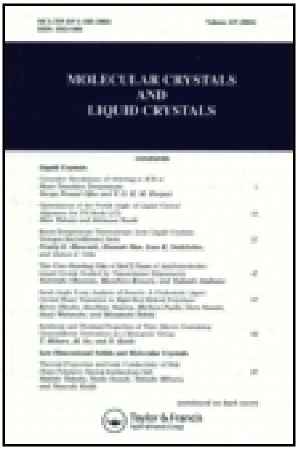

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Chemically Reactive Nanoparticle for Ultra-lowk Applications

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Chemically Reactive Nanoparticle for Ultra-low *k* Applications

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*The introduction of nanometer-sized pores into low dielectric (**k**) materials is the most promising approach in producing ultra-low dielectric constant materials (**k** < 2.2). However, since the increased pores in low-**k** films lowered the mechanical strengths, it is important to optimize the mechanical properties by controlling the pore morphologies such as pore size, its size distribution and interconnectivity. We prepared nanoporous low-**k** films by using a chemically reactive cyclodextrin (TESCD) as a porogen to acquire chemical bonding with the low-**k** matrix, poly (methyl trimethoxy silane-co-bistriethoxysilyl ethane). The porosity of nanoporous low-**k** films linearly increased with porogen loading, which indicated great compatibility between porogen and matrix, and its dielectric constant was as low as 2.2 (from 3.0) at 40% of porogen loading. Nanoindentor was applied on the nanoporous low-**k** films prepared by either TESCD or poly(caprolactone) porogen to measure elastic modulus and surface hardness. TESCD porogen resulted in much less reduction in elastic modulus and surface hardness from ∼16 GPa to ∼7.3 and from ∼2.7 GPa to ∼1.0 at 27% of porosity, respectively, while PCL porogen brought about the dramatic decrease in both mechanical properties at the corresponding porosity. This result may be due to the chemical bonding between TESCD and the matrix during its crosslinking reaction, which led pores.*

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Keywords: mechanical properties; pore morphologies; TESCD porogen; ultra low-*k* materials

INTRODUCTION

Since the decrease in the feature dimension of semiconductor devices causes the increase in signal delay (RC delay), cross-talk (noise) and power consumption, the recent development of semiconductor chips requires lower dielectric (k) materials [1,2]. For example, the next 50 nm devices call for ultra low dielectrics below 2.0 [3].

One of the ways to decrease k is the introduction of nanometer-sized air ($k \sim 1.0$) into low-k matrices such as organosilicate glasses with k value of $2.7 \sim 3.0$ and pores are generally obtained by sintering a thermally degradable material, called porogen, from the nanohybrids of an organic porogen and an organosilicate matrix [4,5]. To obtain ultra-low dielectrics below k value of 2.0, based on low-k organosilicate matrix, more than 30% of porosity is needed. In addition, higher mechanical strengths such as elastic modulus and surface hardness are required to withstand chemical-mechanical polishing (CMP) process. Therefore, the control of pore morphologies is critical in preparing the ultra-low k dielectrics since the pore structures as well as pore size and its size distribution seriously affect the mechanical strength of nanoporous low-k materials.

Although there are many sacrificial porogens such as star polymers and block copolymer, they resulted in macroscopically phase-separated domains of porogens during the cross-linking of organosilicate matrix due to the nucleation and growth mechanism and thus the resultant macropores led to the dramatic decrease in the mechanical strength at higher porosity.

