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Communications

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

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Introduction

In the International Technology Roadmap for Semiconductors (ITRS), new low dielectric insulating materials with bulk dielectric constant below 2.1 are required to minimize the interconnect delay caused by high densities of devices and wiring for high-performance chips.[1] Among many possible candidates for ultra low dielectric materials, nanoporous organosilicate thin films are one of the most promising candidate materials since their dielectric constant can be continuously reduced by the incorporation of nanopores within the films. Various nanoporous low dielectric films have been realized using poly(methyl silsesquioxane) (PMSSQ) as a matrix material with a wide variety of pore generating materials (porogens) such as star-shaped polymers,[2,3] block copolymers,[4,5] cyclodextrines,[6-8] norbornenes,[9,10] dendrimers,[11,12] and hybrid type porogens.[13,14]

However, reliability issues still remain 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 porogens are needed.

In present study, we introduce two types of porogens to realize porous low dielectric films and observe the effect of porogens on the electrical and mechanical properties for nanoporous films.

Experimental

Materials. A PMSSQ copolymer,[15] which has been used as a matrix material with a number average molecular weight of 1,250 g/mol, was synthesized by the addition of 10 mol% of 1,2-bis-trimethoxysilyletane (BTMSE) to 90 mol% of methyltrimethoxysilane (MTMS). Star-shaped polycaprolactone (PCL) (M_n=4,220 g/mol) and Tetronic (150R1, BASF) (M_n=8,000 g/mol), as shown in Figure 1, are used as porogens. The PMSSQ copolymer was mixed with 10, 20, and 30 wt% porogens in methyl isobutyl ketone (MIBK). The solution was spun cast on piranha treated silicon wafers at 3,000 rpm for 30 sec. Films prepared with PCL and Tetronic porogens were cured under nitrogen at 420 and 450 °C, respectively.

Characterization. The refractive indices of porous low dielectric films were measured with a variable-angle multi-wavelength ellipsometer (Gaertner, L2W16C830). FTIR measurements were carried out using a JASCO FTIR 200 spectrometer. Mechanical properties of low dielectric films were measured by using a nanoindenter (Nano Indenter®

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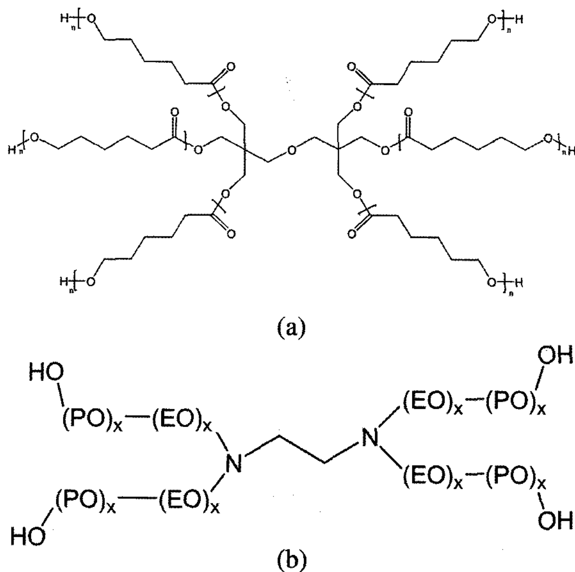

Figure 1. Pore generating materials: (a) Polycarprolactone (PCL) porogen and (b) Tetronic porogens.

XP, MTS Corp.) in the continuous stiffness measurement mode. Apparent modulus values were collected at the relative displacement of 0.05 from the film surface. Dielectric constants were measured in the metal-insulator-metal (MIM) configuration with evaporated aluminum electrodes at 1 MHz using a HP4284 LCR meter.

Results and Discussion

Measured refractive indices of porous films gradually decrease with the porogen loading for both porogens tested. Volume fraction porosity for the films can be obtained by the Lorentz-Lorenz 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 porous film. Figure 2(a) shows the change in refractive index as a function of porogen loading. For both porogens, the refractive indices decrease with the increase in porogen loading, which implies that the porous structure is successfully achieved without further pore collapse for both porogens. Calculated porosity based on the Lorentz-Lorenz equation is plotted in Figure 2(b). It is noted that the Tetronic porogens yield the higher porosity than the PCL porogens at a given porogen loading.

