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新式兩相多孔性低介電材料及其製程之探討 (I)

“Study of novel 2-phase porous low-k materials and process interactions (I)”

計畫編號：NSC94-2215-E-009-076-

執行期間：94 年 02 月 01 日 至 95 年 07 月 31 日

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Abstract

Porosity is inevitably needed for dielectric materials with k below 2.5 in either 45 nm node or beyond. However, several key issues related to as-deposited porous dielectrics (k < 2.5) have been identified from their process integration. For example, porosity brings challenges on how to form a continuous metal diffusion barrier onto the exposed porous dielectric cross-section by etching step without reliability issue. In addition, porous low-k materials are mechanically weak compared to SiO_2, indicating that they are prone to be damaged during CMP process.

In order to circumvent the reliability issues encountered in integration of as-deposited porous dielectric, in this 3-years research project, a Solid-First^{TM} scheme is employed for the preparation of low-k dielectric. We intend to examine the impact of medium-high temperature “porogens” in methylsilsesquioxane (MSQ) matrix on the materials properties of the MSQ/porogen, compared to those in dense MSQ and porous low-k directly formed after dielectric deposition. At first year, the mechanical properties of these three low-k system used in different integration schemes were investigated using nanoindenter and FTIR analysis for different porogen loading (porosity). The modulus of 2-phase films is higher than its porous form, and even better than dense one, for porogen loading below a critical quantity (~30%), which can be attributed to its enhanced degree of crosslinking in MSQ matrix. This implies that 2-phase low-k materials system can pass the CMP test while avoiding the barrier reliability issue.

In the next year (2006-2007), we propose to characterize key materials properties such as dielectric constant of the novel 2-phase materials, and its process interactions with major backend processing steps as a function of porogens. This involves the studies on adsorption/desorption kinetics of moisture in three low-k systems, and different energy source to shorten required porogen decomposition time and examine its kinetics. In addition, their interactions with plasma etching chemistries in terms of etch characteristics, compatibility and process integration.

I. Introduction

The increasing of propagation (RC) delay becomes a limiting factor for ultra-large-scale integration (ULSI) of integrated circuits whose dimensions reduce beyond 130 nm [1]. As device technologies in 45 nm node and below, low-k materials with k < 2.5 are being fervently developed in order to reduce the increasing RC delay in the backend interconnects. So far, it is well recognized that incorporation of porosity is critical to the search of viable low-k materials with k < 2.5 for 45 nm technology node and beyond. The conventional porous low-k dielectric is generally formed after deposition of matrix with porogens, then burning out the porogen at high temperature. Several showstopper issues, However, related to as-deposited porous dielectrics (k < 2.5) have been identified from their process integration; namely: (1) device reliability due to large pore size (> 15 Å), (2) RC variation due to roughness in dielectric from etching, and (3) its wet chemical compatibility [2]. To circumvent these roadblocks, this calls for new approach in materials design and its integration. A novel Solid-First™ approach in materials and integration has been proposed by Shipley Company to defer the formation of lower k, porous dielectric after completing a metal layer, and then thermally remove the sacrificial porogen in the two-phase dielectric film [3]. But, there is little understanding of its materials properties either as-deposited or after the removal of porogen, any film shrinkage, the effect of thermal decomposition temperatures of porogens on upper process temperature, and more importantly its interactions with processing modules such as chemical-mechanical polish (CMP) and patterning steps.

A commercial, spin-on organosilicate such as MSQ was used as the matrix and high-temperature porogens were employed as the sacrificial component. The amphiphilic block copolymers (ABCs), such as Poly(styrene-block-4vinypyridine) and Poly(styrene-block-ethylene-random-butylene-block-styrene) (PS-b-P4VP and PS-b-PE-b-PS), could be used as ideal porogens since they offer the advantages of microphase morphologies for controlling the pore shape and size. It is postulated that intermolecular hydrogen bonding [4-6] significantly improved the miscibility of the MSQ/ABCs hybrid and thus aggregation would not occur during curing. The amphiphilic characteristic of the MSQ is changed to hydrophobic because of the condensation of the Si–OH groups to the Si–O–Si linkages during the thermal curing. Hence, microphase separation is expected through the hydrophobic amphiphilic interaction between MSQ and ABCs [7].

