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Synthesis, Pore Morphology, and Dielectric Property of Mesoporous Low-*k* Material PSMSQ using a Reactive High-Temperature Porogen, TEPSS

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A high-temperature reactive porogen, triethoxy(polystyrene)silane (TEPSS) (M_w=3,500 g/mole), suitable for late-porogen removal integration scheme has been synthesized in *p*–xylene via atom transfer radical polymerization. TEPSS was then grafted onto poly(methyl-silsesquioxane) (MSQ) matrix (k=2.9) to circumvent possible phase separation between matrix and porogen in the hybrid approach and porogen aggregation. Our results shows porous low-k MSQ films possess uniform pore size, 24 nm for porosity up to 40%, primarily due to low PDI and reactive porogen, and the dielectric constant is decreased to 2.37 at 40% porosity. In addition, less porogen aggregation was observed at porogen loading ~40 v%.

Introduction

For the application of ultra-low-k dielectrics (k ≤ 2.5) as ILD for 32 nm node and beyond, large porosity is introduced into low-k materials matrix using porogens which is burned out immediately after dielectrics deposition or after completion of a Cu/low-metallization layer in a late-porogen removal scheme. The common method for preparing porous low-k films is to mix porogen into a matrix, and then spin-coat the matrix/porogen solution onto a substrate. For spin-on dielectrics with large porosity, the pore size is relatively large with wide distribution compared to the porous dielectrics deposited by plasma-enhanced chemical vapor deposition (PECVD) method using small molecules as the porogen. The large pores in the porous spin-on dielectrics may be caused by the aggregation of porogen in the solution at room temperature [1] and in the spin-coated film during the curing step. Large pore size and interconnected pores may detrimentally degrade the mechanical strength of ultra-low-k films [2]. However, for a mechanically robust low-k material and better reliability at trench sidewall, it is highly desirable to have small and well-dispersed pore sizes with tight distribution in the low-k films [3,4]. Approaches such as fast heating rate in the cure step or addition of surfactants [5] had been undertaken to retard the porogen aggregation in the solution and casted film to improve the pore size and distribution in porous low-k materials with limited success.

To overcome these issues, Nguyen *et al.* reported the fabrication of the nanoporous MSQ films via a star-shaped poly(ϵ-caprolactone) porogen in the PMSSQ/PCL hybrids [6]. Pore sizes of nanoporous PMSSQ films were smaller than 20 nm in size. Further, Ree *et al.* demonstrated the use of six-armed poly(ϵ-caprolactone) (mPCL6) as a reactive

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porogen in the MSQ matrix [7]. Pore sizes of porous low-k films which used mPCL6 as porogen was observed around 5 nm with 40% porogen loading [8]. However, such porogens cannot be used in the late-porogen removal integration scheme due to their low thermal stability.

In this study, a high-temperature, reactive porogen with siloxane backbone and polymer chains of well-controlled molecular weight is designed and synthesized for the preparation of low-k dielectrics suitable for the late-porogen removal integration scheme. In specific, a reactive high-temperature porogen, triethoxy-(polystyrene)silane (TEPSS) was synthesized in *p*-xylene by atom transfer radical polymerization (ATRP) [9] to obtain tight molecular weight distribution, then grafted onto the poly(methyl-silsesquioxane) (MSQ) matrix to circumvent possible phase separation between matrix and porogen in the conventional hybrid approach. The chemical structures and thermal characteristics of TEPSS reactive porogen and TEPSS-grafted MSQ (PSMSQ) were examined and verified by ^{1}H-NMR, ^{29}Si-NMR, and thermogravimetric analyzer (TGA), respectively. The morphology and pore size of porous PSMSQ low-k films were investigated by scanning electron microscopy (SEM). The porosity and dielectric property of porous PSMSQ low-k film were measured by x-ray reflectometry (XRR) and C-V dot.