Dielectric constants and mechanical properties were measured and listed in Table I. Dielectric constants for the films prepared with the PCL porogens, as shown in Table I(a), decrease down to 2.21 at 22% porosity. Both modulus and

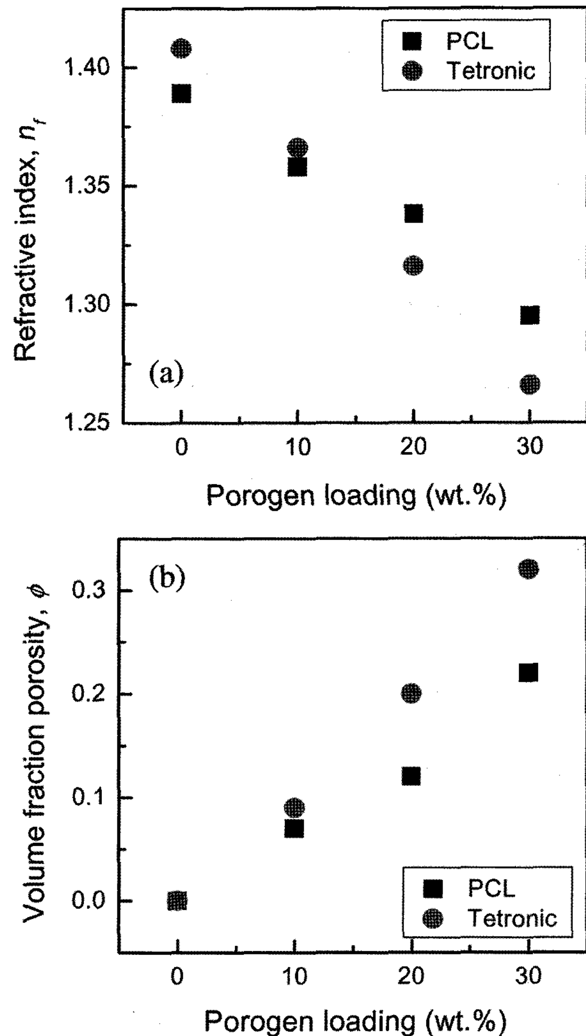

Figure 2. Refractive index (a) and volume fraction porosity (b) of porous films.

Table I. Electrical and Mechanical Properties of Porous Films Prepared with (a) PCL 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

hardness are also reduced by increasing the porosity. Up to the 10 wt% porogen loading, modulus initially drops sharply and then gradually decreases. In contrast, Tetronic porogens reduce the dielectric constant and modulus of porous films to 2.08 and 2.45, respectively, at 32% porosity. It is noted that films prepared with Tetronic porogens yield higher porosity and modulus and lower dielectric constant than those with the PCL porogens.

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

To investigate the origin of difference in modulus as a function of porosity for porous films prepared by both PCL and Tetronic porogens, FTIR spectra were measured and shown in Figure 4. Full FTIR spectra for porous films prepared with PCL and Tetronic porogens with different porogen loadings are represented in Figures 4(a) and 4(b), which show Si-C vibration at 768 cm^{-1}, vibration of Si-O-Si with functional groups at 1130 cm^{-1}, Si-O-Si network vibration at 1030 cm^{-1} and Si-CH_3 deformation at 1270 cm^{-1}. Typically, as the condensation between Si-OH groups progresses, the peak at 1130 cm^{-1} reduces and at the same time, the peak at 1030 cm^{-1} increases by the formation of Si-O-Si network structure. When the FTIR spectra for both porogens are further investigated from 950 to 1250 cm^{-1} in detail, as shown in Figures 4(c) and 4(d), there are different peak ratios between 1030 and 1130 cm^{-1} for porous films.[16] In the case of porous films prepared with the PCL porogens, Si-O-Si network structure is suppressed by the addition of porogens.

