Material Issues for Nanoporous Ultra Low-k Dielectrics

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Abstract

Using the molecularly designed porogen (pore generating agent) approach, novel nanoporous low-k materials with improved mechanical properties have been achieved based on poly(methylsilsesquioxane), PMSSQ, structure. Two different methods, microphase separation system and grafted porogen system, were adopted to realize nonporous ultra low-k dielectrics with superior mechanical properties. We found that the behavior of dielectric constant as well as thin film modulus depends on the molecular structure of a porogen. Within the decomposition temperature windows of grafted porogens, a low-k material with k < 2.2 and Young's modulus > 6 GPa was achieved. These results indicate that it is possible to design and fabricate nanoporous thin films with balanced low dielectric constant and robust mechanical properties, which are highly desired for microelectronic industry.

Introduction

Since low-k dielectrics have been regarded as a necessary choice to elevate IC (integrated circuit) performance for next generation integration technology, tremendous efforts worldwide have been devoted to the development of low-k materials with k < 2.8 ~ 3.0 that are targeted for the 130 nm device technology.[1] The International Technology Roadmap (ITRS) anticipates that low-k dielectrics below 2.5 for the 90 nm node should soon be lowered to 2.0 or less for the future technology node by 2010. The dielectric constant of a given material can be continuously lowered by introducing porogens, leaving behind air-filled nanopores (k ~ 1), into insulating films. A variety of pore generation methods have been utilized to create ultra low-k (k < 2.2) dielectrics with k value as low as 1.5.[2-8] However, the choice of low-k material that can meet the integration and reliability requirements[9], while still maintaining the low k value, remains elusive because of fundamental material limitations of nanoporous low-k dielectrics originate from the reduced density. Consequently, the design strategy for low-k materials to have balanced electrical (low k) and mechanical (high E) properties becomes increasingly necessary. In present study, we show a few examples in ultra low-k (k < 2.2) materials employing a variety of porogen molecular structures.

Sample Preparation
a. Microphase separation system

MSSQ:BTMSE copolymer, which is used as a matrix material, was prepared by the addition of 10 mol % "bridged" BTMSE monomers to methyltrimethoxysilane (MTMS). A star-shaped aliphatic core porogen, a Tetronic (150R1, BASF) block copolymer and a modified Gemini surfactant are employed as pore generating polymers (porogens) and chemical structures are shown in figure 1. The copolymer matrix precursor was mixed with 10, 20, and 30 wt. % porogen in methyl isobutyl ketone (MIBK) or 1-butanol. Solution was spun cast at 3000 rpm for 30 seconds. Films prepared by the aliphatic porogens were cured under nitrogen at 420 °C for 1 hour while other films were cured at 450 °C under N_2 atmosphere.
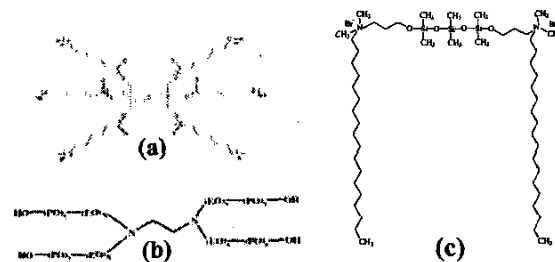

Fig. 1 Pore generating polymers: (a) aliphatic core porogen, (b) Tetronic, and (c) modified Gemini surfactant.

b. Grafted porogen system

A variety of monomers containing pore generating moieties were initially prepared by first the synthesis of porogen moieties and then the graft of the porogen moiety to alkoxy silanes by hydrosilylation and were subsequently copolymerized with methyltrimethoxysilane (MTMS) and/or 1,2 bis-trimethoxysilylethane (BTMSE) to yield polymers denoted as A, B, and T. For A, porogen moieties were grafted to the MSSQ backbone and bridged BTMSE is introduced in the case of T. On the other hand, porogen moiety in B was linked to the silane backbone by two covalent bonds. All the prepared polymers are readily spun cast and their molecular weights were confirmed by GPC. ^{1}H NMR spectra also confirmed that A, B, and T polymers contain 8, 13, 10 mole% of porogens, respectively.

Results and Discussion
a. Microphase separation system

Refractive indices of porous films gradually decrease with the porogen loading for the three types of porogens

tested. Volume fraction porosities of the films are calculated by the Lorent-Lorentz equation:

$$\frac{n^2-1}{n^2+2} = (1-\phi)\frac{n_0^2-1}{n_0^2+2}$$

where, n_0 is the measured refractive index of the matrix material, and, n is the measured refractive index of the nanoporous film. Figure 1 shows refractive index and volume fraction porosity as a function of porogen loading. It is noted that Tetronic porogens yield the highest porosity at a given porogen loading.
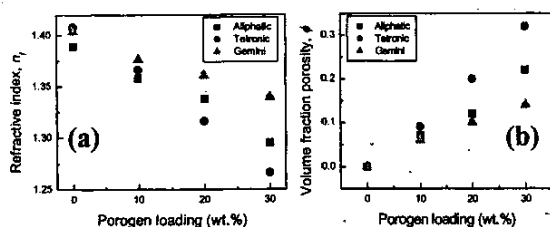

Fig. 2 Refractive index (a) and volume fraction porosity (b) of nanoporous films.

