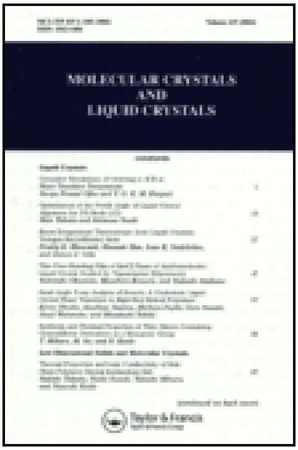

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Low Dielectric Nanoporous Poly(methylsilsesquioxane) (PMSSQ) Films via Inorganic/ Organic Hybrids

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Two types of methylsilsesquioxanes (MSSQ) were used as base matrix materials for nanoporous films. The hydrophilicity of MSSQ was controlled by copolymerization for the improved miscibility between MSSQs and star-shaped poly(caprolactone) (PCL) as a porogen. Linear relationship holds between porosity/refractive index and vol% of porogen upto 30%. Dielectric constant of porous MSSQ film could be reduced to 2.2 at the porosity of 30 vol%. Dielectric constant was very sensitive to the content of hydroxyl group of MSSQ and the the latter was reduced by treating surface silanols with hexamethyldisilazane.

Keywords Methylsilsesquioxane (MSSQ); nanoporosity; dielectric constant; thin film; copolymeriation, dehydroxylation

INTRODUCTION

As the feature dimension in integrated circuits continues to shrink, both signal delays and the crosstalk between metal interconnects are expected to be serious problems in the next generation chips. A key to the problems is to lower the dielectric constants of inter-layer dielectrics by incorporation of air bubbles in them [1]. When star-shaped poly(caprolactone) is used as a nanotemplate, the amount of hydroxyl (–OH) groups in MSSQ should be controlled to obtain nanoporous MSSQ. In this study we successfully controlled them by copolymerizing methyltrimethoxysilane (MTMS) with 1,2- bis trimethoxysillethane (BTMSE). We studied the effect of temperature and the amount of porogen on the dielectric constants. MSSQ thin films were also dehydroxylated to reduce the dielectric constant.

EXPERIMENTAL

Materials: MSSQ (GR650F, TECHNEGLAS) oligomer (M_n ~ 2,000 g/mol) was used as received and MSSQ copolymers (CMSSQ) were synthesized by the procedure described in detail elsewhere [2]. PCL (P30; 6 arm, DP = 6) as a pore-forming material (porogen) was also synthesized.

Preparation of MSSQ Thin Film and Dehydroxylation Treatment: Pure MSSQs (20 wt%) and hybrid MSSQs/PCL (P30 content: 10, 20, 30 vol%) solutions in methyl isobutyl ketone (MIBK) were loaded into a disposable syringe and passed through a 0.2 μm PTFE filter. For MIS capacitor, the filtered solutions were spun on Si-wafer at 2,500 rpm for 30 sec. After thermal curing of MSSQ, an array of Al dots which were approximately 2000 Å thickness and 5.0 mm diameter, was deposited by a thermal evaporator.

Cured CMSSQ films were dehydroxylated by spinning hexamethyl-disilazane (HMDS) at 2000 rpm for 30 sec and heating at 400 °C for 2 hours. The chemical reaction of HMDS with surface silanols is:

$$2Si\text{-}OH + (CH3)_3\text{-}Si\text{-}NH\text{-}Si\text{-}(CH_3)_3 \rightarrow 2Si\text{-}O\text{-}Si\text{-}(CH_3)_3 + NH_3.$$

Measurements: Dielectric constant was calculated from the saturated maximum capacitance value in C-V curve. Refractive indices (n) of the hybrid thin films were measured by the variable angle multi-wavelength ellipsometer using a different light beam (633nm, 835nm).

RESULTS AND DISCUSSION

2 different types of MSSQ materials were used as a base matrix material for the incorporation of nanoporosity. As shown in Fig. 1, dielectric constants decreased a little with the increasing curing temperature due to the reduction in the –OH functional group. Higher dielectric constants of CMSSQ indicate a large amount of –OH functional group. NMR indicated that 5% and 10% BTMSE CMSSQs contained 13.6% and 15.5% of -OH group, respectively.

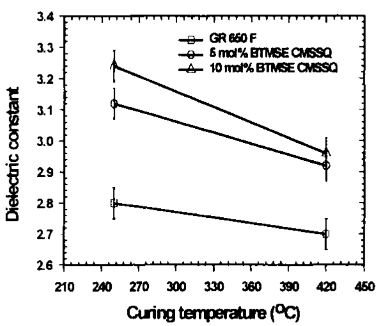

FIGURE 1 Dielectric constants of various MSSQ thin films as a function of curing temperature.

TABLE 1 Dielectric Constants of CMSSQ Films by MIS Structure

Sample	Curing T	Dielectric constant	
		Before HMDS	After HMDS
5 mol% BTMSE CMSSQ	420 °C	2.92 ± 0.08	2.67 ± 0.03
10 mol% BTMSE CMSSQ	420 °C	2.96 ● 0.06	2.61 ± 0.05

But CMSSQ's higher dielectric constants were reduced by dehydroxylation with HMDS. With increasing amount of –OH group the miscibility of MSSQ and PCL was improved.

Fig. 2 shows the refractive index and porosity of CMSSQ/PCL hybrid thin films after the decomposition of PCL at 430 °C. Porosity was calculated from the measured refractive index by the Lorentz-Lorentz equation. Refractive index and porosity showed a liner relationship with vol% of porogen. According to the value of dielectric constant calculated by Maxwell-Garnet equation, dielectric constant of the CMSSQ/PCL hybrid thin film could be reduced down to 2.2 when 30 vol% PCL was added. The detailed measurements on dielectric constants of nanoporous MSSQ thin films are in progress.

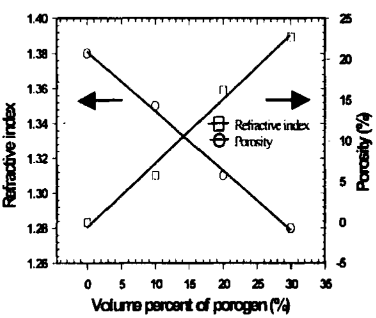

FIGURE 2 Refractive index and porosity of CMSSQ (10 mol% BTMSE copolymer) / PCL hybrid thin film cured at 420°C

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