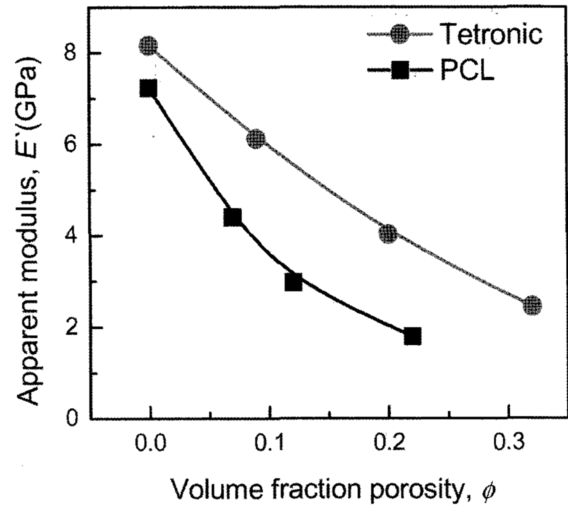

Figure 3. Apparent modulus as a function of volume fraction porosity for porous films prepared with PCL and Tetronic porogens.

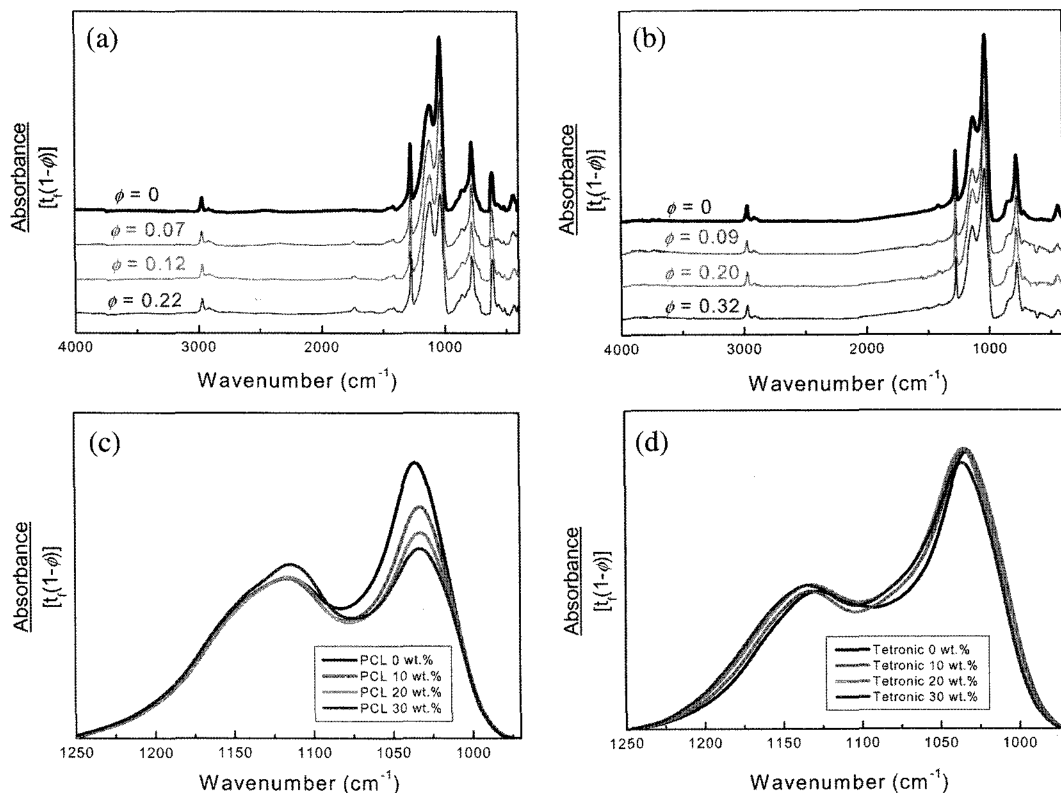

Figure 4. FTIR spectra of porous films prepared with PCL porogens ((a), (c)) and Tetronic porogens ((b), (d)) after curing.

Si-O-Si network structure and thus the Si-O-Si network vibration at 1030 cm^{-1} is reduced by increasing the porogen loading. It has already been reported that the PCL porogens hinder the formation of Si-O-Si network structure by the 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 the porogen loading.

Conclusions

Two types of porogens were tested to prepare porous low dielectric films. PCL 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 significant matrix-porogen interactions and thus result in higher mechanical properties with lower dielectric constant, when compared with the PCL porogens.

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