increase of R_2. The amount of functional end-groups is also affected by the R_2 value as expected, as shown by the change of the amount of functional end-groups as a function of the R_2 value in Table 2. High molecular weight polymers, which have undergone more condensation reactions, have a relatively small percentage of functional end-groups and the amount of –OH group increases with R_2 values. From ^{29}Si NMR data, the number of Si–O–Si linkage on Si atom could be identified and it was confirmed that all the PMSSQ polymers we prepared contained only T_2 (silicon atoms bound with two bridging oxygen and one terminal oxygen) and T_3 (silicon atoms bound with all three bridging oxygen) structures as previously determined in the literature [20,21].

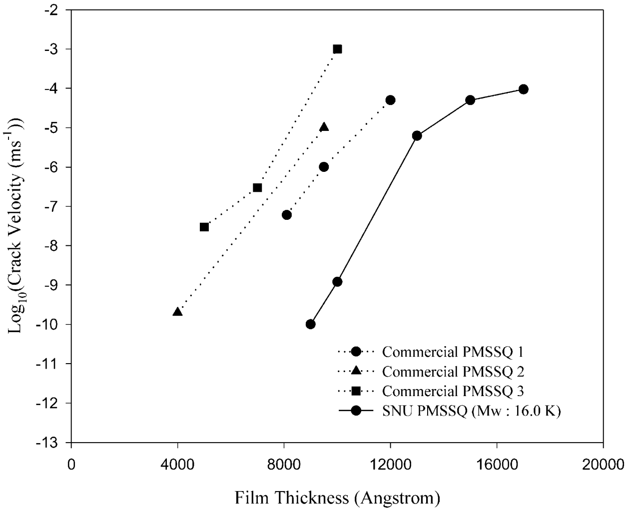

Fig. 1. Comparison of crack propagation velocities for various PMSSQ films in water as a function of film thickness. The data for commercial PMSSQs were taken from Ref. [22] and our sample with M_w of 16,000 is denoted as SNU PMSSQ in the figure.

Thin films of PMSSQ polymers with a high content of functional end-groups were prepared from methyl isobutyl ketone (MIBK) solution by spin-coating on silicon wafers followed by curing to 430°C, and their mechanical and electrical properties were examined. Upon initiating a crack by loading weights on the film with microvickers indenter, the crack propagation velocity was measured and compared with the values reported by Cook and Liniger [22], who measured the crack velocities as a function of film thickness for various PMSSQ samples obtained from commercial sources. As shown in Fig. 1, the crack propagation velocity is found to increase exponentially with film thickness as predicted by theory [22], but the absolute value varies tremendously with the polymer samples. In this regard, our PMSSQ sample with $M_n = 3,200$ and $M_w = 16,000$ (GPC data based on polystyrene standards), prepared in 43% (w/w) in THF with $R_1 = 0.03$ and $R_2 = 1.6$, exhibits most promising mechanical properties. For example, our experiments show that this PMSSQ film of ca. 1.0 μm thickness exhibits an average crack velocity smaller than of 10^{-10} m/s in water as shown in Fig. 1. This value is found to be significantly smaller, by ca. 10^4, as compared with the most favorable value reported in Ref. [22].

This improvement in the mechanical properties could be due to different microstructures of PMSSQs depending on the polymerization mechanism prevalent in various synthetic conditions. In the conventional acid-catalyzed reaction conditions with a high water content, a complete hydrolysis of MTMS generates methylsilanetriol ($MeSi(OH)_3$) first [23]. The preferred intermolecular condensation of the methylsilanetriol proceeds to produce PMSSQs containing a large amount of T_2 type Si units, which are highly branched without forming ladder-type structures. As a result, PMSSQ samples from commercial sources like those reported in Ref. [22] (which are most likely prepared by this conventional method) tend to have relatively low molecular weights ($M_w < 6{,}000$) and large amount of polar functional end-groups (Si–OR, up to ~40%) [24]. The PMSSQ polymer prepared in the refluxing THF solution with a relatively small amount of water, however, has a high M_w (up to 130,000 when a concentrated monomer solution (43%, w/w) was polymerized at $R_2 = 2.2$) and contains relatively small amount of polar functional end-groups (Si–OH and Si–OMe, lower than 15.5%).

In this regard, it is important to note that analysis of our polymerization products in the low molecular weight region, as monitored by Graphite Plate Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (GPLDI-TOF-MS), revealed that partially hydrolyzed products of MTMS started the condensation reaction [25]. As a result, the PMSSQs prepared in our synthetic condition always contain Si–OMe polar end-groups along with Si–OH groups (Table 2). Another important feature of our synthetic system is that the intramolecular condensation was more favorable than the intermolecular condensation, even at the very early stage of polymerization, generating ladder-type PMSSQ oligomers. As pointed out in the literature [23,26], the hydrophilic/hydrophobic balance of oligomeric PMSSQs in the polymerization solution is believed to be quite important. If the polymerization is carried out in a polar condition (high water content or biphasic system), the initially formed oligomers should take conformations where the hydrophilic silanol (Si–OH) groups point outward and hydrophobic methyl and siloxane chains are placed in the inner region. Such conformations tend to favor intermolecular condensations yielding highly branched PMSSQ. In our polymerization system, where the polymerization occurs in a relatively non-polar condition (low water content), the preferable positions of the silanol and the methyl groups would be reversed. This reversed conformation prefers the intramolecular condensation to yield ladder-type structures, followed by the intermolecular condensation through the terminal silanol groups to increase the total molecular weight. It is expected that PMSSQs generated from these partially organized polymers with ladder-type structures could produce more organized dielectric films during the so-called secondary condensation process at around 200–250°C, which may result in improved mechanical properties.

In order to confirm this possibility, we are currently performing detailed characterizations of various PMSSQ samples prepared by the current method and also by normal conventional method, employing GPC and light scattering experiments for dilute solutions and X-ray scattering experiments for thin solid films.

As shown in Table 2, the molecular weight of PMSSQ and the amount of functional end-groups do not seem to significantly affect the refractive indices of the cured PMSSQ thin films. Dielectric constants of the PMSSQ thin films prepared in this study were found to be ca. 2.7 in close agreement with the literature values [17]. Detailed studies of introducing porogen polymers and generating nanometer-size pores in the fully cured PMSSQ matrices are currently under investigation.

In summary, we have developed a simple synthetic method to control the molecular weight and microstructure of PMSSQ as well as the amount of functional end-groups. Thin solid PMSSQ films fully cured to 430°C showed quite promising mechanical and electrical properties. This novel simple synthetic method for preparing PMSSQs will be used to prepare the next-generation low-dielectric thin film insulators, which incorporate closed cell pores of nanometer-size scale.

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