We synthesized a chemically reactive nanoparticular porogen to inhibit the phase separation of the porogen in a low-k matrix during its cross-linking process by introducing alkoxysilane (Si–OR) or silanol (Si–OH) in cyclodextrin molecules using allylation and hydrosilylation reaction (Fig. 1). Cyclodextrin is a series of cyclic oligosaccharides containing six to eight glucose units linked by α-1,4-linkages and its molecular size is approximately $1.4 \sim 1.7$ nm. Organosilicate matrix used in this study was poly(methyl trimethoxy silane-co-bistriethoxysilyl ethane) {poly(MTMS-co-BTESE)} which contained 50 mol% of BTESE (BTESE50). BTESE50 exhibited k value of ~ 3.0 and elastic modulus of ~ 16 GPa, the latter of which was 5 times higher than that of commercial organosilicate (PMSSQ). To investigate the effect of pore morphologies on mechanical properties of nanoporous low-k films,

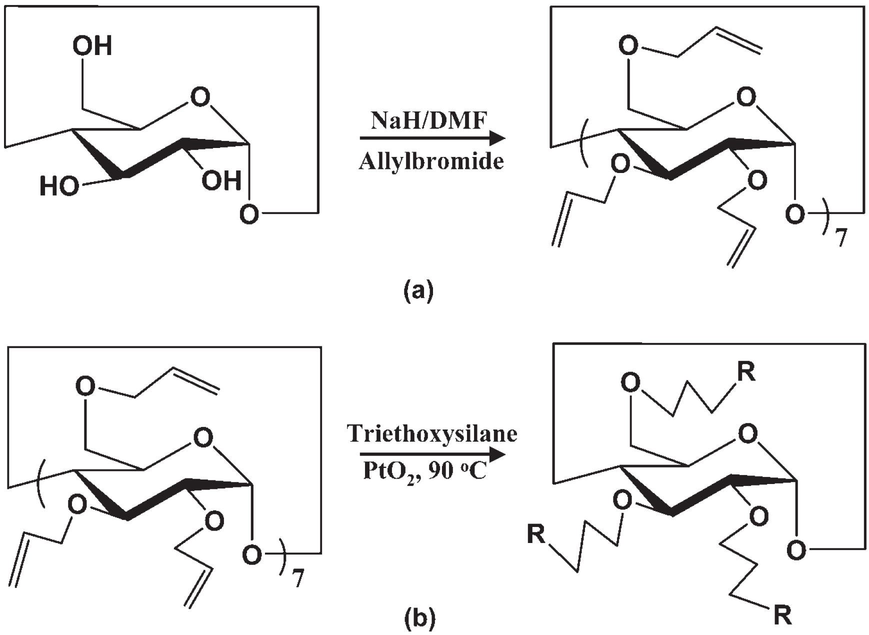

FIGURE 1 The synthetic scheme of triethoxysilyl β-cyclodextrin (TESCD): (a) allylation and (b) hydrosilylation.

nanoindentor was applied on the nanoporous low-*k* films prepared by either TESCD or poly(caprolactone) star polymer (PCL) porogen as a function of porogen loading. The porosity and dielectric constant were estimated from the change in the refractive indices of nanoporous films.

EXPERIMENTAL

Triethoxysilyl cyclodextrin (TESCD) as a chemically reactive porogen was synthesized by allylation and hydrosilylation reaction [6–8]. For allylation, 4 mmol β-cyclodextrin was dissolved in 45 ml of DMF by stirring and the prepared solution was added to NaH solution that was suspended in 70 ml of DMF. After stirring for 1 hr at the room temperature, the solution of allylbromide (21 ml) was added dropwise. The resulting mixture was stirred for 1 hr at 0°C and for 3 hr at 25°C. For hydrosilylation, the perallylated cyclodextrins were dissolved in equimolar triethoxy silane and stirred with platinum oxide (PtO_2) as a catalyst at 85°C for 5 hr. The obtained hydrosilylated cyclodextrins was then purified to remove PtO_2 using activated carbon. To prepare

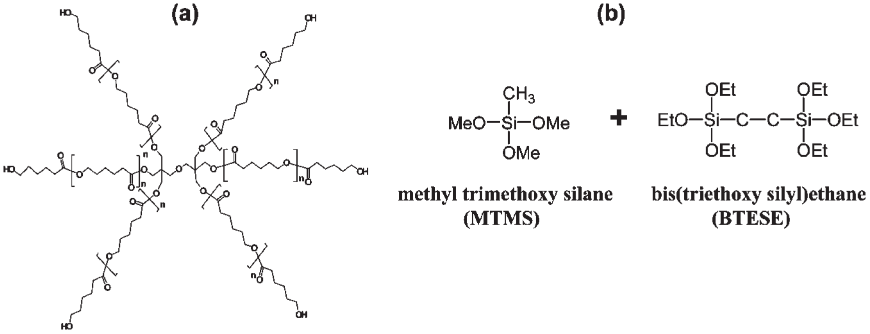

FIGURE 2 The chemical structures of (a) poly(caprolactone) (PCL) and (b) poly(MTMS-co-BTESE) copolymer.

