New Approach for the Preparation of Nanoporous Polyorganosilicate Low-k Films

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ABSTRACT: The distribution of pores and the mechanical properties of materials are the key factors in preparing satisfactory low-k films. In the present study, a kind of silsesquioxane-polyethylene glycol (SSQ-PEG) was synthesized and used as a template to make the distribution of pores more even in the low-k films. The crosslinking density of films could be adjusted by the sol-gel of tetramethoxysilane/dimethoxydimethylsilane with various proportions. The porosity of films could also be adjusted with different proportions of pendant PEG chains introduced. A dielectric constant as low as 2.1 had been achieved for nanoporous polyorganosilicate films with good tenacity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1238–1243, 2007

Key words: dielectric properties; polysiloxanes; templates; crosslinking

INTRODUCTION

With the rapid development of ultra-large-scale-integration, a new low dielectric constant material is needed to replace the current interlayer dielectric: silicon dioxide ($k = 4.0$). To withstand the rigors required for integrated circuit fabrication, the low-k materials should meet other requirements, including excellent thermal stability, strong adhesion to substrates, good mechanical properties, low moisture uptake, and high breakdown fields.[1] In recent years, several classes of low-k materials[2] have been explored including organic, inorganic, hybrid, fluorinated, or nonfluorinated materials and deposited by spin-on, chemical vapor deposition or via freeze drying.[3–6]

A method of reducing the dielectric constant of such interlayer material is to incorporate within the insulating film very small, uniformly dispersed pores or voids. One class of promising low-k materials is organosilicate polysilsesquioxanes. Most thin polysiloxane films are made directly by the tetramethoxysilane sol-gel process.[7] These films have very high crosslinking density so that they can very easily be cracked during spin coating and annealing. To reduce the stress inside the system, dimethoxydimethyl silane is introduced to cohydrolyze with tetramethoxysilane. It can strengthen toughness of the materials due to the reduced crosslinking density of the matrix.[8–10]

The way the template is added to the materials directly influences the mechanical properties of the materials. In some reports,[11–13] the templates were mixed with sol solution in physical way. The organic chains in the templates would be enriched by macrophase separation during thermal decomposition, and the nanopores in the final materials were not well distributed. In another report,[14] the templates joined the crosslinking co-network, and those parts of crosslinking structure were destroyed. It made the mechanical properties of the materials fallen when the materials were annealed.

We described herein a process for making low dielectric constant films from SSQ-PEG by hydrosilylation of PEG mono allyl ether and hydrogen silsesquioxane. SSQ-PEG acted as the template in this new polysiloxane crosslinking system. The silsesquioxane-base part joined the crosslinking system, but the polyethylene glycol pendant chain did not. As a result, the template could evenly be distributed at a molecular level. The porosity of the annealed film could be adjusted with different proportions of pendant PEG chains introduced. A thin film with low crosslinking density was achieved by a molar ratio $\sim$ 1:2 of tetramethoxysilane/dimethoxydimethyl silane selected. The film showed good tenacity, and its hardness was well kept during annealing (Fig. 1).

