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Communications

Preparation of Nanoporous Poly(methyl silsesquioxane) Thin Films Derived from Chemically Linked Carbon Cages

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Introduction

Recently, there has been a considerable interest in the development of low dielectric constant (low-k) materials in order to minimize the so-called resistance-capacitance signal delay upon the shrinkage of the feature size of ultra large-scale semiconductor integration (USLI) devices.[1] Among many low-k candidates, poly(methyl silsesquioxane) (PMSSQ) with the empirical formula of $(RSiO_{3/2})_n$ have extensively been explored due to the intrinsic low dielectric constant (k~2.8), the fairly hydrophobic character after curing, and the high thermal stability up to 500 °C.[2,3] To further decrease the dielectric constant of PMSSQs, pores should be incorporated into the film and such porous PMSSQ films have conventionally been prepared by the removal of thermally labile molecular templates or pore generating materials (porogens) within the film.[4-8] However, it has been realized that the blending of porogens with matrix organosilicates often causes significant phase separation, resulting in films with interconnected pore structure and poor thermo-mechanical properties.[3,9] Recently, this blending approach has further been improved in some cases through the surface modification of nanosized molecules or the finely-tuned polymerization.[10-13]

On the other hand, as an alternative to the blending approach, the covalently bonded template approach, involving porogens chemically linked to organosilicate precursors, can suppress the massive phase separation and can have a possibility to yield attractive low-k materials with controlled porosity and porous structure. Nanosized moieties such as alkyl and norbonene groups have been covalently bonded to the polymer backbone based on silsesquioxane and/or silica matrix and this approach has further been extended to organic-inorganic hybrids composed of poly(methyl methacrylate) (PMMA) or PAMAM dendrimers grafted to silsesquioxane.[14-17] Although these approaches have extensively been studied, there still exists a room for the optimization of porogen systems with practical control of pore size and distribution.

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Experimental

Characterization. ^{1}H NMR spectra were obtained at room temperature using a Bruker (AVANCE) 500 MHz. The NMR spectra were taken in deuterated chloroform for monomers and in acetone-d_6 for the copolymers. Thermal gravimetric analysis (TGA) was performed using a TA model 2050 TGA instrument under N_2 flow at a heating rate of 10 °C/min. The solid samples were heated from 50 up to 900 °C. The weight loss of the samples (TG curves) was collected. Volatile compounds evolved after curing under N_2 were recovered in bulk and analyzed by GC-MS (GC System, HP 6890). FT-IR measurements were performed on a JASCO FT/IR 200 spectrometer. Baseline corrected infrared spectra were obtained for films on silicon wafers in absorbance mode at room temperature. The refractive indices 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. Mechanical properties of all the PMSSQ films were measured by a nanoindenter (Nano Indenter® XP, MTS Corp.) in the CSM (continuous stiffness measurement). The dielectric constants were measured in the metal-insulator-metal (MIM) configuration, with evaporated aluminum electrodes at 1 MHz using a HP4284 LCR meter. Field emission scanning electron microscopy (JEOL 6330F) was used to investigate the cross sectional structure of the thin films. Spin coated films were cut into small pieces and fixed vertically on a sampling holder to analyze the internal structure. In order to minimize the film damage by electron beam and to obtain clear images, Au was sputtered onto the thin films.

Materials. All the reagents used in present study were purchased from Aldrich, Gelest, and TCI and used as received unless otherwise specified.

4-Adamantan-1-yl-phenol (2). A solution of 1-bromoadamantane, **(1)** (10.0 g, 46.5 mmol) and phenol (35 g, 372 mmol) was refluxed overnight at 120 °C under the N_2 atmosphere. The mixture was poured to 1,000 mL hot water and washed three times to remove excess phenol. The product was filtered and dried under vacuum to give **(2)** as a white solid. Yield: 10.2 g (96%) ^{1}H NMR ($CDCl_3$):δ 7.24 (d, -ArH-, 2H), 6.78 (d, -ArH-, 2H), 4.61 (s, -OH, 1H), 2.08 (br, adamantyl, -CH-, 3H), 1.88 (adamantyl, -CH_2-, 6 H), 1.76 (ada-

mantyl, -CH_2-, 6 H). GC-MS (m/z): 228.