nanoporous low-*k* films, an inorganic matrix called BTESE50 was synthesized by sol–gel reaction of MTMS and BTESE monomers as shown in Figure 2 and the experimental procedure was described in detail elsewhere [9]. To investigate the effect of pore morphologies on the mechanical properties of nanoporous films, the PCL was used as a reference and the detailed synthetic procedures were described elsewhere [10].

For the measurement of dielectrical and mechanical properties of nanoporous low-*k* films, BTESE50 matrix and TESCD porogen were dissolved in butanol/pentanol (50/50 wt%) mixture solution at 30 wt%, respectively and mixed together to make proper ratios of porogen to matrix from 0 to 40 vol%. The mixed solutions were dropped on a silicon wafer through a syringe with a 0.2 µm PTFE filter, and then spun at 2500 rpm for 30 s. The spin-coated films were heated to 250°C at 3°C/min under nitrogen and cured for 2 hr at that temperature and further heated to 430°C and held for 1 hr. Thickness and refractive indices of nanoporous low-*k* films were measured by a variable angle multi-wavelength ellipsometer (L116C, Gaertner Scientific Corp.). The mechanical properties of nanoporous films were determined by using Nanoindentor (MTS Corp.).

RESULTS AND DISCUSSION

^{1}H NMR spectroscopy confirmed the synthesis of TESCD porogen by using allylation and hydrosilylation reaction as shown in Figure 3. The vinyl peaks around 5.0 and 6.2 ppm indicated the successful allylation of cyclodextrin hydrates and the new C–C peaks around 0.6 and

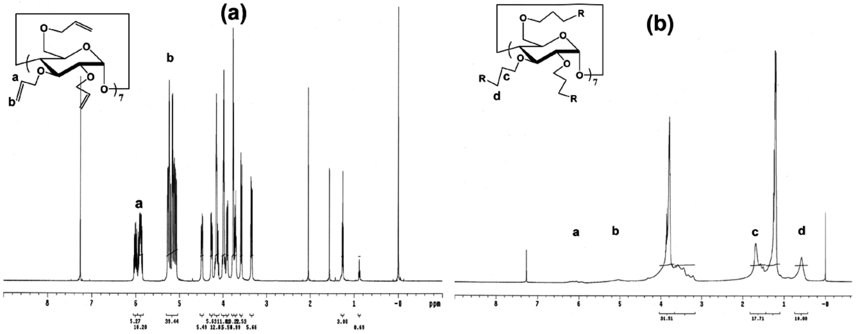

FIGURE 3 ^{1}H NMR spectra of (a) allylated-cyclodextrin and (b) TESCD.

1.7 ppm resulted from hydrosilylation along with the disappearance of the vinyl ones.

Figure 4 shows thermogravimetric analysis (TGA) of TESCD porogen. It showed the slight weight decrease up to 300°C due to the cross-linking reactions of TESCD functional groups (–OH) and then it began to decompose above 300°C along with peak temperature around 350°C. The small amount of residue after 500°C might be due to the creation of siloxane (Si–O–Si) linkages through the condensation reaction of the ethoxy groups. Figure 5 presents refractive indices, estimated porosity (P) and k values of nanoporous films, which were