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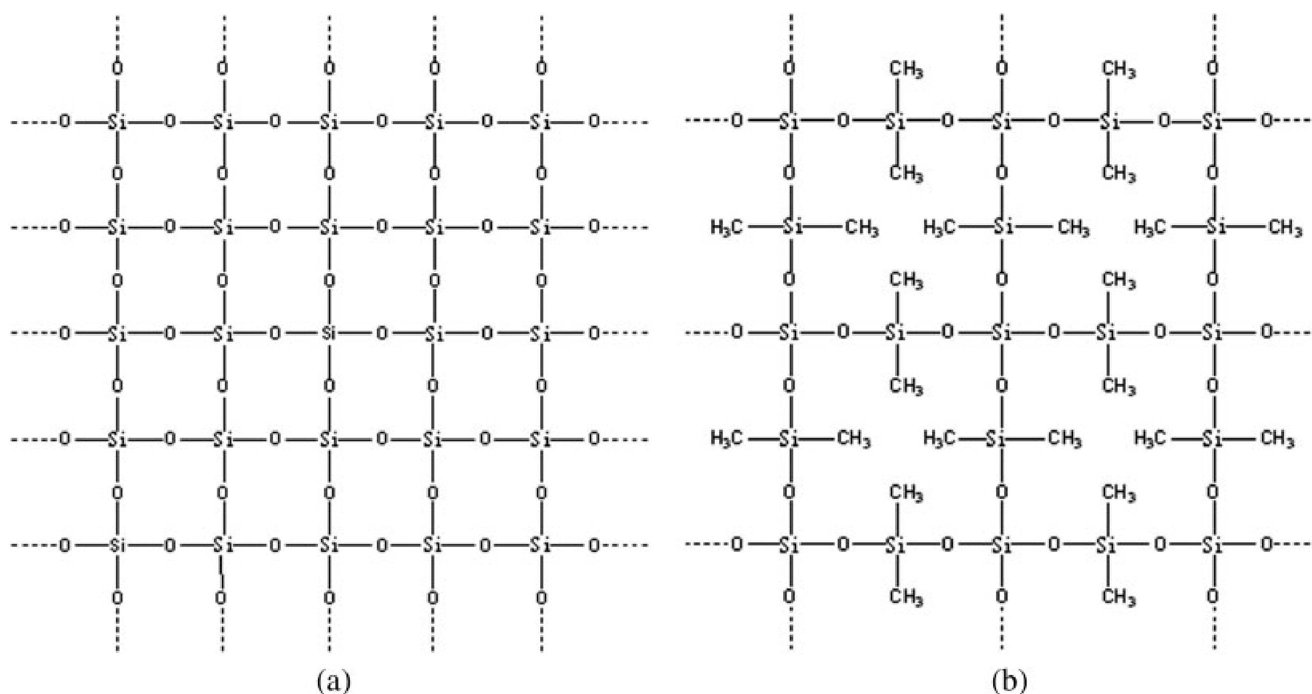


Figure 1 Crosslinking structure of (a) silica (b) tetramethoxy/dimethoxydimethyl silane with a molar ratio about 1 : 2.

EXPERIMENT DETAILS

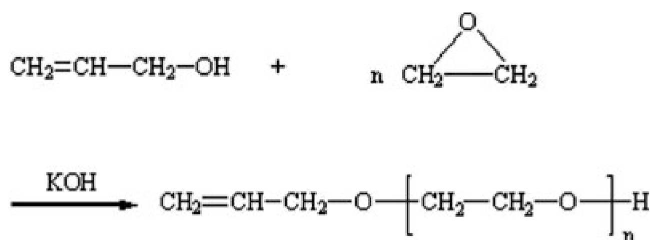
Materials

Tetramethoxysilane, hydrogen silsesquioxane [HSi $(OCH_3)_3$] (M = 122), dimethoxydimethyl silane, tetrahydrofuran, KOH, benzene, chloroplatinic, and allyl alcohol were purchased from Shanghai Chemical Co. (Shanghai, People's Republic of China) and used as received. Wafers N (1,1,1) were purchased from Bexin Sci. Co. (Shanghai, People's Republic of China). Oxirane was purchased from Yangzi Petrochemical Co. (Nanjing, People's Republic of China).

Synthesis and film preparation

Synthesis of allyl-polyethylene glycol

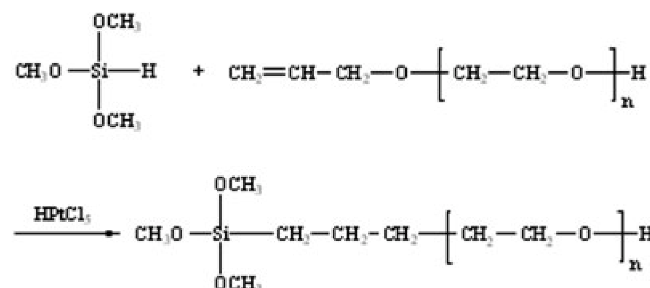
The synthesis of general PEG could be found in the literature.[15] The functionalized polymer used in this study was the same one as used in the references.[16–17] The synthesis and isolation of allyl-polyethylene glycol were done by JuTian Chemical Co. (Nanjing, China). The main synthesis procedure adopted by JuTian Chemical Co. is briefly described as below. A mixture of 0.50 mol (29 g) of allyl alcohol and 0.023 mol (1.28 g) of KOH was first refluxed. After KOH was completely dissolved, 10 mL of benzene was added and distilled to eliminate produced water in the mixture. The mixture was then allowed to heat to 110–130°C in an autoclave with stirring. Following that, 11.0 mol (484 g) of oxirane was gradually added until the reaction finished. The reaction is shown in Scheme 1.