Experimental

Materials

Styrene (Aldrich, 99%) was distilled and stored at 5°C. Copper(I) bromide (CuBr) (Sterm Chemicals, 98%) was sublimated before using and stored at 15°C. Methyltrimethoxysilane (MTMS) (Acros, 97%), *N,N,N'*,*N''*,*N''*-pentamethyldiethylenetriamine (PMDETA) (Acros, 99^{+}%), hexafluorophosphoric acid (HPF_6) (Acros, 60 wt%), and (3-chloropropyl)(triethoxy)silane (CPTES) (TCI, 95%), were used as-received. Tetrahydrofuran (THF) (Echo, 99%) was distilled to keep anhydrous before use. *P*-xylene (Aldrich, 99%) was used as-received.

Synthesis of Triethoxy(polystyrene)silane (TEPSS)

CuBr(I) (2.0×10^{-3} mole) was added to a 100mL two-necked flask equipped with a magnetic stirring bar and a condenser. After sealing, the flask was degassed for 1.5 hours. Subsequently, CPTES (1.0×10^{-3} mole) as initiator, solvent (4 ml) (p-xylene), and styrene (5.0×10^{-2} mole) were degassed by three freeze–pump–thaw cycles in order to remove the dissolved oxygen, respectively. After pre-treatment, solvent, PMDETA (2.0×10^{-3} mole), and CPTES were transferred into the flask, which was immediately sealed under argon. Styrene was then added into this flask, which was then degassed to remove oxygen by three freeze–pump–thaw cycles. The mixture was placed in an oil bath and stirred at 80°C for 12 hours under argon atmosphere. At the end of the polymerization reaction, the flask was quenched in cold water, subsequently diluted with THF. Afterwards, Cu^{2+} was removed through an alumina column. The reactive porogen TEPSS was obtained by precipitating the solution into alcohol and drying in the vacuum overnight. The molar ratio of styrene/CPTES was chosen at 500:1 to obtain a TEPSS.

Synthesis of MSQ from MTMS using Sol-gel Reaction

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Methyltrismethoxysilane (MTMS) ($2.4x10^{-2}$ mole), distilled water (DI water) ($1.8x10^{-2}$ mole), and hexafluorophosphoric acid solution (HPF_6) ($3.0x10^{-4}$ mole) were added into an alumina dish, which was then heated in an oven at 80°C for 7.5 minutes. The function of DI water was to hydrolyze MTMS, while the function of HPF_6 was to dehydrate MTMS and initiate sol-gel reaction.

Grafting TEPPS onto MSQ through Sol-gel Reaction.

TEPSS (1.6 $x10^{-6}$ mole) was first dissolved in 2 ml THF in a 100 ml flask. Upon the completion of the MSQ sol-gel reaction, MSQ ($1.6x10^{-3}$ mole) was immediately added into the flask. Afterwards, 0.06 g of dilute HCl (10%) were added into the flask slowly. This reaction was carried out at 50°C in an oil bath under N_2 atmosphere for 14 h. The grafting reaction product was named PSMSQ. The ratio of TEPSS/MSQ was increased from 0.001:1 to 0.02:1 to increase the loading of high-temperature reactive porogen, TEPSS. (*i.e.* the porosity in the low-k MSQ matrix after the burn-out of porogens.)

Preparation of Porous Low-k Film

PSMSQ was dissolved in THF to form a 20 wt% solution. Prior to coating, the solution was filtered through a 0.2 µm PTFE filter (Millipore Inc.). The PSMSQ solutions were spin-coated at 2000 rpm on a silicon wafer. The PSMSQ film was sequentially baked at 100°C for 1 minute, then cured on a hot plate preheated at 200°C for 30 minutes to form a crosslinked MSQ structure. The TEPSS reactive porogens were thermally decomposed at 400^oC for 90 minutes to form a porous low-k MSQ films. The nominal thickness of PSMSQ film is 150 nm, unless specified otherwise.

Measurements

The chemical structures of TEPSS and PSMSQ were first validated by ^1H-NMR spectra and ^{29}Si-NMR spectra, respectively. ^1H-NMR spectra were recorded in solution using a Bruker AC-300P (300 MHz) spectrometer, with the tetramethylsilane (TMS) proton signal as an internal standard. ^{29}Si-NMR spectra for powder samples were carried out by a Bruker DSX-400WB NMR spectrometer.