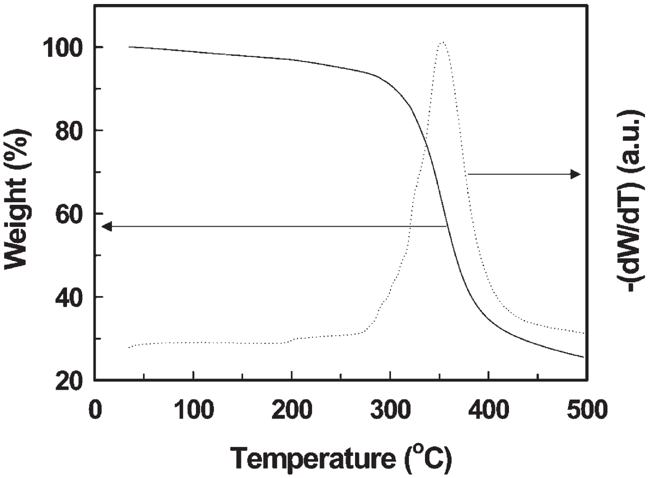

FIGURE 4 TGA thermogram of TESCD.

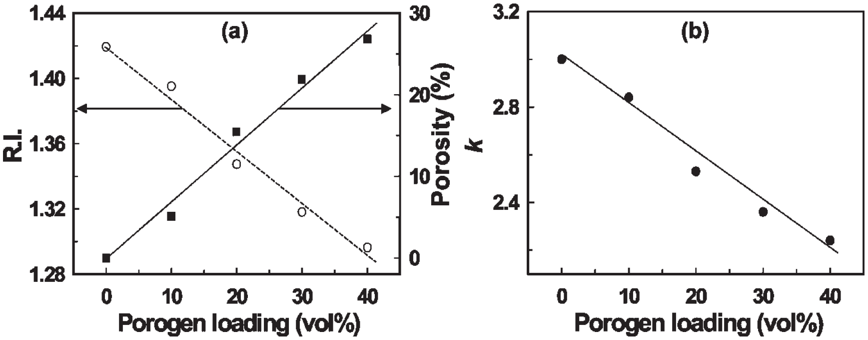

FIGURE 5 Optical and dielectric properties of nanoporous low-k films as a function of porogen loading: (a) refractive index and porosity and (b) dielectric constant.

calculated by Lorentz-Lorenz equation [11]:

$$\frac{n_0 - 1}{n_0 + 2}(1 - P) = \frac{n - 1}{n + 2} \tag{1}$$

where n_0 and n are the refractive indices of the inorganic matrix and nanoporous films, respectively. The porosity linearly decreased with porogen loading and well matched with the amount of porogen loading, which was implicative of no collapse in nanoporous low-k films. The k values of nanoporous films estimated by Maxwell-Garnet equation decreased from 3.0 to 2.2 at 40 vol% of porogen loading [11]:

$$\frac{k_0 - 1}{k_0 + 2}(1 - P) = \frac{k - 1}{k + 2} \tag{2}$$

where k_0 and k are the measured dielectric constants of the matrix and nanoporous films.

Figure 6 shows the effect of porogen loading on elastic modulus (E) and surface hardness (H) of nanoporous low-k films as a function of h/t_f, where h is the indentor displacement and t_f is the film thickness. The increased E above 0.1 of h/t_f was attributed to the substrate effect, while the hardness seemed to be less susceptible to the substrate effects than the modulus [12,13]. BTESE50 copolymer matrix presented E and H values of about 16 and 2.7 GPa, respectively, which were approximately 5 times higher than PMSSQ homopolymer. The increase in the porogen loading resulted in the decreased mechanical strengths due to the increased porosity. According to the Gibson and Ashby [14], the relationship between E and porosity (P) was predicted