Scheme 1 Synthesis of allyl-polyethylene glycol.

Synthesis of SSQ-PEG

In this study, 0.010 mol (9.50 g) of allyl-polyethylene glycol and 0.012 mol (0.888 g) of hydrogen silsesquioxane were mixed in a 1 : 1.2 molar ratio; 50 mL of tetrahydrofuran was then added as solvent and chloroplatinic acid added as catalyst at 60°C for 4 h under nitrogen atmosphere (Scheme 2). The hydrosilylation addition reaction was monitored by Fourier



Scheme 2 Synthesis of silsesquioxane-polyethylene glycol.

transform infrared (FT-IR). After the Si—H absorption band in the spectra (not listed in this report) disappeared, the received SSQ-PEG was used directly as solution in the next step without isolation.

Preparation of sol solution

A class of typical precursor polymer solutions of porous silicate used in this work was prepared by mixing tetramethoxysilane, dimethoxydimethyl silane, and SSQ-PEG with an acid catalyst and solvent at 60°C under nitrogen atmosphere. A typical composition of the solution was tetramethoxysilane/dimethoxydimethyl silane/SSQ-PEG/H_2O/HCl/tetrahydrofuran in a 1 : 2 : 0.2 : 4.6 : 0.02 : 50 molar ratio. The film with 30% of polyethylene glycol base (−PEG) could finally be achieved. Thin films with 45% of −PEG, 60% of −PEG and 0% of −PEG were prepared in the same way.

Film preparation

The films were obtained by spin-on process. Before film deposition, the silicon wafers (1,1,1) were boiled in H_2SO_4+H_2O_2 solution and heated to 80°C for 1 h to remove particles on the surfaces. The process was divided into three steps at room temperature. At the first step (5000 rpm), 5 mL of solution was dripped on wafers. Next, a rinsing stage (7000 rpm) was used to get rid of the edge bead of precursor, which might induce crack when drying. At the final step (2000 rpm) the residual solvent was removed by spin drying. The crosslinking structure of the thin film polysiloxane was shown in Figure 2.

After drying at room temperature for 30 min, films were kept in a 5°C/min ramp of temperature from room temperature to 450°C, and baked at 450°C for 2 h. The annealing treatment was wholly carried out under a nitrogen environment.

Characterization

13C-NMR spectra of APEG were recorded on a Bruker Avance 300 spectrometer at room temperature operating at 300 MHz, $CDCl_3$ as solvent and tetramethylsilane as internal standard. FT-IR spectra were obtained on a Nexus 870 spectrometer using the membrane as samples.

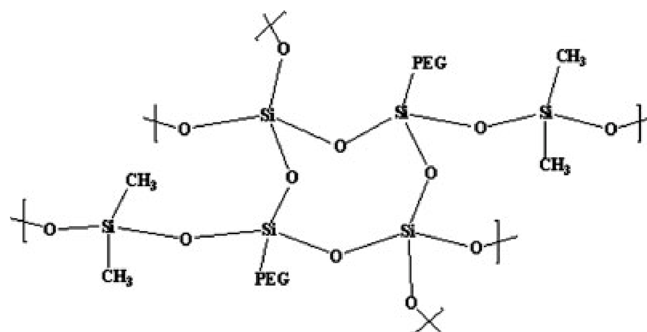


Figure 2 Film structure with PEG chain added.