1-(4-Allyloxy-phenyl)-adamantane (3). A solution of **(2)** (2.0 g, 8.8 mmol), K_2CO_3 (3.6 g, 26 mmol) and allyl bromide (2.3 mL, 26 mmol) was refluxed in acetone (25 mL) at 80 °C for 12 h. The mixture was allowed to cool to room temperature (rt), K_2CO_3 was filtered off and the filtrate was concentrated under reduced pressure. The product was further dried under vacuum for 24 h in order to give **(3)** 2.4 g of light yellow solid. Yield: 2.4 g (89%). ^{1}H NMR ($CDCl_3$):δ 7.27 (d, -ArH-, 2H), 6.87 (d, -ArH-, 2H), 6.07 (m, -CH=, 1H), 5.44 (m, CH_2=, 2H), 5.26 (m, CH_2=, 2H), 4.52 (d, -CH_2-, 2H), 2.08 (s, adamantyl, -CH-, 3H), 1.88 (adamantyl, -CH_2-, 6H), 1.71 (adamantyl, -CH_2-, 6H). GC-MS (m/z): 268.

3-[(4-Adamantan-1-yl-phenoxy)-propyl]-trimethoxysilane (4). A 25 mL three-necked flask equipped with a condenser/N_2 inlet and a stir bar was charged with 0.15 g 1% Pt on carbon (7.7 μmol). The flask was flushed with nitrogen for a few minutes and trimethoxysilane (2.85 mL, 22.4 mmol) and **(3)** (2 g, 7.5 mmol) were added by syringes. The mixture was stirred at 80 °C for 24 h. After being cooled to rt, ethanol (20 mL) was added and the solution was filtered by a 0.2 μm membrane filter. The filtrate was evaporated under reduced pressure to give a transparent oil of 2.8 g. Yield: 2.75 g (94.5%). ^{1}H NMR ($CDCl_3$): δ 7.26 (d, -ArH-, 2H), 6.83 (d, -ArH-, 2H), 3.93 (t, -CH_2-, 2H), 3.82 (s, -OCH_3-, 9H), 2.05 (br, adamantyl, -CH-, 3H), 1.88 (adamantyl, -CH_2-, 6H), 1.74 (adamantyl, -CH_2-, 6H), 0.75 (t, -CH_2-, 2H). GC-MS (m/z): 390.

Synthesis of PMSSQs. As a typical example, compound **(4)** (2.0 g, 2.6 mmol), 1,2-bis-trimethoxysilylethane (1.4 g, 5.3 mmol) (BTMSE), methyltrimethoxysilane (2.5 g, 18.2 mmol) (MTMS), and THF (12.2 g) were added into a 50 mL three-neck, round-bottom flask. At 25 °C, HCl dissolved in H_2O was added dropwise into the vigorously stirred reaction mixture over 30 min. After 30 min, the reaction mixture was refluxed at 60 °C for 10 h, cooled to room temperature and 30 mL of diethyl ether was added. The organic layer was extracted with H_2O (3 × 30 mL) and was dried over Na_2SO_4. The solvent was evaporated off under reduced pressure to yield a 1.84 g in white solid form. ^{1}H NMR (d-Acetone): δ7.26 (br, -ArH-, 2H), 6.85 (br, -ArH-, 2H), 5.74 (br, -OH, 1H), 3.95 (br, -CH_2-, 2H), 2.06 (adamantyl, -CH-, 3H), 1.89 (adamantyl, -CH_2-, 6H), 1.78 (adamantyl, -CH_2-, 6H), 0.85 (br, -CH_2-, 6H), 0.83 (br, -CH_2CH_2-, 4H), 0.13 (br, Si-CH_3, 3H).