According as previous report, we compared the materials properties and processing characteristics among the following three types of materials (a) "solid-only" low-k materials from matrix only, without porosity as control, (b) 2-phase low-k materials (matrix + porogen) which interact with all backend processing steps, and (c) the porous low-k materials after the removal of porogen phase in order to elucidate the impact of such porogens and Solid-First™ scheme shown in Figure 1. The compatibility of copolymer porogens/matrix/solvents and the effect of 2 porogens with different decomposition temperatures on the formation of low-k materials, and thermal stability were investigated. In addition, the mechanical properties of MSQ/porogen at 300 and 400 °C were compared and assessed for their integration feasibility.

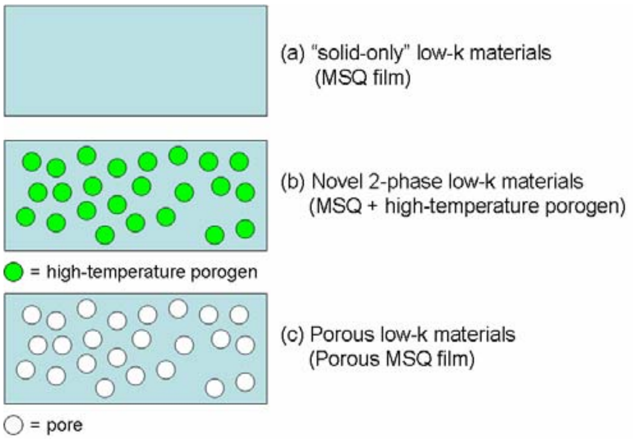

Figure 1. Three model low-k materials systems for comparative study on the impact of high-temperature porogens.

II. Experimental section

1. Materials and Film preparation

The low dielectric constant material, MSQ used as the matrix was obtained from Gelest Inc. as clear to white flakes. PS-b-P4VP (10% PS) copolymers and PS-b-PE-b-PS (21% PS) copolymers as the porogens were obtained from Sigma-Aldrich Co. Their chemical structures are illustrated by Figures 2 (a) through (c), respectively.

MSQ was dissolved in tetrahydrofuran (THF) to form a 5 wt% "solid-only" solution. For 2-phase films, MSQ was first dissolved in n-butanol, and then porogen was mixed at various loading to form a 5 wt% solution. The solution was first filtered through 0.45 µm PTFE filter (Millipore Inc.), then spun onto (100) silicon wafer at 2000 rpm for 60 seconds at room temperature. The prepared film was then baked at 30, 50, 80, and 100 °C for 30 min sequentially, then at 150 °C overnight. Then the sample was cured in a quartz tube furnace under N2 at a heating rate of 2 °C/min up to different final temperatures from 200 to 450 °C with 50 °C interval for 30 min.

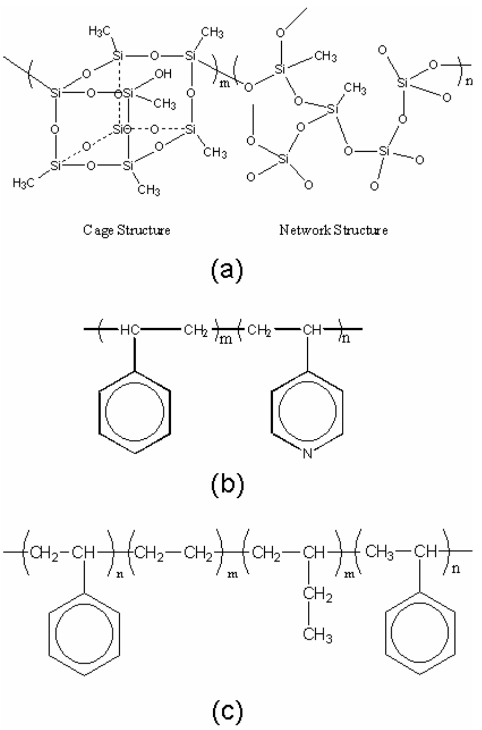

Figure 1. The molecular structures of (a) MSQ as the low-k matrix; (b) PS-b-P4VP, and (c) PS-b-PE-b-PS as the high-temperature porogens.

2. Thin film characterization

The study of thermal decomposition temperature of porogens, whose mass loss was less than 2%, was carried out under a nitrogen atmosphere using a TGA Q500 (TA Instruments). The temperature scan speed was 10 °C/min and the temperature ranges from 30 to 600 °C. The porosities in porous low-k films were measured by Brunauer-Emmett-Teller (BET) analyzer. The measurements was performed using NOVA 1000e (Quantachrome Instruments) with relative pressure (P/P_0) from 1 to 0.