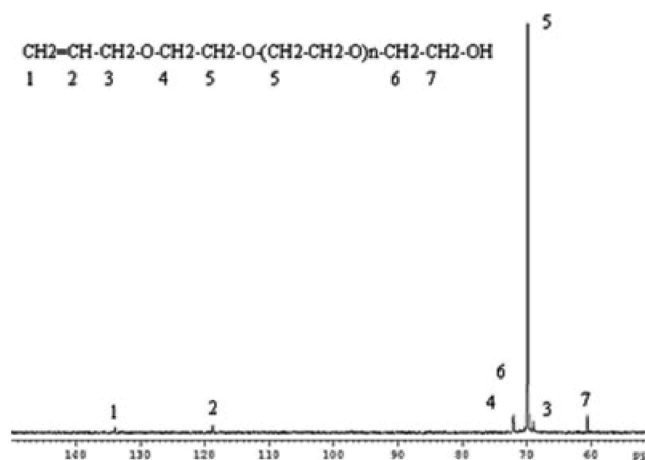


Figure 3 13C-NMR spectrum of allyl-polyethylene glycol.

The film morphology of surface and section was obtained by a HITACHI X-650 SEM spectrometer, the resin surfaces were coated with a thin layer of gold before observation and an acceleration voltage of 10–20 kV was used. The film morphology of surface was also obtained by Seiko SPI3800N AFM spectrometer.

The hardness of the film was performed with Nicro Hardness Tester HV-1000. The samples were stamped using an ASTM 1708 standard die and were tested using the crosshead speed of 50 mm/min at room temperature (∼ 18°C) under 50% humidity. The capacitance of films was measured with an HP4145B semiconductor parameter analyzer.

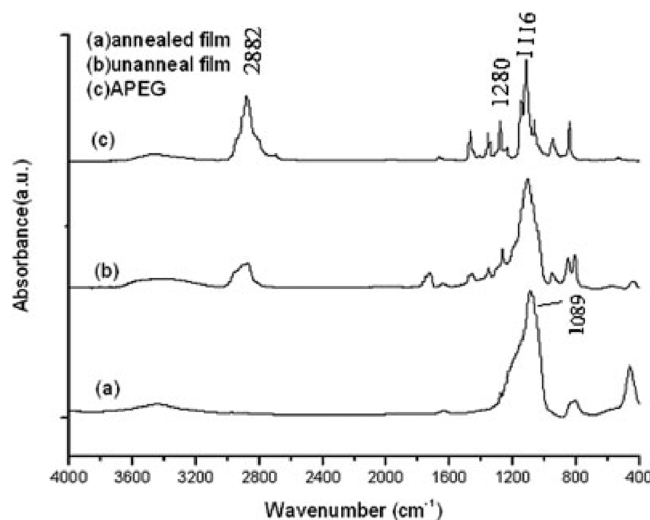


Figure 4 FTIR spectra of (a) allyl-polyethylene glycol (b) thin film before annealing and (c) thin film after annealing.

