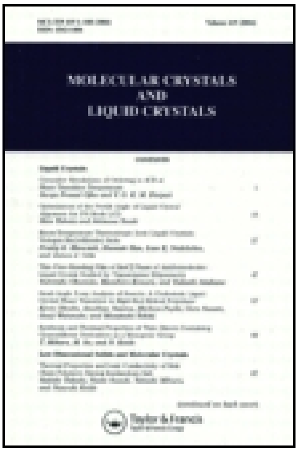

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Characteristics of Low-*k* Nanoporous Poly(methylsilsequioxane) Thin Films

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Nanoporous poly(methyl silsesquioxane) (PMSSQ) was obtained by sintering organic/inorganic nanohybrids. The porogen was cyclosiloxane with four poly(ethylene glycol) arms for better miscibility with PMSSQ. As the porogen content in the hybrid increased up to 30 vol%, the porosity of the calcined PMSSQ film increased up to 24%, and the *k* values decreased as low as 2.12. However, the interconnected pore structure was observed at the porogen content above 25 vol%. The miscibility was improved compared to poly(caprolactone)-based porogens and the pore size was indistinguishable even at SEM resolution.

Keywords Poly(methylsilsesquioxane); Low dielectric constant; Nanopore; Interconnection; Cell structure

INTRODUCTION

As the feature dimension of IC chips shrinks, new dielectric materials with dielectric constant (*k*) less than 2.0 are required by 2004 [1]. The compatibility of porogen with PMSSQ was very important in controlling the pore size and its distribution. Cyclosiloxane with four poly(ethylene glycol)-arms was synthesized and its hydrophilic feature will result in better miscibility with PMSSQ and then a smaller pores during crosslinking of PMSSQ. The dielectric properties were characterized by LCR meter and cross-section was examined by SEM. The interconnectivity of pores was determined by AC conductivity measurement.

EXPERIMENTAL

We spin-coated the solution mixture of methylsilsesquioxane (MSSQ) prepolymer and porogen. The porogen was cyclosiloxane with four poly(ethylene glycol) arms (Figure 1). The hybrids were cured at 250 °C for 30 minutes under inert atmosphere. Nanoporous PMSSQ films were obtained by sintering organic/inorganic hybrids at 420 °C for 1 hour.

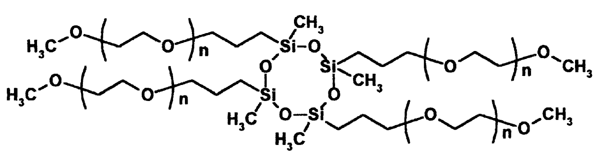

FIGURE 1. Poly(ethylene glycol)-arm tetramethylcyclosiloxane (n ~ 16.3)

The refractive indices were measured with an ellipsometer and the porosity of nanoporous films was estimated by the Lorentz-Lorentz equation.

RESULTS AND DISCUSSION

Table 1 shows that the measured dielectric constant (*k*) of the nanoporous PMSSQ films and it decreased down to 2.12 at the porogen content of 30 vol%. The measured k values were fairly well matched with theoretical values, which were calculated from the Maxwell-Garnett equation.

Figure 2 shows the FE-SEM images of the nanoporous PMSSQ films coated on Si wafers. No pores were observable in PMSSQ films even at the microscopic magnification of ×50,000. It suggests that the dimension of pores in the PMSSQ film may be less than ~ 10 nm based on previous results [2].

TABLE 1. Characteristics of Nanoporous PMSSQ Films Prepared with Different Porogen Contents

Porogen content in hybrid (vol%)	Refractive index	Porosity (%)	Theoretical *k*	Measured *k*
0	1.395 ± 0.03	0		2.75 ± 0.07
10	1.355 ± 0.04	8.2	2.50	2.52 ± 0.05
20	1.313 ± 0.03	17.2	2.28	2.34 ± 0.08
30	1.283 ± 0.03	24.0	2.08	2.12 ± 0.05

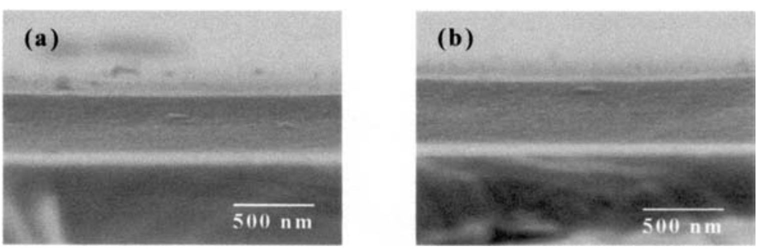

FIGURE 2. FE-SEM cross sectional images of nanoporous PMSSQ film with the porogen content of (a) 10 wt% and (b) 20 wt%.

The interconnectivity of pores was indirectly determined by measuring AC conductance of nanohybrids prepared at 250 °C. A sudden increase in ac conductance was observed at the porogen content between 20 vol% and 30 vol%, which may imply the change of the pore structures from closed cells to open cells. Consequently, the upper limit of porogen content for the closed-cell structure should be ~ 25 vol%, which limits the practical k of the nanoporous PMSSQ films to about 2.3.

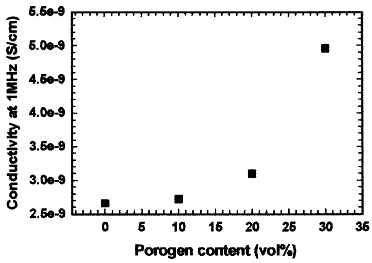

FIGURE 3. Ac conductivity of PMSSQ films with different porogen contents.

CONCLUSIONS

According to the SEM images of the nanoporous PMSSQs the new porogen definitely improved miscibility with MSSQ and resulted in very smaller pores, which is speculated to be less than ~ 10 nm. Ac conductivity measurement on nanohybrids may be a good way to determine the interconnectivity of pores in the nanoporous PMSSQs.

Acknowledgments
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