The chemical makeup and structural transformation in the MSQ matrix and MSQ/porogen 2-phase system as a function of temperature were studied using a Fourier-transform infrared spectroscopy (FT-IR). The measurements were performed using a MAGNA-IR Technology Protage 460 (Nicolet Inc.) in transmission mode with 32 scans at 4cm^{-1} spectral resolution. Measurements of refractive index and film thickness were made using an n&k Analyzer 1280 (n&k Technology, Inc.) at the wavelengths ranging from 190 to 900 nm.

Nanoindentation tests were carried out using a Nanoindenter (MTS, Nano Indenter XP system) with a Berkovich tip and continuous method to obtain reduced modulus (E_r), and then the Oliver-Pharr method was applied to determine the elastic modulus (E) of various low-k films [8].

III. Results and Discussion

Chemical and structural change of MSQ films at various curing temperatures at 50, 150, 250, 300, 350 to 400 °C were first characterized by FTIR as shown in Figure 3. The Si-CH_3 absorption bands are found at 1273 and 781 cm^{-1}, respectively and the corresponding CH_3 absorption band appears around 2972 cm^{-1}. The two peaks at 1130 and 1035 cm^{-1} can be assigned to Si-O in the cage and network structures. Two distinct changes can be observed in Figure 3. The board O-H stretching band around 3400 cm^{-1} and the Si-O stretching of the Si-OH bond at 903 cm^{-1} decrease in intensity gradually and disappear when temperature is greater than 300 °C. This suggests that the condensation reaction of the Si-OH group takes place. Another distinct change is related to the peak intensities between 1000 and 1200 cm^{-1}. Finger 3 is FTIR absorption spectra of pure MSQ cured at various temperatures, which magnified from Figure 2. The intensity of the Si-O-Si absorption band of the cage structure at 1130 cm^{-1} decreases with increasing curing temperature, while the Si-O-Si absorption band of the network structure at 1030 cm^{-1} shows the opposite trend. This indicates the transformation of the cage structure into the network structure through thermal curing. In addition, the degree on the cross-linking of the MSQ was determined by FTIR analysis to be 50% at 100 °C and 80% at 400 °C, respectively. The major difference among the MSQ cured at 300, 350 or 400 °C is their network/cage structure ratio, which may affect the mechanical strength.

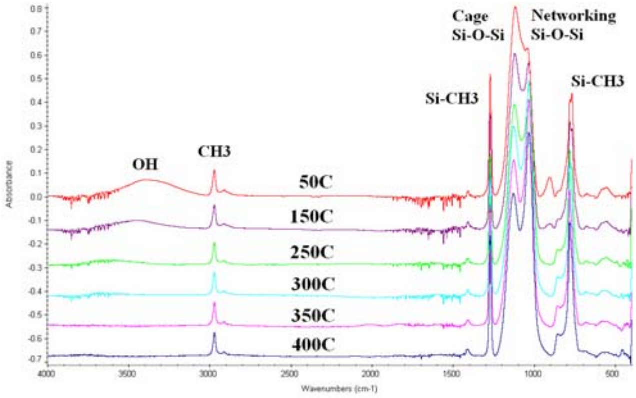

Figure 2. FTIR spectra of the MSQ films cured at various temperatures.

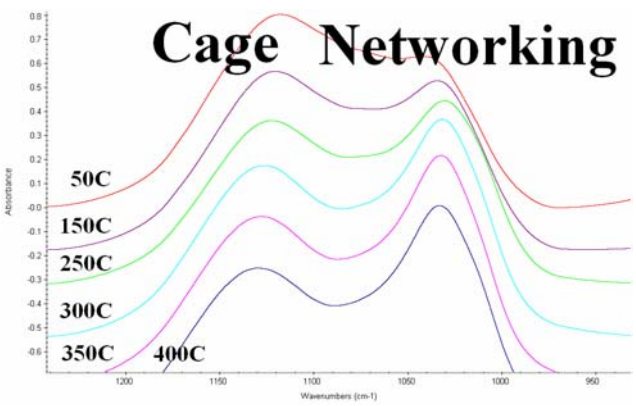

Figure 3. The Si-O-Si of MSQ transformation from cage to networking structure cured to various temperatures.