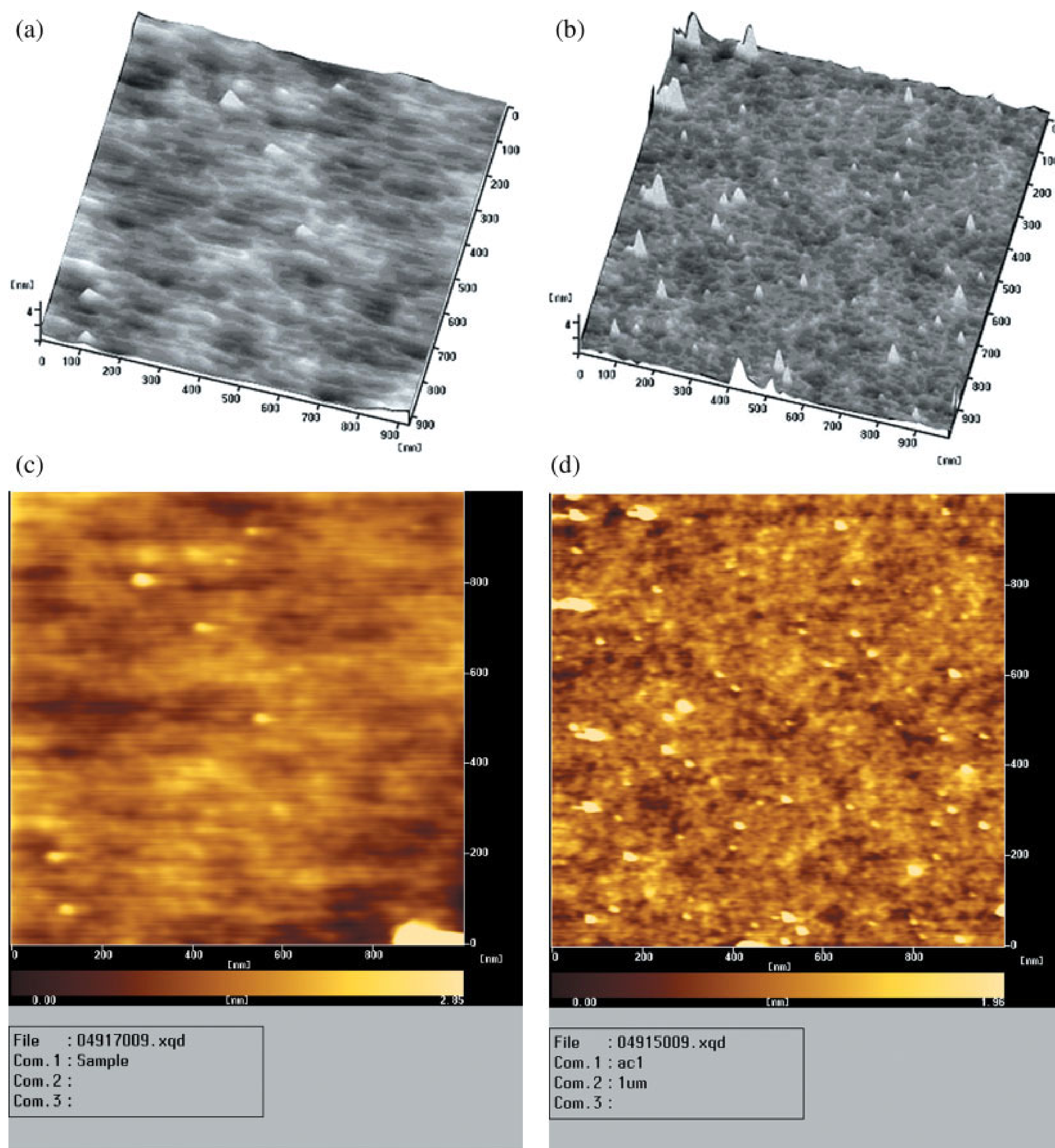


Figure 5 AFM 3D images of (a) the film with 0% of -PEG, and (b) the film with 60% of -PEG. AFM 2D images of (c) the film with 0% of -PEG, and (d) the film with 60% of -PEG. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Characterization of allyl-polyethylene glycol

The chemical shifts of different carbons in allyl-polyethylene glycol were marked from 1 to 7 and shown in 13C-NMR spectrum. The area of peak 7 was 1 and the area of peak 5 was 37, the molecular weight (M) of APEG could then be calculated: $M = 37 \times 14 + 16 \times 19 + 14 + 13 + 14 + 16 + 14 + 14 + 17 = 924$. To avoid the calculation of minor deviation due to the Nuclear Overhauser Effect, another method was used. While 58.17 of the hydroxyl content of allyl-polyethylene glycol adopted, the molecular weight (M*) of APEG could be calculated as follow: $M^{*} = 1 \times 56.1$

$\times$ 1000/58.17 = 964. Both results were close to the molecular weight as we designed (Fig. 3).

Characterization of SSQ-PEG

The FTIR spectra of the allyl-polyethylene glycol and thin films before and after annealing were shown in Figure 4. The —CH_2— stretch bands at 2882 cm^{-1} and C—O—C stretch at 1280 cm^{-1} were attributed to the PEG chain. The broad peaks of Si—O—Si stretching at 1089 cm^{-1} were observed both in (a) and (b) spectra (Fig. 4), while there was only a sharp peak of C—O—C stretching at 1116 cm^{-1} appeared in (c) spectrum (Fig. 4). This finding implied that the PEG chain was surely added into the thin films when —SSQ base joined the crosslinking system, and the PEG chain decompounded completely after annealing.

