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Effect of Pore Generating Materials on the Electrical and Mechanical Properties of Porous Low-k Films

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1. Introduction

Porous organosilicate thin films have attracted much interest as ultra low dielectric materials for the IC (integrated circuit) application since the dielectric constant of a given material can be continuously lowered by introducing pores into insulating films [1-3]. However, reliability issues are still remaining because of poor mechanical properties of the nanoporous low-k dielectrics originating from the reduced density. To balance between electrical and mechanical properties, material design strategies for the matrix material and the pore generating material (porogen) are needed. In present study, we introduce two types of porogens to realize porous low dielectric films and observe the effect of pore generating materials on the electrical and mechanical properties for nanoporous films.

2. Experimental

MSSQ:BTMSE copolymer, which is used as a matrix material, was prepared by the addition of 10 mol % “bridged” BTMSE monomers to methyltrimethoxysilane (MTMS). Star-shaped aliphatic core porogens and Tetronic (150R1, BASF) block copolymers are used as pore generating polymers (porogens), as shown in Figure 1. The copolymer matrix precursor was mixed with 10, 20 and 30 wt% porogens in methyl isobutyl ketone (MIBK). The solution was spun cast at 3000 rpm for 30 seconds. Films prepared with aliphatic porogens and Tetronic porogens were cured under nitrogen at 420 °C and 450 °C.

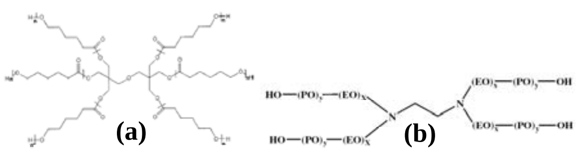

Fig. 1 Pore generating materials: (a) aliphatic core porogen and (b) Tetronic porogens.

3. Results and Discussion

Refractive indices of porous films gradually decrease with the porogen loading for both porogens tested. Volume fraction porosity of the films can be obtained 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 a nanoporous film. Figure 2 shows the change in 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.

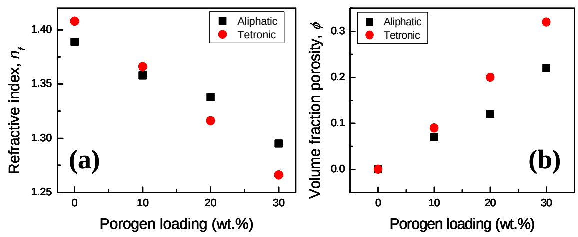

Fig. 2 Refractive index (a) and volume fraction porosity (b) of porous films.

Dielectric constants and mechanical properties were measured and listed in Table 1. Dielectric constants for the films prepared with aliphatic porogens, as represented in Table 1(a), decrease down to 2.21 at 22 % porosity. Both modulus and hardness are also reduced by increasing the porosity. At 10 wt% porogen loading, modulus drops sharply and then gradually decreases. In contrast, Tetronic porogens reduce the dielectric constant and the modulus of porous films to 2.08 and 2.45, respectively, at 32 % porosity. Films prepared with Tetronic porogens yield higher porosity and lower dielectric constant than those with aliphatic porogens.

Table 1. Electrical and mechanical properties of porous films prepared with (a) aliphatic porogens and (b) Tetronic porogens

(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

To compare mechanical properties, moduli obtained with aliphatic porogens and Tetronic porogens are plotted as a function of porosity, as shown in Figure 3. It is evident that films prepared with Tetronic porogens yield higher modulus than the films prepared with aliphatic porogens.

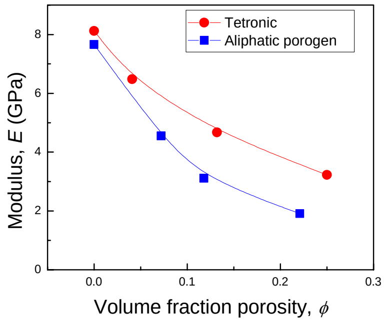

Fig. 3 Apparent modulus as a function of volume fraction porosity for porous films prepared with aliphatic and Tetronic porogens.

To observe the effect of porogens on the matrix structure, FT-IR spectra were measured and shown in Figure 4. Aliphatic porogens hinder the formation of Si-O-Si network structure and thus the Si-O-Si network vibration at 1030 cm^{-1} is reduced by increasing the porogen loading [4]. It has been already reported that aliphatic porogen hinders the formation of Si-O-Si network structure by matrix-porogen interaction [3]. For the films prepared with Tetronic porogens, however, there is no significant change in the matrix structure. The Si-O-Si network vibration at 1030 cm^{-1} is almost intact by varying porogen loading.

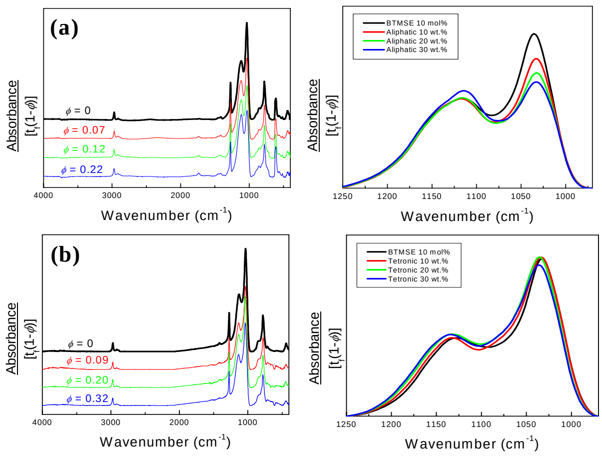

Fig. 4 FT-IR spectra of porous films prepared with (a) aliphatic porogens and (b) Tetronic porogens after curing.

3. Summary

Two types of porogens were used to prepare porous low dielectric films. Aliphatic porogens as well as Tetronic block copolymer porogens generate pores within the films thus lowering the dielectric constant. Tetronic porogens, however, yield porous films without the matrix-porogen interactions and result in higher mechanical properties with lower dielectric constant, when compared with aliphatic porogens.

Acknowledgements

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References

[1] C. V. Nguyen, et al, Chem. Mater. 1999, 11, 3080.
[2] Y. Toivola, et al, J. Electrochem. Soc., 2004, 151, 45.
[3] Q. R. Huang et al, Chem. Mater. 2002, 14, (9), 3676.
[4] Socrates, G., Infrared and Raman Group Characteristic Frequencies: Tables and Charts. John Wiley & Sons: New York, 2001.