# Nanoporous Ultra Low-k Dielectrics Prepared with Covalently Bonded Adamantylphenol Pore Generators

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### 1. Introduction

Nanoporous organic and inorganic thin films provide a variety of potential applications such as intermetallic dielectric materials, optical components, sensor elements, and substrates for biological applications.<sup>1</sup> The most straightforward way to realize thin films containing pores in nanometer size is to introduce sacrificial porogens (pore generating materials) into the thin films, where porogens are removed leaving behind air-filled nanopores. In semiconductor industry, this approach is particularly valuable since ultra low-k dielectrics with k values as low as 1.5 can only be achieved with porosity.<sup>2</sup> However, nanoporous materials have inherently poor mechanical stability owing to their reduced density. Therefore, the preparation of low-k thin films with improved mechanical properties is an important issue in the integration of low-k materials in semiconductor industry.<sup>3</sup> Recently, as an alternative to the incorporation of porogens into a host film through blending, the introduction of porogens by covalent bonding to the matrix materials has extensively been studied because it can suppress the massive phase separation that is often observed in the blending approach and this new approach can suggest possibility to yield attractive low-k materials with controlled porous structure and improved mechanical properties.<sup>4</sup>

In present study, we report the formation of nanoporous organosilicate thin films with robust mechanical and low dielectric properties using adamantylphenol porogens covalently attached to poly(methyl silsesquioxane) (PMSSQ). In order to be applied as intermetallic dielectrics, nanoporous films with desirable electrical and mechanical properties can be achieved due to the thermal decomposition of adamantylphenol groups as well as the partial formation of silica structure.

#### 2. Results and Discussion

Figure 1 shows a schematic on the organosilicate copolymer where PMSSQ copolymers were synthesized by the sol-gel copolymerization with methyltrimethoxysilane (MTMS) for a given amount of various comonomers, which were prepared by the direct hydrosilylation between trimethoxysilane and adamantylphenol served as a porogen. All the prepared copolymers are readily spin coatable. Figure 2(a) and (b) show the changes in dielectric constant (*k*) and refractive index ( $n_f$ ) of prepared copolymer thin films cured under N<sub>2</sub> purge. As a reference, k-value of a PMSSQ film is 2.75, which is in good agreement with the previous reported value.<sup>5</sup> For all the films tested, *k*-values and refractive indices initially decrease with curing



Fig.1 Schematic structure of prepared organosilicate copolymers.





temperature due to the formation of porous structure by the decomposition of porogens and the removal of silanol groups through polycondensation. The k-values of ADRand ADP-PMSSQs reduce to 2.17 and 2.57 after curing at 450 and 400 °C, respectively. Above 400 °C, it is interesting to note that both k-value and refractive index of the ADP-PMSSO increases after passing through the minimum value. The decomposition of porogens was further confirmed by FT-IR. Figure 3(a) shows the FT-IR spectra of an ADR-PMSSQ film cured under N<sub>2</sub> purge. The infrared spectra show that the peak intensity at 2910 cm<sup>-1</sup> due to the asymmetric stretching of CH in the adamantane groups notably decreases above 300 °C together with the peaks at 1514 cm<sup>-1</sup> and 1256 cm<sup>-1</sup> assigned to phenyl groups attached to the adamantane moieties and ether groups, respectively, and nearly disappears at 450 °C. This spectroscopic evidence confirms the thermal decomposition of the porogens. Infrared spectra of ADP-PMSSQ at different temperatures are also similar to that of ADR-PMSSQ. For the ADDP-PMSSQ, however, a small amount of residual organics is retained after curing at 450 °C. With temperature, absorbance band due to the ladder-like Si-O stretching at around 1040 cm<sup>-1</sup> also increases as well as the reduction of bands assigned to cage-like Si-O stretching at 1140 cm<sup>-1</sup>. This result suggests that structural rearrangement from the cage-like structure to the ladder-like network further proceeds by the polycondensation during heat treatment and the decomposition of porogens, implying the formation of dense films.<sup>6</sup>



Fig. 3(a) FT-IR spectra showing the structural changes of ADR-PMSSQ film with curing temperature. (b)  $^{29}$ Si CP-MAS NMR spectra for ADR- and ADDP-PMSSQ after curing at 450 °C. The ssb in the spectra denotes the spinning sideband.