In next step, we investigate the decomposition temperatures of porogens and the thermal stability in MSQ/porogens and MSQ films to determine the upper temperature limit of Solid-First^{TM} scheme. Thermal gravimetric analyses (TGA) showed that the di-block copolymer porogen, PS-b-P4VP (curve a), and tri-block copolymer porogen, (curve b) had the decomposition temperature (T_d) about 305 °C and 380 °C at heating rate of 10 °C/min and were completely removed above 380 and 410 °C under N_2 atmosphere, respectively as shown in Figures 3. Since isothermal heating by hot-plate or furnace is commonly used in semiconductor fabrication processing, these high-temperature porogen were further confirmed to be fully removed at 400 and 500 °C after 2 hours, which are still reasonable for practical applications.

For a porogen/MSQ system using 10% PS-b-P4VP di-block copolymer, the T_d is increasing to 325 °C as observed in Figure 3 curve c, which is higher than the decomposition temperature of neat porogen. This can be attributed to the intermolecular hydrogen bonding between N atom of pyridine and OH group of MSQ, which in turn delay the decomposition temperature of the 2-phase system.

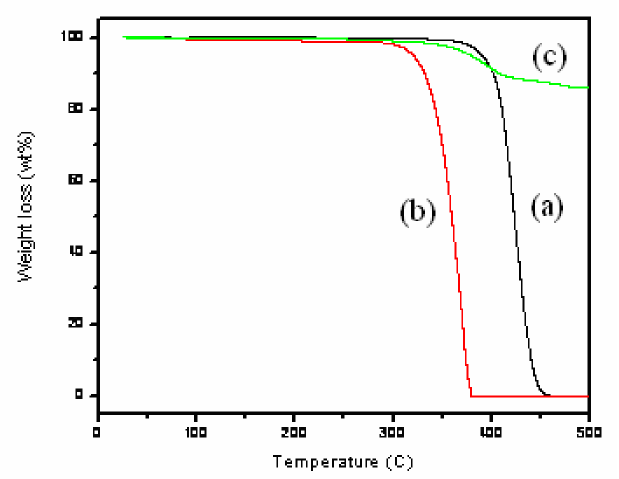

Figure 4. The TGA curves of (a) PS-b-PE-b-PS, (b) PS-b-P4VP and (c) MSQ with 10% PS-b-P4VP.

FT-IR is also employed to track any change of porogen in the MSQ/porogen films at various temperature to determine the upper temperature limit of Solid-First^{TM} scheme. For PS-b-P4VP, the characteristic peaks are 1400 to 1600 cm^{-1} attributed to aromatic C-N, C-C, and 2900 to 3025 cm^{-1} attributed to aromatic and alkyl chain C-H. Spectral analysis of MSQ/ PS-b-P4VP 2-phase films at temperature ranging from 100 to 400 °C in Figure 5 showed the characteristic peaks of porogen still existed at 320 °C and below, but the intensity of the C-N absorption peak has become weaker after 320 °C, 30 minutes curing. Finally, the characteristic peaks of PS-b-P4VP porogen completely disappeared after pyrolysis at 350 °C.

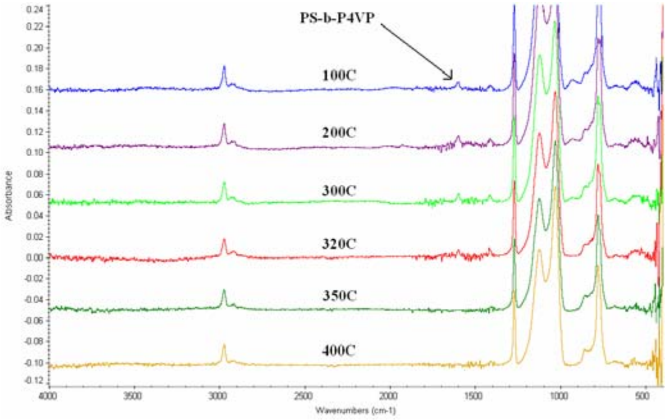

Figure 5. FTIR spectra of the MSQ films with 10% PS-b-P4VP as a porogen cured to various temperatures.