The number-average (M_n), weight-average (M_w) molecular weight, and the molecular weight distribution (*i.e.* polydispersity, PDI), were determined by gel permeation chromatography (GPC) using a Waters chromatography unit interfaced with a Water 2414 differential refractometer (Waters Corporation, Ashland), and using tetrahydrofuran (THF) as an eluant and polystyrene as the standard. TGA was employed to measure the decomposition temperatures of TEPSS and PSMSQ using TA Q500 (TA Instruments). The temperature was raised from 100°C to 900°C in nitrogen at 10°C/min.

The density of porous MSQ film was measured by XRR. The films were scanned by D8 Discover, Bruker with Cu Kα source (λ=0.154 nm) using ω-2θ method with a scanning angle ranging from 0° to 2° at an increment of 0.002°. Porosity was then calculated by the Eq. 1.

$$\rho = \rho_s (1-p) \qquad (1)$$

where ρ is film density (g/cm^3), ρ_s is silica density (1.63 g/cm^3), and "p" refers to porosity.

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The pore morphology of porous low-k films was examined by using a dual beam FIB/SEM (Nova Nanolab 2000 system, FEI Company) system. The pore size and distribution were calculated using Image J analysis [10] of >200 pores in the SEM graphs. The film thicknesses of PSMSQ and porous MSQ film were measured using n&k Analyzer 1280 (n&k Technology, Inc.) at wavelengths ranging from 190 to 900 nm. The dielectric constant of porous low-k MSQ film was measured by C-V dots (Keithley 590 C-V Analyzer) with a sweeping frequency of 1 MHz based on Metal/Insulator/Metal (MIM) configuration at room temperature.

Results and Discussion

Synthesis of Triethoxy(polystyrene)silane (TEPSS) and TEPSS-grafted MSQ (PSMSQ)

(a) Synthesis of TEPSS by using ATRP. In order to obtain a siloxane-functionalized polystyrene, TEPSS as a reactive and high-temperature porogen, the synthesis was carried out at 80 ^{o}C by adding styrene as monomers, CPTES as initiator, CuBr/PMDETA as catalyst using ATRP method [11] as schematically illustrated in Figure 1. *p*-xylene was selected as the solvent for synthesizing TEPSS due to its better control of its molecular weight. In specific, TEPSS, with a low molecular weight (3,500 g/mole) and a low PDI (1.12) were used in this study, and the yield of TEPSS was 58% as shown in Table I.

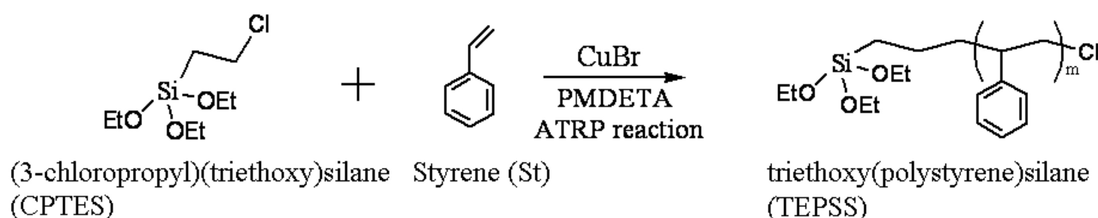

Figure 1. The synthesis route of TEPSS

Table I. The number-average (M_n) molecular weight, weight-average (M_w) molecular weight, PDI, and yield of TEPSS.

	M_n (g/mole)	M_w (g/mole)	PDI	Yield
TEPSS	3900	3500	1.12	58%

(b) Grafting TEPSS onto MSQ through Sol-gel method. The oligomer MSQ was synthesized and prepared in good yield by sol-gel method as outlined in Figure 2(a). MSQ has siloxane groups on the end caps when MSQ was synthesized from monomer MTMS. TEPSS was grafted onto MSQ with siloxane groups by sol-gel reaction through the reaction between MSQ and TEPSS in dry THF as shown in Figure 2(b). This yields reaction product, PSMSQ.