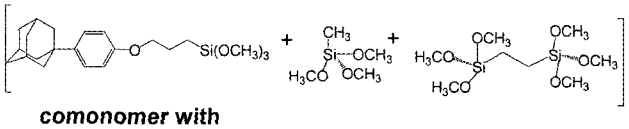
As a reference sample, copolymer with BTMSE of 20 mole % was also prepared using the same reaction condition described above. ^{1}H NMR (d-Acetone): δ5.76 (br, -OH-, 1H), 3.50 (br, -OCH_3-, 3H), 0.85 (br, -CH_2CH_2-, 4H), 0.12 (br, -$SiCH_3$-, 3H).

Preparation of PMSSQ Thin Films. The PMSSQ thin films were prepared by spin-coating from solutions dissolved in MIBK with a concentration of 20 wt%. The silicon wafer pre-treated with piranah solution (H_2SO_4/H_2O_2 70/30 by v/v) was typically spun at 2,000 rpm for 30 sec and coated films were then cured at a desired set temperature for 2 h after preannealing the film at 250 °C for 30 min with a home-made furnace under N_2 purge.

Results and Discussion

In present study, we introduce a new class of porogens based on adamantane groups, providing nanoscale molecular carbon cages of 7 Å and a sublimation temperature of *ca.* 210 °C.[18] To synthesize PMSSQs containing chemically linked porogens, trialkoxysilane comonomers chemically linked to adamantylphenol porogens were prepared by the hydrosilylation and the comonomer was then copolymerized with methyltrimethoxysilane (MTMS) and 1,2 bis-trimethoxysilylethane (BTMSE), as schematically shown in Figure 1. The analysis of ^{1}H NMR spectra confirms that the PMSSQ polymers contain 8.8 mole% adamantylphenol porogens.

To investigate the pore forming capability of chemically linked adamantylphenols in the silsesquioxane matrix, the thermal behavior of PMSSQs with and without porogens and adamantylphenol itself was measured with thermal gravimetric analyzer (TGA), as shown in Figure 2(a). The low molecular weight adamantylphenol shows the complete weight loss just above 200 °C. When the adamantylphenol groups are chemically liked to the silsesquioxane matrix, the weight loss of such porogens is shifted to a temperature above 400 °C, indicating that the adamantylphenol templates are good pore forming candidates for copper interconnects. On the other hand, the PMSSQ without porogens does not show such a massive weight loss above 500 °C. Also, the weight loss below 200 °C is due to the loss of methanol and water originating from polycondensation of the matrix.[17] Thermally activated loss of porogens is further monitored by infrared spectroscopy. Figure 2(b) shows the changes of infrared spectra of PMSSQs with curing temperature. The peak intensity at 2910 cm^{-1} assigned to the adamantane groups notably decreases above 350 °C along with the peak at 1514 cm^{-1} assigned to the phenyl groups and completely disappears above 450 °C. Figure 2(c) shows the change of the peak intensity corresponding to phenylether groups around 1256 cm^{-1}, which is known to have the lowest bond dissociation energy.[19,20] As curing temperature is increased, the peak intensity starts to reduce and completely disappears



comonomer with chemically linked pore generator **MTMS** **BTMSE**

Figure 1. Synthesis of PMSSQ terpolymers. The comonomer with a chemically linked porogen was synthesized by hydrosilylation.