On the other hand, the peak intensity of Si-O-Si in the ADDP and ADR-PMSSQ is stronger than that for the ADP-PMSSQ since more Si-O-Si bonds are formed from the bridging condensation compared with the grafting during the hydrolytic condensation of alkoxysilanes. It is thus expected that both thermal and mechanical stabilities of ADR-and ADDP-PMSSQ are higher than those of the ADP-PMSSQ due to the formation of dense structure in the bridge-PMSSQ. <sup>29</sup>Si CP-MAS NMR spectra, shown in Figure 3(b), of ADR- and ADDP-PMSSQ demonstrate the emergence of Q<sub>4</sub> resonance (tetra-coordinated Si-O structure) at around - 110 ppm after curing at 450 °C, implying the significant formation of SiO<sub>2</sub> bonds. Since the Q4 resonance is not observed for uncured copolymers as well as for cured PMSSQ homopolymers, this result indicates that the decomposition of porogens is accompanied by the formation of tetra-coordinated Si-O structure that enhances mechanical properties of the matrix. The origin of the Q<sub>4</sub> resonance is believed to be due to the decomposition of residual propenyl groups and the nucleophilic attack by silanol group after the decomposition of porogens, as reported previously.7 Mechanical properties of prepared copolymer thin films measured with a nanoindenter in dynamic contact mode (DCM) are summarized in Table 1. As all the measured values are reported at 50 nm of relative displacement, which is only around 1/10 of the deposited film thickness, the substrate effect on the data could be safely neglected. Moreover, the elastic modulus and surface hardness of a PMSSQ film measured as a reference film were also similar to the values reported previously.<sup>5</sup> After curing at 400 °C, the modulus of ADP-PMSSQ is lower than the dense, nonporous PMSSQ while the modulus of ADDPand ADR-PMSSQ is higher than that of the PMSSQ homopolymer. On the other hand, moduli of all the films are significantly increased after curing at 450 °C. Even with the decomposition of porogens in the ADR-PMSSQ, the modulus increases up to 6.16 GPa, which is believed to be due to the high crosslinking density and the partial formation of SiO<sub>2</sub> structure, maintaining the nanopore structure as evidenced by the low dielectric constant.

Table I Mechanical properties of PMSSQ thin films\*

Film	ADP <sup>a</sup>	ADDP <sup>b</sup>	ADR <sup>b</sup>
Elastic modulus (GPa)	$2.76\pm0.06$	$5.53\pm0.06$	$6.16\pm0.01$
Surface hardness (GPa)	$0.32\pm0.01$	$0.72\pm0.01$	$0.75\pm0.02$

\*measured using a nanoindenter. All films were cured at 400  $^{\rm o}C^a$  and 450  $^{\rm o}C^b$  under  $N_2.$ 

## 3. Conclusions

By introducing covalently bonded adamantylphenol porogens into a silsesquioxane-based matrix, nanoporous thin films with balanced low dielectric constant (k ~ 2.2) and superior mechanical properties (E  $\sim$  6.2) were realized by the formation of nanoporous organosilicate structure caused by the decomposition of porogens and the high crosslinking density based on the bridged precursor structure. The decomposition of porogens also led to the formation of silica structure by depropenylation and necleophilic attack of silanol groups. Since the number of bonds as well as the bond structure linking between the porogen and the matrix can be controlled, this strategy to design nanoporous thin films from organosilicate precursors containing covalently bonded porogens can be further optimized by changing the porogen structure, the number and type of covalent bonds, and the bond dissociation of the chemical structure linking the porogen and the matrix.

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