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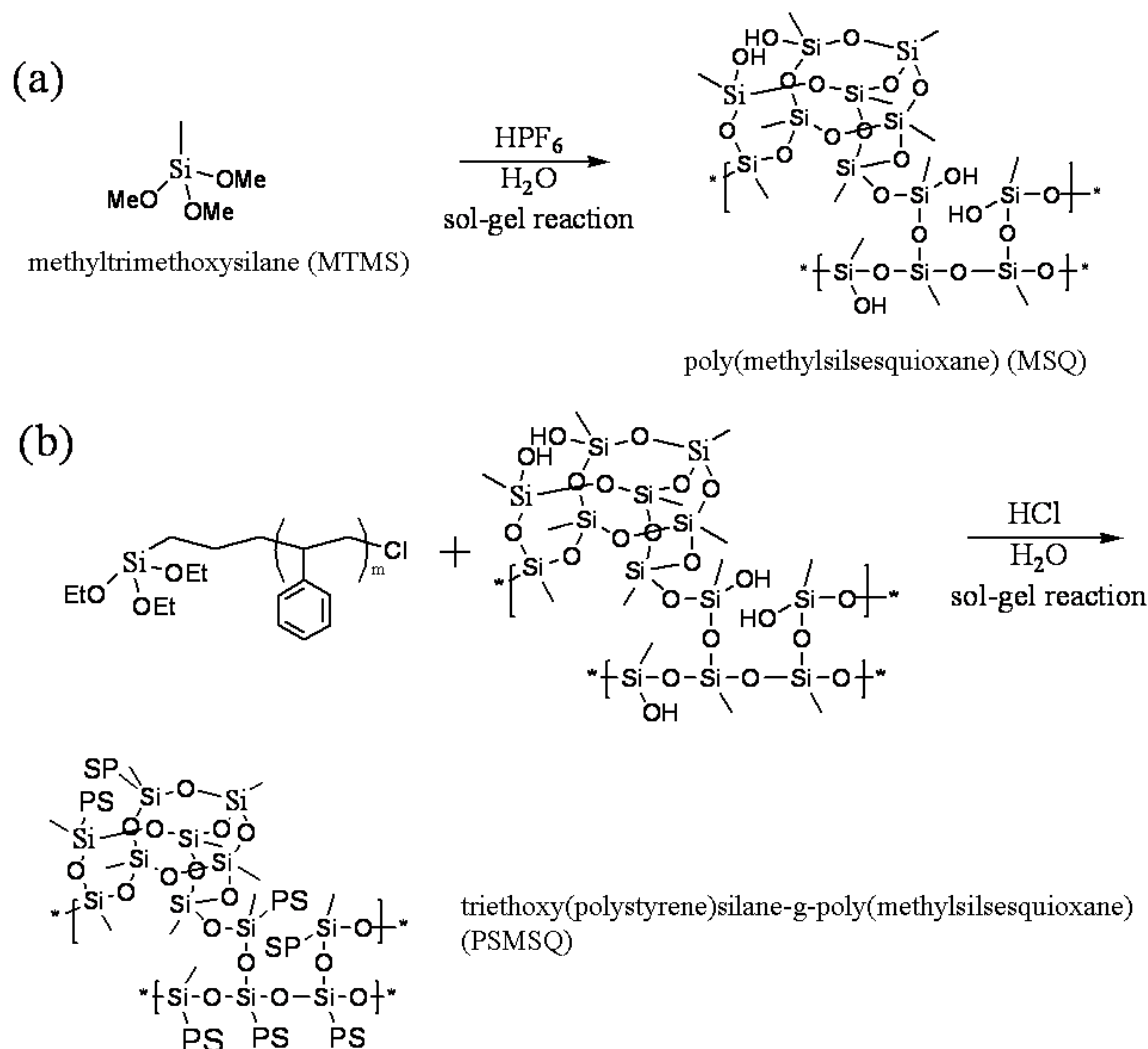

Figure 2. (a) synthesis route of MSQ from MTMS by sol-gel method, and (b) synthesis of PSMSQ by grafting TEPSS onto MSQ.