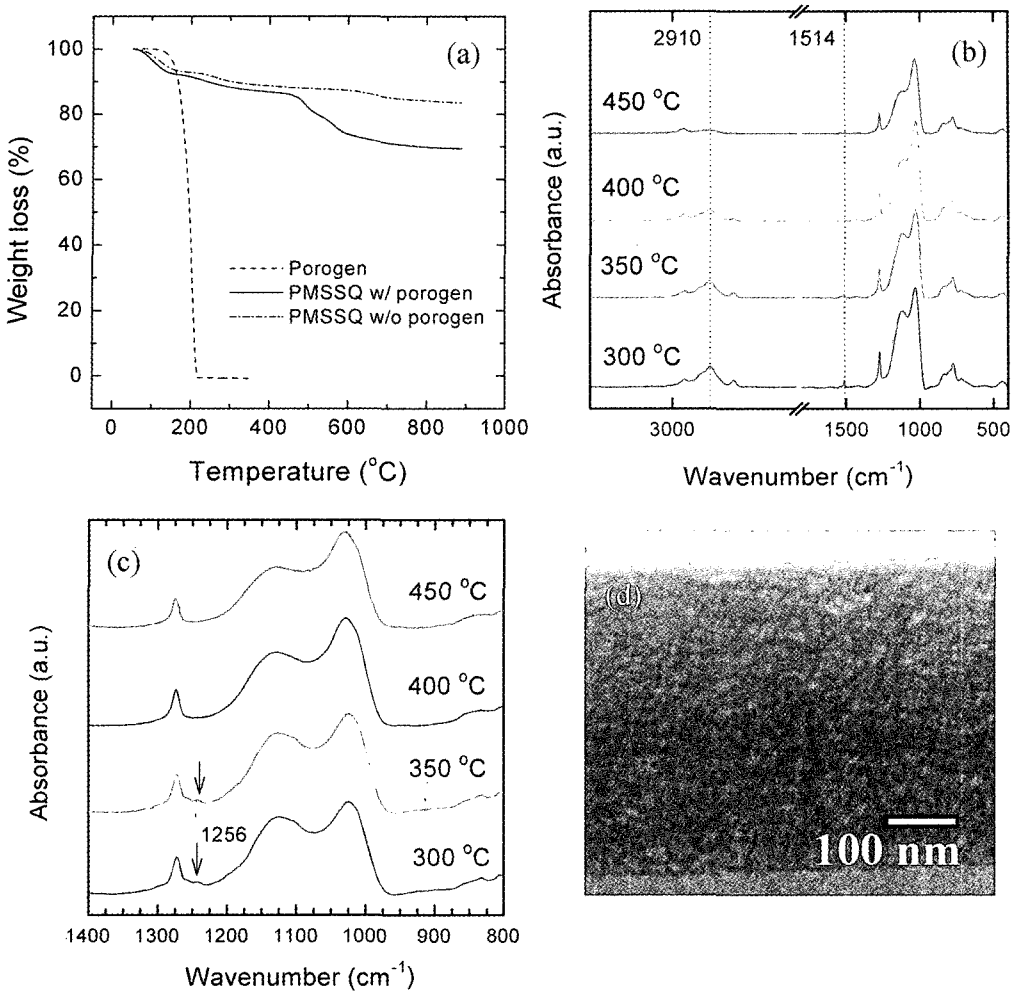


Figure 2. (a) TGA scans of PMSSQ with and without chemically linked porogens and adamantylphenol porogen itself measured under N_2 with a heating rate of 10 °C/min, (b) Changes in the FT-IR spectra of PMSSQ films with curing temperature, (c) Expanded FT-IR spectral region representing the Si-O-Si vibrational modes in Figure 2(b), (d) A cross-sectional FE-SEM micrograph of a PMSSQ film with chemically linked porogens cured at 450 °C.

after curing at 400 °C. These spectroscopic data confirm that the adamantylphenol porogens are removed through the cleavage of ether bonds.