For the rest of this report, we focus on the thin film properties at 300 °C for Solid-First^{TM}, 2-phase MSQ/porogen films and at 400 °C for porous low-k after removal of porogen. The insert in Figure 6 shows the relationship between porogen loading and porosity as measured by BET. The porosity of low-k films increases from 6.5 to 36.4% as the porogen loading increases from 10 to 40%. The refractive indices of porous films versus porosity are shown in Figure 6. The refractive index of porous film decreases linearly from 1.38 to 1.20 as the porosity increases from 0 to 37%. Table 1 summarizes the refractive index (n), optical dielectric constant by Maxwell relation ($\varepsilon_{film}=n^2$) and ideal mixing rule [$\varepsilon_{film}=(1-\varphi)\varepsilon_{MSQ}+\varphi\,\varepsilon_{porogen}$, φ =volume fraction of porogen] for porous films with various porosity. The deviation of optical dielectric constant from the estimated value by ideal mixing rule increases with increasing porosity. This implies that the porosity and its internal surface area may contribute to the increased moisture uptake, which in turn raises refractive index and optical dielectric constant.

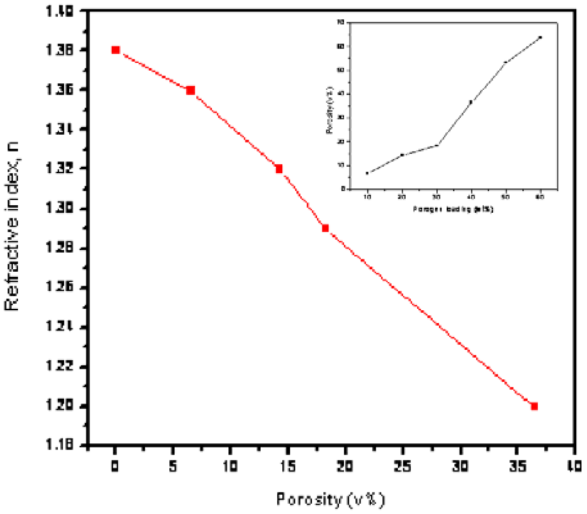

Figure 6. The refractive indices of porous MSQ as a function of porosity. Insert shows the correlation between PS-b-P4VP loading and porosity.

Table 1. The optical properties of various porous MSQ films.

Porosity (%)	0	6.5	14.3	18.2	36.4
Refractive index (n)	1.38	1.36	1.32	1.29	1.20
Optical dielectric constant ($\varepsilon_{film}=n^2$)	1.90	1.85	1.74	1.66	1.44
($\varepsilon_{film} = (1+\varphi)\varepsilon_{MSQ} + \varphi\,\varepsilon_{porogen}$)	1.90	1.84	1.69	1.62	1.27

Mechanical strength of low-k dielectric is one of significant concern in the backend processing such as chemical-mechanical polish (CMP) and die/packaging interaction. To evaluate the applicability of using MSQ/porogen through backend processes, elastic modulus was measured using nanoindentation technique. The elastic modulus of three low-k materials systems, MSQ at 400 °C and MSQ/PS-b-P4VP at 300 and 400 °C, are shown in Figure 7. The moduli of the porous films cured at 400 °C drop with increasing the porosity. Furthermore, for 2-phase films cured at 300 °C, the modulus for film with 10% porogen, 5.4 GPa is much higher than that of pure MSQ, 3.5 GPa, and then the modulus decreases with increasing the porogen (PS-b-P4VP) loading from 10 to 60%. In general, 2-phase films cured at 300 °C are stronger than those of porous MSQ with 10 to 50% porogen loading. The incorporation of porosity or porogen into dense low-k materials lowers its density, which reduces mechanical properties such as elastic modulus.

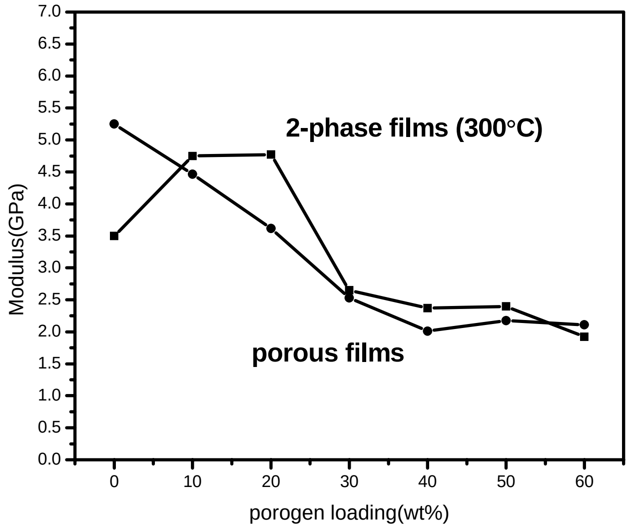

Figure 7. The correlation between PS-b-P4VP lading and modulus.