Chemical Structure and Thermal Properties of TEPSS and PSMSQ

(a) Chemical Structures of TEPSS and PSMSQ. The chemical structure of TEPSS was confirmed by ^{1}H-NMR spectra as shown in Figure 3. From ^{1}H-NMR spectra, two characteristic signals of TEPSS are located: (1) in the 6.45-7.18 ppm range representing the aryl protons of styrene units and (2) in the 1.25-1.84 ppm range assigned to the methylene protons of styrene backbone. Moreover, signals located in the 3.6 ppm range are attributed to -Si-$(OCH_3)_3$ end group. From the ^{1}H-NMR result, it is shown that TEPSS has been successfully synthesized by ATRP method. Figure 4 exhibits the ^{29}Si-NMR spectra of (a) MSQ and (b) PSMSQ baked at 60°C. Two types of silicon atoms are located at -54 ppm and -69 ppm, which correspond to T^2 and T^3 species, respectively. T^2 refers to silicon nuclei with hydroxyl group termination, [RSi-$(OSi)_2$OH] or [RSi-(OSi)(OR)OH], and the chemical shift is from -54 ppm to -61 ppm. Beside, chemical shift of [RSi-(OSi)(OR)OH] would close to -54 ppm, and [RSi-$(OSi)_2$OH] would close to -61 ppm. On the other hand, T^3 represents three -O-Si bonds and one alkane group, [RSi-

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$(OSi)_3$], and the chemical shift is from -64 ppm to -69 ppm [12-14]. In this study, T^3 peak has been normalized to check the change of T^2 peak on MSQ and PSMSQ. It can be seen that T^2 peak of PSMSQ is closer with -54 ppm than MSQ. It means that PSMSQ has more [RSi-(OSi)(OR)OH] structures than MSQ, due to the triethoxysilyl side group of TEPSS are less reactive than the trimethoxysilyl side group of MSQ [15]. On the other word, in the same sol-gel condition, the trimethoxysilyl side group would become [RSi-$(OSi)_2$OH] structure largely. However, the triethoxysilyl side group maintain [RSi-(OSi)(OR)OH] structure and become to [RSi-$(OSi)_2$OH] structure slowly. Therefore, when TEPSS was grafted onto MSQ, the triethoxysilyl side group would decrease siloxane condensation and cause PSMSQ has more [RSi-(OSi)(OR)OH] structure. Thus, the results of ^{29}Si-NMR confirmed that TEPSS has been grafted onto MSQ successfully.