It is important to note that adamantylphenols are recovered in bulk after curing at 450 °C, indicating that the porogen moieties are sublimed after the cleavage of ether bonds, resulting in nanoporous structure.[21,22] Upon curing, the band at 1040 cm^{-1} also increases due to the structural rearrangement from a cage-like Si-O-Si structure to a network structure, resulting in the formation of more dense film structure.[23] The cross-sectional FE-SEM micrograph for a PMSSQ film cured at 450 °C is shown in Figure 2(d). The SEM image clearly shows the cross-sectional textures due to the difference in electron density between nanopores and the matrix. Since there is no such texture observed for the PMSSQ without porogens, this result indicates that nanoporosity is created after the removal of porogens.[24]

Figure 3 shows the changes in both dielectric constant (k), measured in MIM (metal-insulator-metal) configuration, and refractive index, obtained from ellipsometry, of PMSSQ films containing chemically linked carbon cages, cured under N_2 purge. Overall, the behavior of dielectric constant is well consistent with the change of refractive index with curing temperature. Both dielectric constant and refractive index of PMSSQ films decrease with curing temperature. Due to excessive silanol groups and unremoved phenyl groups, the k-values of PMSSQ cured below 400 °C are higher than the k-value of a PMSSQ film without porogens (n_f~1.39, k~3.0). The k-value of PMSSQ reduces down to 2.12 after curing at 450 °C. The reduction in both k-value and refractive index is believed to originate from the formation of nanopores within the film by the removal of chemically linked porogens. Mechanical properties of the PMSSQ thin films were also measured with a nanoindenter in dynamic

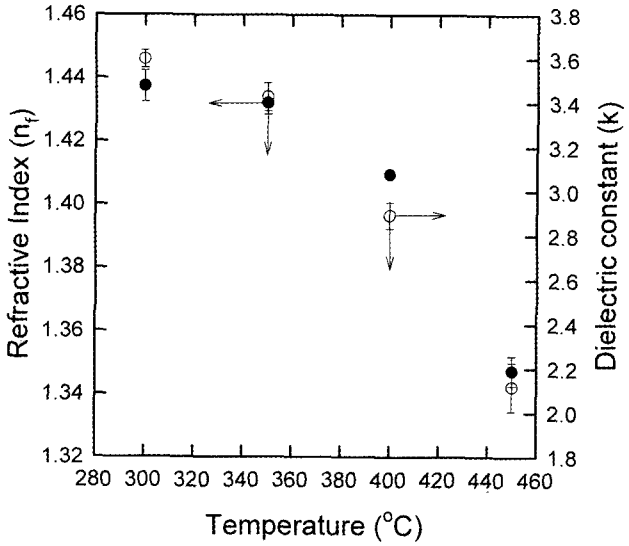


Figure 3. Changes of refractive index and dielectric constant of PMSSQ films with curing temperature.

contact mode (DCM). The modulus of PMSSQ after curing at 450 °C shows 3.8 GPa, which is slightly higher than 3.4 GPa of dense PMSSQ homopolymer.

In summary, we realized nanoporous low-*k* thin films with mechanically robust properties using adamantylphenol porogens chemically linked to the PMSSQ matrix. By direct thermal sublimation of adamantylphenol porogens through the bond cleavage leaving behind nanoporous structure, polysilsesquioxane films with reduced refractive index and low dielectric constant were prepared, which have potential applications ranging from low-*k* dielectrics to anti-reflection coating materials to pore-based sensing devices.

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(19) The calculation of bond dissociation energy (BDE) was performed at B3LYP/6-311+G(3df,2p) level using optimized geometries at the B3LYP/6-31G(d) level, B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d). All the calculations were performed with the Gaussian 98 program. The estimated results show that the C_6H_5O-R bond has the lowest BDE of 53.3 kcal/mol, which is in good agreement with the previous result.[20]
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(21) GC-MS data of recovered products shows a strong peak (m/z = 228) corresponding to adamantylphenol. ^{1}H NMR spectra also confirm the existence of signals at 6.78 and 1.87 ppm corresponding to the adamantylphenol moiety.
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(24) Porous structure of the films was further investigated using the nitrogen adsorption isotherm. For the measurement, spin-coated films were cured at 450 °C and scraped off the substrate to yield powder specimens. All the isotherms show the typical Type I isotherms with unclosed hysteresis, representing microporous materials with pores below 5 nm.