FT-IR spectra of porous films with different types of porogens are shown in figure 2. The Si-O-Si network peak at 1030cm^{-1}, normalized with film thickness and porosity, decreases with the porogen loading in the case of aliphatic porogen. The relative ratio of the Si-O-Si networking peak at 1030 cm^{-1} to the Si-O-Si cage peak at 1130 cm^{-1} also clearly decreases with the addition of aliphatic porogen.
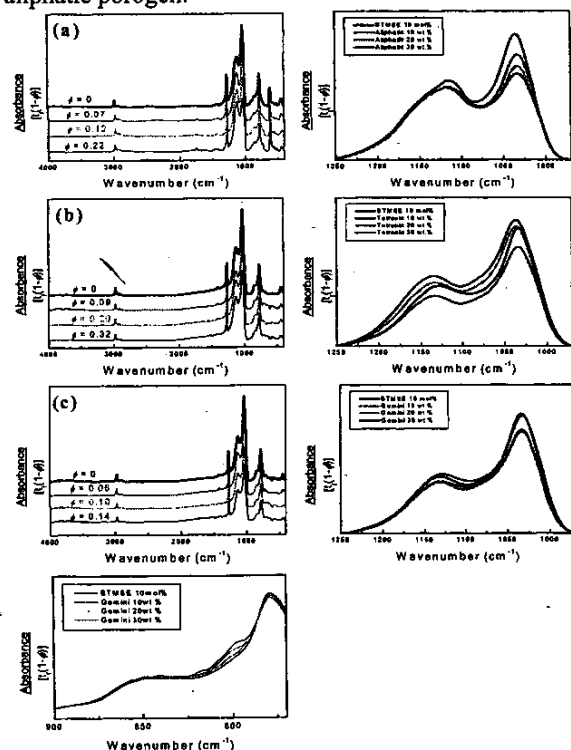

Fig. 3 FT-IR spectra of porous films prepared by (a) aliphatic porogens, (b) Tetronics, and (c) modified Gemini surfactant after curing.

On the other hand, Tetronic block copolymer and modified Gemini surfactant do not seem to disturb the matrix condensation: the relative ratio of the Si-O-Si network peak to the Si-O-Si cage peak does not change significantly. The Si-$(CH_3)_2$ peak at 800 cm^{-1} was also observed for the films prepared by the modified Gemini surfactants. It is also observed that this peak at 800 cm^{-1} increases with the loading of modified Gemini surfactant. This implies that the siloxane groups on the modified Gemini surfactant recombine with matrix.

Table 1. Electrical and mechanical properties of porous films prepared by (a) aliphatic porogens, (b) Tetronics, and (c) modified Gemini surfactants

(a)	Modulus (GPa)	Hardness (GPa)	k-value	Porosity
0	7.53 ± 0.06	1.33 ± 0.06	2.86	0
10	4.46 ± 0.13	0.78 ± 0.04	2.63	0.07
20	3.15 ± 0.13	0.51 ± 0.04	2.42	0.12
30	2.14 ± 0.13	0.33 ± 0.02	2.21	0.22

(b)	Modulus (GPa)	Hardness (GPa)	k-value	Porosity
0	8.16 ± 0.10	1.21 ± 0.02	2.82	0
10	6.12 ± 0.08	0.88 ± 0.02	2.71	0.09
20	4.20 ± 0.05	0.58 ± 0.02	2.48	0.20
30	2.45 ± 0.06	0.36 ± 0.01	2.08	0.32

(c)	Modulus (GPa)	Hardness (GPa)	k-value	Porosity
0	7.88 ± 0.13	1.18 ± 0.03	2.80	0
10	6.35 ± 0.09	0.91 ± 0.03	2.69	0.06
20	4.63 ± 0.11	0.63 ± 0.03	2.43	0.10
30	4.00 ± 0.08	0.54 ± 0.02	2.40	0.14

The electrical and mechanical properties are listed in table 1. Aliphatic porogens yield low dielectric constants but show poor mechanical properties. Tetronic block copolymers, however, show low dielectric constant as well as acceptable mechanical properties.

Modified Gemini surfactant has the lowest porosity at a given porogen loading. At 20 wt.% of loading, the modified Gemini surfactant sample has a lower dielectric constant and a higher modulus relative to the Tetronic porogens. This can be explained by the existence of possible interfacial reaction between siloxane groups in the surfactant and the matrix and the existence of Si-$(CH_3)_2$ in FT-IR probably lowers the polarity of the films resulting in films with low dielectric constants.

b. Grafted porogen system

Figure 4(a) shows the structural changes of a **B** film measured with FT-IR after curing under N_2 purge. Infrared spectra show that the peak intensity at 2910 cm^{-1} due to the asymmetric stretching of porogen groups notably decreases above 300 °C together with the peak at 1514 cm^{-1} assigned to phenyl groups attached to the porogen moieties and these peaks almost disappear at 450 °C. Upon curing, the absorption band at 1040 cm^{-1} increases due to the structural rearrangement from a