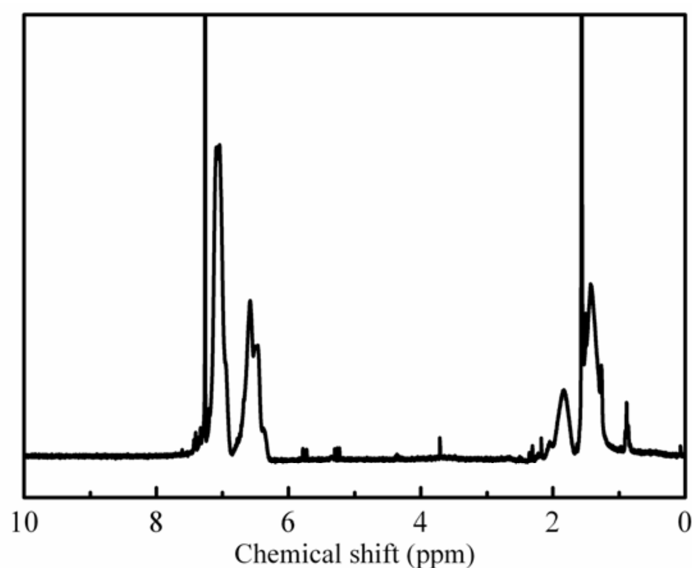

Figure 3. ^{1}H-NMR spectra of TEPSS

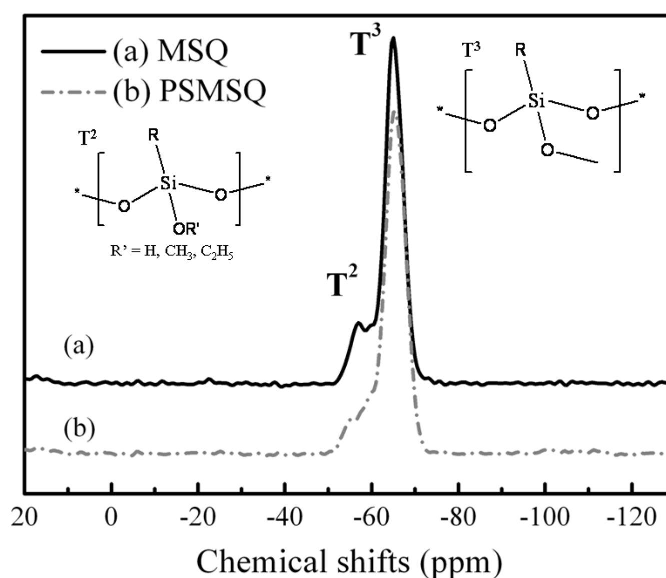

Figure 4. ^{9}Si-NMR spectra of MSQ and PSMSQ

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(b) Thermal properties of TEPSS and PSMSQ. In this paper, we can use not only ^{29}Si-NMR but TGA analysis to demonstrate that TEPSS has been grafted onto MSQ. Thermo-gravimetric curve of TEPSS is shown in Figure 5(a) under nitrogen at a ramp rate of 10 °C/min. The decomposition temperature of TEPSS was investigated to determine the maximum processing temperature of the porous low-k film. As illustrated in Figure 3(a), reactive porogen, TEPSS, had a high decomposition temperature (T_d) of 362°C, at which weight loss 5% occurred. Moreover, TEPSS could be completely removed at T > 435°C under N_2 atmosphere in dynamic mode. In addition, TEPSS can be completely removed at 400°C for 1 hour in static mode as shown in Figure 5(b), and the 8% residual was silane skeleton. As a result, TEPSS is confirmed to be an excellent porogen for a porous low-k dielectric in late-porogen removal scheme. Next, the thermal stability of MSQ and PSMSQ in nitrogen using TGA are shown as in Figure 6. MSQ showed a high thermal stability with a mere 2.5% weight losses for temperature ranging from 200°C to 600°C. The TGA of PSMSQ showed 1% weight loss from 376°C to 460°C. The weight loss can be attributed to the decomposition of the long chain polystyrene in TEPSS. The T_d of grafted PS in PSMSQ was calculated to be 383°C, which is 21°C higher than the T_d of TEPSS (362°C). The increased T_d of styrene in PSMSQ is due to the confinement and interactions of styrene long chain by the MSQ matrix structure.

