1 Introduction

As the ultralarge scale integrated (ULSI) circuits are becoming smaller, it is required to reduce the significant resistance/capacitance (RC) delay, crosstalk noise and power consumption for the next generation semiconductors (<25 nm devices). Recently, considerable attention has been focused on the replacement of organosilicates which has dielectric constant of k ~ 2.7.

One of the most promising way to achieve the material with lower dielectric constant is to introduce nano-sized pores (k = 1) into the matrix. This approach is on the basis of the incorporation of a thermally degradable material, which is called porogen.

When the high porosity is introduced into organosilicates, their mechanical properties deteriorate substantially due to aggregation of pores above a certain amount of porosity. Thus, these mechanical properties is questionable about applying to real semiconductor fabrication such as chemical mechanical polishing (CMP). The poor mechanical properties directly related to the incompatibility between organosilicates and pore generating materials (porogens). Therefore, it is crucial to control their compatibility in order to secure high mechanical properties in addition to uniform distribution of nano-sized pores.

In this work, we synthesized the copolymer prepared by copolymerization of methyl trimethoxysilane (MTMS) and a small amount of an ethylene-bridged organosilicate [(bis(1,2)-trimethoxysilyl)ethane, BTMSE], which exhibited better mechanical properties.

We used differential thermogravimetric analysis (DTGA) and dielectric relaxation measurement to estimate qualitatively the degree of interaction between porogens and organosilicate matrices by measuring decomposition and glass transition temperatures of porogens. In addition, the structural changes of PCL hybrids with MSSQ and BTMSE 10% copolymer respectively were measured by FT-IR spectroscopy during curing process.

2 Experimental

Organosilicate matrix was prepared by copolymerization of methyl silsesquioxane (MTMS) with bis-triethoxysilyl ethane (BTMSE, 10 wt%). As porogen, star-shaped poly(e-caprolactone) (PCL) with 8-arms was prepared. Each materials was dissolved in n-butyl acetate at 30 wt% and mixed together to make nanohybrids with proper ratios (from 0 to 50 wt%). After homogeneous hybrid solution was filtered with 0.2 µm Acrodisc CR PTFE filter, it was dropped directly onto a glass substrate placed in vacuum oven. Then, nanohybrids were prepared by spinning the solutions on a Si wafer at 2,500 rpm for 30 sec and cured at 250 ºC for 30 min. The heating rate was 3 ºC/min by 430 ºC and then it was cured for 1 hour under the nitrogen atmosphere. For the dielectric relaxation measurement, the solution was spin-coated on a glass substrates with patterned bottom Al electrodes and cured at 250 ºC for 2 hours under nitrogen atmosphere. Then, a top electrode was evaporated on cured samples at 5 x 10^3 torr or less. The dimensions of Al electrodes were 5 mm in diameter and 1,000 Å in thickness.

The transmission FT-IR measurements were used to monitor the structural changes of organic/inorganic hybrids during thermal curing to 430 ºC. Thermogravimetric analyzer (TGA 2950, TA instruments) was used to measure decomposition temperature (Td) and its shift depending on the degree of interaction. The heating rate was 3 ºC/min from 30 to 500 ºC under nitrogen atmosphere. The
dielectric relaxation measurements were conducted with LCR meter (Hewlett-Packard 4194A). Tan δ was acquired during heating cycles and temperature varied from −200 to 200 °C at a rate of 5 °C/min. The frequency ranged from 10 to 500 kHz and the amplitude was 0.1 V.

Dielectric constants of porous BTMSE films were measured with metal-insulator-semiconductor (MIS) configuration using (Hewlett-Packard 4284A). The thickness of nanohybrids and porous films were obtained by α-step profiler (Model 25087) and a variable angle multi-wavelength ellipsometer (L116C, Gaertner Scientific Corp.). The morphology of porous organosilicate films was observed by FE-SEM (JSM-633OF, JEOL, Japan).

3 Results and discussion

The effect of BTMSE content on the composition of the MTMS-co-BTMSE copolymer was shown in table 1. As the BTMSE mol% increased, the concentration of Si-CH$_2$ in copolymer increased linearly, which indicated that most of the added BTMSE units were incorporated into copolymers. Also, contents of Si-OH increased with BTMSE mol%. That means it could control the amount of the hydroxyl group in the copolymers by adjusting the contents of BTMSE mol%. Thus, it affected the compatibility between porogens and matrix.

FT-IR spectra of 40% PCL hybrids with both MSSQ and BTMSE 10% copolymer is shown in figure 2. The hybrids were treated as a function of temperature from 25 °C to 430 °C. For both MSSQ and BTMSE 10% copolymer, the FT-IR spectrum was characterized by Si-O-Si stretching modes at 1000–1180 cm$^{-1}$, -CH$_3$ symmetric deformation modes at 1270 cm$^{-1}$ and the Si-OH stretching vibration at 930 cm$^{-1}$. For PCL porogen, the carbonyl (-C=O) stretching band at ≈1730 cm$^{-1}$ is the most distinct one. The relative intensities of Si-O-Si stretching modes in both matrices were related to curing temperature. At 25 °C, the ≈1130 cm$^{-1}$ band was strong than ≈1030 cm$^{-1}$ band. However, at higher temperature (T> 250 °C), ≈1030 cm$^{-1}$ band was stronger. It suggested that the cross-linking degree of both matrices increased with curing temperature.