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cage-like symmetric Si-O-Si structure to an asymmetric Si-O-Si network structure, which is related to the formation of a more dense film structure.
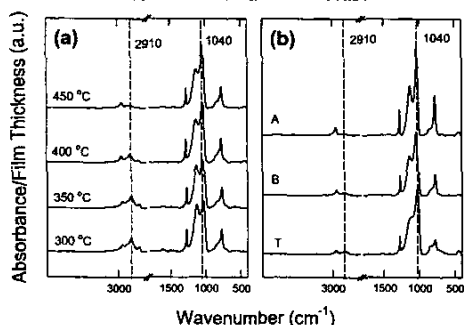

Fig. 4 FT-IR spectra showing the structural changes of B film with temperature (a) and A, B, and T films after curing at 450 °C.

Figure 4 (b) shows infrared spectra of *A*, *B*, and *T* films after curing at 450 °C. For all the films tested, it is confirmed that the grafted porogens are almost removed. In addition, absorbance intensities at 1040 cm^{-1} in *B* and *T* are stronger than that for *A*. As a result, it is expected that thermal and mechanical stabilities of *B* and *T* are higher than that of *A* due to the formation of a dense film structure. Figure 5 shows the behavior of refractive index (n_f) and dielectric constant (k) for *B* with curing temperature. For all the films examined, *k*-values and refractive indices decrease with curing temperature due to the formation of porous structure by the decomposition of the grafted porogens and also the removal of silanol groups by polycondensation. *k*-values of *A*, *B*, and *T* reduce to 2.67, 2.17 and 2.12 after curing at 450 °C, respectively. For *A*, the *k*-value of 2.57 after curing at 400 °C is lower than 2.67 at 450 °C, signaling the possible collapse of pores in the films by the introduction of bulky free-rotating porogens. On the other hand, the collapse of pores was observed for *B* and *T* samples. This observation supports the idea that the introduction of bridge-type comonomer such as BTMSE increases the thermomechanical stability of a film.
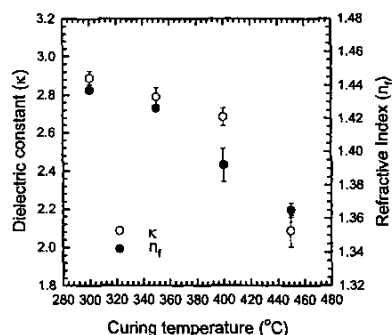

Fig. 5 The change of dielectric constant and refractive index with curing temperature for a B film.

Table 2 shows the mechanical properties for low-k materials with different molecular structures of grafted porogens. As mentioned earlier, the elastic modulus of A is lower than those of *B* and *T* after curing. On the other hand, B and T show moduli of 6.16 GPa and 3.76 GPa that are higher than 3.40 GPa of non-porous PMSSQ in spite of the pore formation in the film as evidenced in the low k values. This is believed to be due to the high crosslinking density by the incorporation of bridged hexa-coordinated alkoxy groups and the possible formation of SiO$_2$ structure by the dissociation of Si-C bonds, respectively. The tetra-coordinated SiO$_2$ structure is also confirmed by the ^{29}Si CP-MAS NMR spectra.

Table 2. Electrical and mechanical properties of porous films after curing

Film	Modulus (GPa)	Hardness (GPa)	k-value
A	2.71 ± 0.05[a]	0.32 ± 0.01[a]	2.57[a]
B	6.16 ± 0.10[b]	0.75 ± 0.02[b]	2.17[b]
T	3.76 ± 0.06[b]	0.49 ± 0.01[b]	2.12[b]

[a,b]Measured for films cured at 400 and 450 °C, respectively. Nanoindentation data were taken at a relative value of 50 nm.

Conclusion

Nanoporous thin films were prepared two different methods; microphase separation system and grafted porogen system. Dielectric films with balanced low dielectric constant and mechanically superior properties were prepared by the decomposition of porogens chemically grafted to the organosilica matrix. The reduction of dielectric constant is achieved by the removal of grafted porogen moieties, while the increase in mechanical properties is due to the bridged hexa-coordinated alkoxy groups and the additional partial conversion to the tetra-coordinated Si-O bond after removal of the grafted porogens in the case of PMSSQ films containing a bridge-type comonomer.

References

(1) L. Peters, Semiconductor International 2001, May.
(2) C. V. Nguyen, et al, Chem. Mater. 1999, 11, 3080.
(3) H. W. Ro, et al, Polym. Prep., 2002, 43(2), 1166.
(4) H. W. Ro, et al, Polym. Prep., 2001, 42(2), 889.
(5) Y. Toivola, et al, J. Electrochem. Soc., 2004, 151, 45.
(6) S. Mikoshiba, et al, J. Mater. Chem. 1999, 9, 591.
(7) B. Zhong, et al, Polym. Mater. Sci. Eng. 2002, 87, 440.
(8) A. Padovani, et al, J. Electrochem. Soc. 2002, 149, 161.
(9) A. E. Braun, Semiconductor International 2003, May.