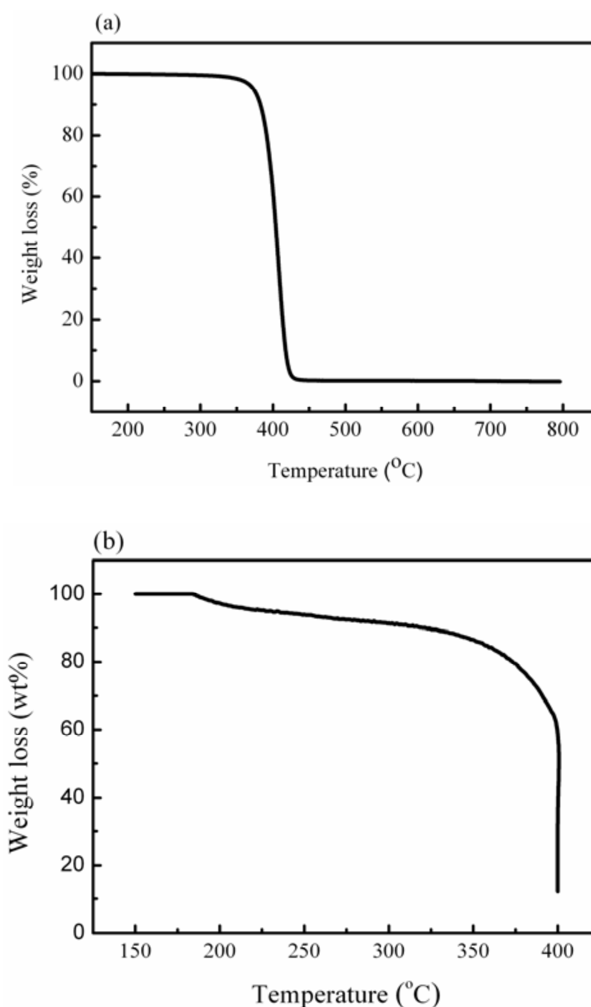

Figure 5. The (a) dynamic, and (b) 400°C isothermal TGA curves of TEPSS

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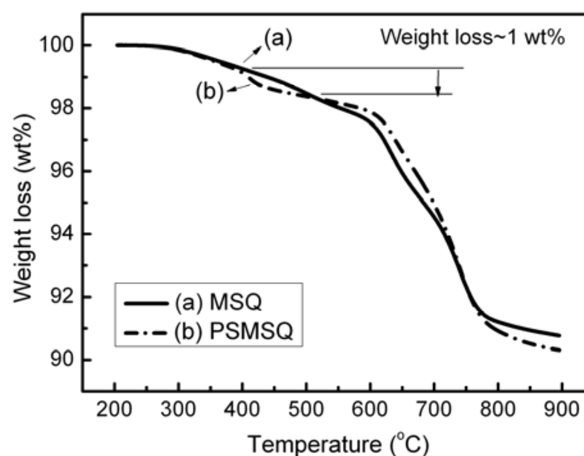

Figure 6. TGA thermograms of MSQ and PSMSQ

Pore Morphology and Pore Size of Porous MSQ Films with Different Porosities

After the chemical structure and thermal properties of PSMSQ are demonstrated, this paper continues to study the changing of porosity in the different porogen loading, and PSMSQ porous films morphology and pore size. The PSMSQ films were prepared by dissolving 20 wt% PSMSQ into THF solution. Moreover, various weight ratios of TEPSS and MSQ were used in this study to change the loading of reactive porogen, and in turn the porosities. The densities and porosities obtained by XRR for various porogen loadings are summarized in Table II. The porosity was increased from 18% to 54%, while the film density decreased from 1.80 to 10.1 g/cm^3 when the porogen loading was raised from 0.4% to 20%. The pore morphology of porous low-k MSQ films at various porosities after the removal of porogen at 400 ^{o}C by using scanning electron microscopy are shown in Figures 7(a) through 7(d): (a) 16%, (b) 27%, (c) 40%, and (d) 54%, respectively. From these top-view SEM graphs, porous PSMSQ films were found to be continuous and smooth. The pores were spherical and uniformly distributed without rod-like, interconnected pores. Pore sizes of PSMSQ porous films were estimated to be 18 nm at 16% porosity, 19 nm at 27% porosity, 24 nm at 40% porosity, and 38 nm at 54% porosity. Compared to the porous MSQ prepared from MSQ/PS hybrid, porous low-k film at ≤ 40% porosity based on PSMSQ through the grafting of reactive TEPSS porogen onto MSQ can deliver smaller, mesoporous ~18-24 nm, which are in spherical shape and uniformly distributed. However, severe pore aggregation was observed for porosity at 54% porosity presumably due to the aggregation of reactive porogen, TEPSS and poor dispersion, at relatively high loading prior to grafting reaction. A better dispersion of TEPSS at high loading in the solvent is critical for fabricating porous low-k MSQ films with porosity > 40 v%.

Table II. The dielectric constant of porous PSMSQ films with various porosities

Porogen loading	Density g/cm^3	Porosity (%)	Dielectric constant	Pore size (nm)
MSQ	2.20	0%	2.90	-
0.4 %	1.80	18%	2.66	18
1 %	1.60	27%	2.45	19
8 %	1.34	40%	2.37	24
20%	1.01	54%	2.30	38