Morphology of thin films

The formations of porous films with surface patterns were demonstrated by AFM (Fig. 5). The pore size in the materials depended on the molecular weight of the PEG, when organic chains such as PEG were used as sacrifice template. The porosity changed with different contents of PEG added. The open pores are presented in the films. The as-deposited film with 0% of PEG was fairly smooth, as shown in Figure 5, while the surface of the film with 60% of PEG was observed with uniformly dispersed 5–20-nm millipores.

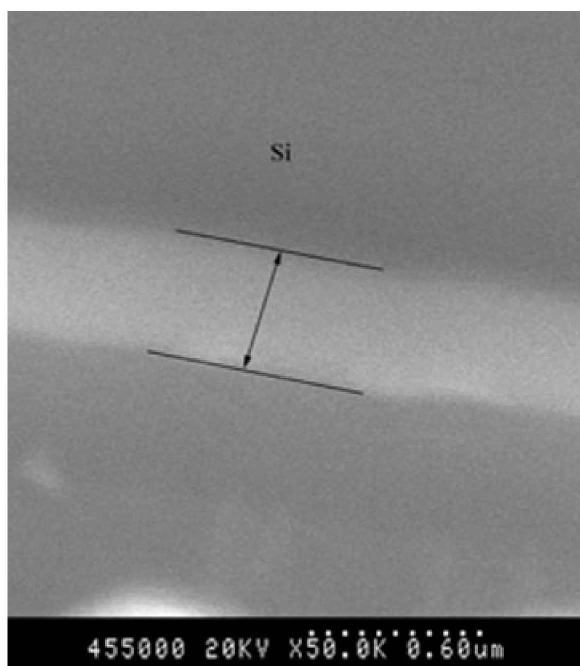


Figure 6 SEM image of film section with 60% of -PEG.

TABLE 1
Porosity, Dielectric Constant (k) and Hardness of the Low-k Porous Films

Sample	Porosity (%)	Dielectic constant	Hardness (GPa)
0% -PEG thin film	0	3.8	0.98
30% -PEG thin film	30	2.3	0.72
45% -PEG thin film	45	2.2	0.71
60% -PEG thin film	60	2.1	0.64

It was also confirmed that the SSQ-PEG as the template was evenly added into the thin films. After annealing, the PEG chains were decompounded; the nanopores were then created reasonably. The thickness of the film with 60% of PEG was observed $\sim$ 300–500 nm by a SEM picture of the film section (Fig. 6).

Mechanical properties and dielectric constant of the thin films

Dielectric constant of the film was calculated by measuring capacitance of the metal–insulator–metal structure using HP4145B semiconductor parameter analyzer according to the following equation:

$$k = C * d/(A * \varepsilon_0) \quad (1)$$

where C is capacitance, d is thickness of thin films, A is the area of thin films, and ε_o is a constant.

The thickness of the films was measured by SEM, and the area of the electrodes on the thin films was 1 cm^2. The hardness and the dielectric constant of the thin films are shown in Table I, which shows that the dielectric constants of the thin films were lower with the amount of PEG content increase, meantime the hardness of the films decreased. The dielectric constant of the thin film with 60% porosity turned out 2.1, and the hardness of the film $\sim$ 0.6 GPa.

CONCLUSION

A series of SSQ-PEG were synthesized and characterized by FTIR and NMR, and used as a template precursor through sol-gel reaction and annealing. After annealing, the films of polysiloxane with dielectric constants of $\sim$ 2.3–2.1 (at 1 MHz) were then achieved with the porosity of $\sim$ 30–60%. The crosslinking system with dimethoxydimethyl silane showed good tenacity. When the porosity of the film was about 60%, the hardness of the film was 0.6 GPa. It reached the minimum requirement of the low-k material used in microelectronic industry. The nanopores in the films appeared in the same aperture and were evenly distributed in the low-k materials because SSQ-PEG was used as template. It is hoped that a class of ultra low-k dielectric materials ($k < 2$)

with good mechanical properties could be made in this way. Further work is underway.

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