FT-IR was also employed to analyze the microstructure of MSQ cured at 300, 400 and 450 °C. The FT-IR spectra between 1350 and 950 cm^{-1} for "solid-only" MSQ films at different curing temperatures are shown in Figure 7. The Si-O-Si stretching peaks at 1130 and 1030 cm^{-1} are assigned to the cage and network structures, respectively. The network Si-O-Si is looser as compared to cage structure. The network/cage ratio is found to increase from 1.25 to 1.53 with increasing curing temperatures from 300 °C to 450 °C. The network/cage ratio of the Si-O-Si peaks is a good indicator of the degree of crosslinking, thus the mechanical strength. [9].

Similar FT-IR analysis was also carried out for 300 °C cured 2-phase films with various porogen loading as shown in Figure 9. Specifically, the network/cage structural ratios are plotted in Figure 10. The ratio increases from 1.25 for pure MSQ at 300 °C to 1.45 for 10% loading, which correlates well with the significant increase of mechanical strength shown in Figure 10, presumably due to the increase in the degree of crosslinking. For loading above 10%, network/cage structural ratio decrease from 1.45 to 1.12 with increasing the porogen loading between 10% and 60%, which confirms the corresponding trend of modulus shown in Figure 10.

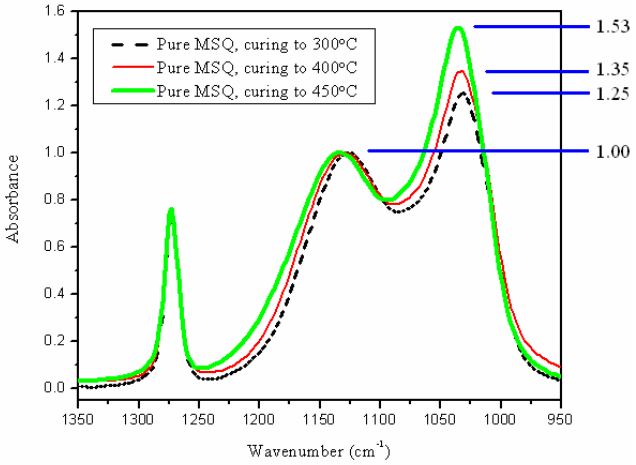

Figure 8. FTIR spectra of "solid-only" MSQ films cured at various temperatures.

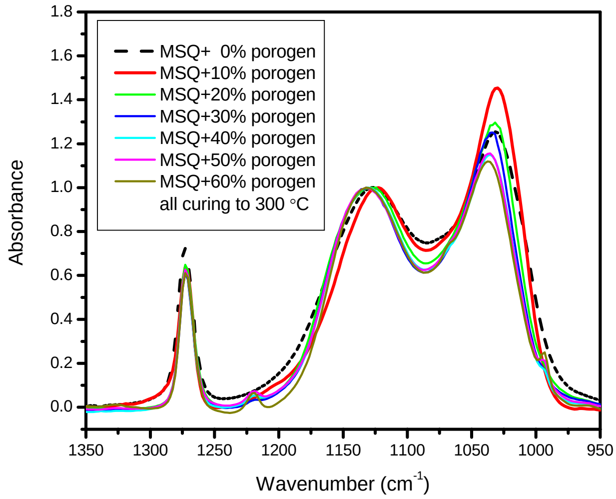

Figure 9. FTIR spectra of MSQ films with various porogen loading cured at 300 °C.

For a porogen loading below a critical quantity (~45% for PS-b-P4VP), porogen acts as a plasticizer, which can provide a better mobility for MSQ molecular chains to come close and crosslink to form more of cage structure schematically illustrated in Figure 11(a). As porogen loading increases above a critical value, the presence of porogen becomes a steric barrier for MSQ molecular chains as schematically illustrated in Figure 11(b), thus reduce the collision probability of MSQ molecular chains for further crosslinking. Therefore, the reduced degree of crosslinking in MSQ with porogen >45% can be account for its lower mechanical strength even compared to those of porous MSQ cured at 400 °C.