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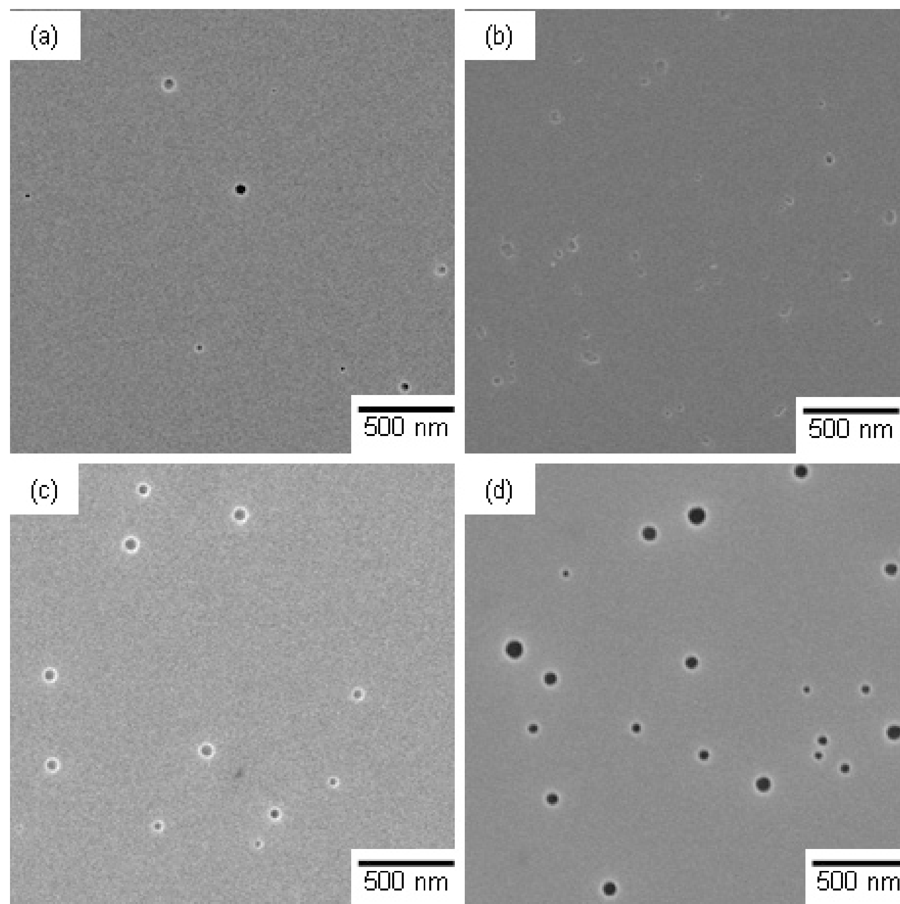

Figure7. SEM viewgraphs of porous low-k MSQ films at various porosities: (a) 16%, (b) 27%, (c) 40%, and (d) 54%

Dielectric Property of Porous Low-k MSQ Films

The dielectric constants of porous low-k MSQ films prepared from PSMSQ films at various porosity are also summarized in Table II. For comparison, the dielectric constant of pure MSQ film was 2.9 (k = 2.9). The dielectric constants of PSMSQ are 2.66, 2.45, 2.37, and 2.30 for porous MSQ films at 18%, 27%, 40%, and 54% porosity, respectively. The dielectric constant decreases with increasing porosity as expected. The result suggests that the dielectric constant of the PSMSQ films decreased with increasing TEPSS loading (*i.e.* increasing PSMSQ films porosity). However, the experimental k values of porous PSMSQ films were higher than theoretical values presumably due to adsorbed water, whose k value is close to 80 [16]. Moisture absorption may be attributed to the residual silanol groups in the low-k films. Efforts in reducing residual silanol groups in the cure step and cautions in the dielectric measurement with appropriate procedures for removing adsorbed moisture have been undertaken. Results will be reported and discussed.

Conclusion

This study introduced a novel method for preparing mesoporous materials, PSMSQ by using a reactive high-temperature porogen, TEPSS, suitable for the late-porogen

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removal integration scheme. In specific, a reactive high-temperature porogen, triethoxy-(polystyrene)silane (TEPSS) (M_w=3,500 g/mole) was synthesized in *p*-xylene by atom transfer radical polymerization (ATRP) to obtain tight molecular weight (MW) distribution, then grafted onto the poly(methyl-silsesquioxane) (MSQ) matrix to circumvent the phase separation between matrix and porogen in the conventional hybrid approach. TEPSS (T_d = 362°C) is confirmed to be an excellent high-temperature porogen as observed from the enhanced T_d of PS in PSMSQ and complete removal of progen at 400^oC for 1 hr. In addition, the extremely low polydispersity by using ATRP and controllable reactivity of high-temperature porogen, TEPSS onto MSQ matrix yielded uniformly distributed and spherical pores (~24 nm) with less aggregation at high porosity up to 40%. The density and the electric properties of porous PSMSQ film were measured by XRR and C-V dots, respectively. The dielectric constant of porous low-k MSQ film was decreased from 2.90 to 2.37 when the porosity was raised from 0% to 40%.

Acknowledgments

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