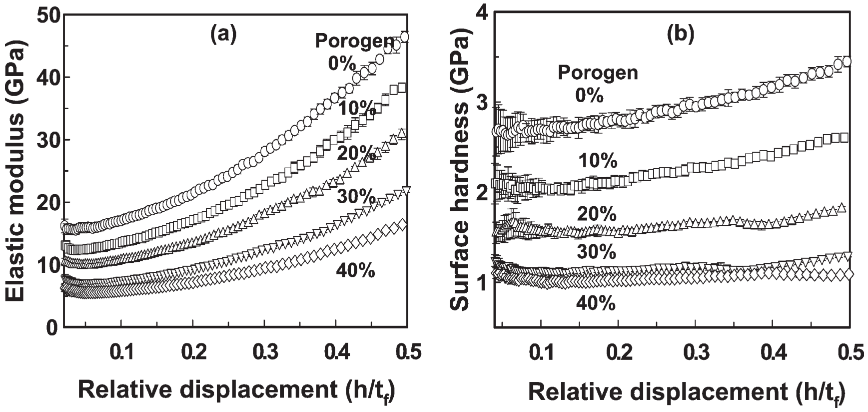

FIGURE 6 The effect of porogen loading on mehanical properties of nanoporous low-*k* films: (a) elastic modulus, and (b) surface hardness.

by the following Eq (3):

$$(E/E_0) \propto (1-P)^n \tag{3}$$

where subscript 0 indicates the modulus of the nonporous matrix. Figure 7 shows the relative elastic modulus (E/E_0) of nanoporous low-*k* films prepared by both TESCD and PCL porogen as a function

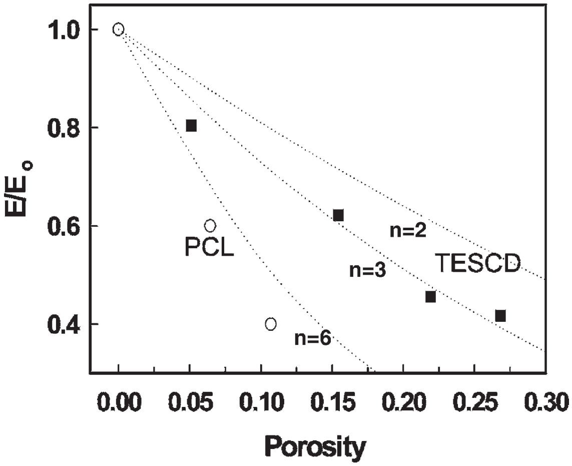

FIGURE 7 The effect of porosity on the relative moduli of nanoporous low-*k* films prepared by different porogen.

of porosity. The dotted lines are the predicted ones for each n value. TESCD porogen resulted in slowly decreased modulus, but PCL brought about the dramatically decreased modulus ($n = 6 \sim 7$). Therefore, it is obvious that the degree of change in the E values upon porosity was seriously influenced by the kind of porogen, which might be related to the degree of phase separation during crosslinking of the organosilicate matrix. TESCD porogen inhibited the phase separation by chemical bonding with the matrix and resulted in the small pore size and narrow size distribution. But, in the case of PCL, which was phase-separated from the hydrophobic matrix during its crosslinking led to the phase-separated domains of the porogen, and consequently the dramatic decrease in the mechanical strength due to the macro-pores.

CONCLUSIONS

It is very important in the preparation of ultra-low k films ($k < 2.2$) to minimize the degree of the decrease in the mechanical strengths by controlling pore morphologies such as pore size, its size distribution and interconnectivity. To inhibit the phase separation of the porogens in a low-k matrix during its crosslinking process, we successfully synthesized a chemically reactive porogen by introducing alkoxysilane (Si−OR) in TESCD through allylation and hydrosilylation reactions. The porosity linearly increased with porogen loading and was consistent with the amount of porogen loading, which implies that no pore collapses occurred during the formation of nanopores. Also, the k value reached down to 2.2 at 40 vol% of porogen loading. The effect of porosity on the mechanical strengths was investigated by measuring elastic modulus and hardness of nanoporous low-k films prepared by both TESCD and PCL porogen. TESCD resulted in remarkably higher mechanical strengths at the corresponding porosity than PCL. This remarkable difference in the elastic modulus might be associated with the pore morphologies since the TESCD porogen inhibited phase separation in low-k matrix by chemical bonding with the matrix, while the increased PCL porogen resulted in the macroscopically phase-separated porogen domains due to the weak physical interactions.

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