The disappearance of the carbonyl adsorption peak means the poly(caprolactone) porogen was decomposed in hybrids. This peak was completely removed by heating to 430 °C. Especially at 25 °C, additional carbonyl adsorption peak existed in BTMSE 10% copolymer but not in MSSQ. It means that porogen interact more strongly with BTMSE 10% copolymer than MSSQ because -OH group of MSSQ had not enough strong interaction with porogen in high porogen loading (40 wt%).

In figure 3, thermogravimetric properties were measured on poly(caprolactone) porogen and its hybrids with both MSSQ and BTMSE 10% copolymer as a function of porogen loading, in 10 wt% porogen loading of both matrices, PCL was decomposed at higher temperature than that of pure porogen. It indicates that PCL molecules in nanodomains were confined. However, over 30 wt% porogen loading in MSSQ, two decomposition temperature appeared. The new decomposition shoulder increased with porogen loading, which suggested that from 30 wt% porogen loading, PCL molecules began to consist of not only nanoscopic domains but also large domains. On the other hand, decomposition of porogen in BTMSE 10% copolymer was occurred at still high temperature. It suggests the existence of one and smaller nanodomain in BTMSE 10% copolymer.

The shift of glass transition temperature (T$_g$) of the porogen could be another way to estimate the degree of interaction between the porogen and organosilicate matrix. Dielectric relaxation measurements were used for the degree of interaction between porogen and matrix by measuring glass transition temperature (T$_g$) of porogen, which were cured at 250 °C for 2 hours. Figure 4 shows tan δ of PCL porogen of frequency on heating cycle. The PCL represents 3 transitions called α (melting), β (T$_g$) and γ (sub T$_g$) transitions presented as bars. The dielectric loss of porogen increased with a frequency and the loss peaks around -60 °C and -100 °C represent glass (or β) relaxation and sub-glass (or γ) relaxation, respectively. In addition, the stepwise change of dielectric loss was occurred around 40 °C, which is corresponding to the melting temperature of porogen. Figure 5 shows tan δ of PCL hybrids with both MSSQ and BTMSE 10% copolymer, which were obtained at 100 Khz. The figure (a) indicated that T$_g$ of porogen was around 40 °C at porogen loading of 16 wt%, which was higher than that of porogen itself. But for porogen loading of 20 wt%
in MSSQ, the $T_g$ of porogen was close to corresponding temperature to the pure porogen. It is because there are large domains as well as nonoscopic domains in hybrids. In figure 5 (b), as expected $\beta$ transitions occurred at higher temperatures in BTMSE nanohybrids up to 35 wt% loadings and $\alpha$ transitions are completely suppressed due to strong confinement effect. But at 40 wt% loading, 2 $T_g$'s are occurred related to different sizes of nano-domains. These results are caused by higher compatibility of BTMSE 10 wt% copolymer with PCL than MSSQ. Therefore, this strong interaction results in confinement effect of porogen in nano-domains by restricting movement of porogen. The $k$ values of porous BTMSE 10% copolymer as a function of porogen loading are shown in Figure 6. As the porogen loading increased, the dielectric constant of BTMSE 10% copolymer linearly decreased down and to 1.8 at 50 wt% porogen loading. Thus, the stable tendency from 0 to 50 wt% loading is related to porosity more intimately than domain size.

4 Conclusions

In FT-IR spectroscopy, the additional carbonyl peak of PCL porogen indicates that BTMSE 10 wt% copolymer has much higher interaction and compatibilities with porogens than MSSQ at room temperature. We have demonstrated that differential TGA and dielectric relaxation spectroscopy were useful tools for qualitatively predicting the degree of interaction or sizes of phase-separated domain in nanohybrids. When the movement of PCL in nano-domains was more restricted by strong interaction, $T_d$ and $T_g$ remarkably shifted to higher temperatures than the pure porogen due to the smaller domain size and confinement effect. BTMSE was more effective in increasing their compatibility, which resulted in the smaller nano-domains. Dielectric constant was more dependent on the amount of pore or porosity rather than their sizes and decreased down to 1.8.

Table 1. $^1$H-NMR Analysis Result of MTMS-co-BTMSE Prepolymers Prepared with Different Contents of BTMSE.

<table>
<thead>
<tr>
<th>BTMSE (mol%)</th>
<th>Si-CH$_3$ (%)</th>
<th>Si-CH$_2$ (%)</th>
<th>Si-OH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>92.9</td>
<td>7.1</td>
<td>14.8</td>
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<td>10</td>
<td>81.8</td>
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</tr>
<tr>
<td>15</td>
<td>73.9</td>
<td>26.1</td>
<td>17.6</td>
</tr>
<tr>
<td>20</td>
<td>67.3</td>
<td>32.7</td>
<td>19.8</td>
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</table>

Fig.1. The chemical structures of 8-arms poly(caprolactone) porogen.
Fig. 2. FT-IR spectra of 40% PCL hybrids with different matrices as a function of curing temperature: 
(a) MSSQ and (b) BTMSE 10% copolymer.

Fig. 3. Differential TGA curves of the PCL and its hybrids with both MSSQ and BTMSE 10% copolymer as a function of porogen loading: 
(a) 10 wt%, (b) 30 wt% and (c) 40 wt%.
Fig. 4. Dielectric relaxation result for poly(caprolactone) at a different frequency.

Fig. 5. Dielectric relaxation spectra of PCL hybrids with different matrices as a function of porogen loading: (a) MSSQ and (b) BTMSE 10% copolymer.

Fig. 6. Dielectric constants of porous BTMSE 10% copolymer as a function of porogen loading.

References