Finally we examine how these novel 2-phase low-k films will fare during chemical-mechanical polish step based on a SEMATECH study that a low-k material can pass the CMP test if its modulus is lager than 4 GPa [10]. For porous MSQ films cured directly at 400 °C, the modulus of porous film becomes lower than 4 GPa when porogen loading is higher than 20% (porosity > 15%). In contrast, 2-phase films prepared by novel Solid-First^{TM} scheme, i.e. cured at 300 °C, possess modulus > 4GPa for even larger porogen loading, ~40% (porosity ~ 35%). That means we can use the same matrix and porogen to design and produce the ILDs with high porosity while the modulus is sufficient to survive backend process such as CMP step and avoid the barrier reliability issue.

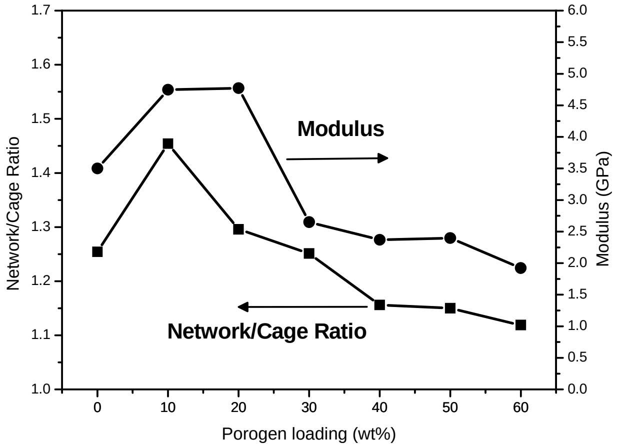

Figure 10. The network/cage ratio and modulus versus various porogen (PS-b-P4VP) loading.

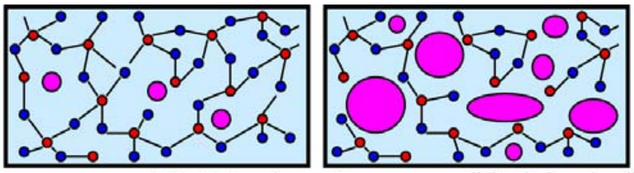
(a) porogen as "Plasticizers" (b) porogen as "Steric barriers"

Figure 11. The porogen affects MSQ cross-linking scheme.

IV. Conclusions

Two high-temperature porogens, PS-b-P4VP copolymers and PS-b-PE-b-PS copolymers, and its 2-phase MSQ/porogen systems were studied for its mechanical and dielectric properties and feasibility in different integration schemes including solid-First^{TM} and state-of-art damascene. The increase of decomposition temperature of the 2-phase porogen/MSQ system was attributed to the intermolecular hydrogen bonding between nitrogen atom of pyridine in PS-b-P4VP and OH group in MSQ. Based on the thermal stability and decomposition data of MSQ/PS-b-P4VP low-k system, the 2-phase films were recommended to be cured at 300 °C for subsequent damascene processing, then the porogen to be removed at 400 °C for 2 hours after CMP step to form metal/porous low-k structure.

The mechanical properties of these materials used in different integration schemes were investigated using nanoindenter and FTIR analysis for different porogen, PS-b-P4VP, loading (porosity). The modulus of 2-phase films is higher than its porous form, and even better than dense one, for porogen loading below a critical level, which can be attributed to its enhanced degree of crosslinking in MSQ matrix due to the plasticization by high-temperature porogen. This implies that 2-phase low-k materials system can pass the CMP test while avoiding the barrier reliability issue. In addition, more aggressive k reduction without failing CMP test can be achieved using a 2-phase low-k materials system.

V. Future Works (2006.08-2007.07)

1. Complete the exploration of extreme

high-temperature porogen with varying molecular weights or surfactants in MSQ/porogen system for Solid-First^{TM} scheme.
2. Complete the characterization on film morphology such as AFM and SEM, and measurement of dielectric constant at 1 MHz using CV-dot technique.
3. Complete studies on adsorption/desorption kinetics of moisture in three low-k materials systems using QCM system.
4. Complete assessment etching characteristics of 2-phase ILD materials.

VI. References

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