

# Control of Pore Size for Superior Ultralow Dielectrics

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## ABSTRACT

The shrinkage of the device for higher performance of microelectronics demands new ultralow dielectrics. Incorporation of pores is most promising way to reduce dielectric constant. However, conventional pore generating materials (porogen) have resulted in large pore sizes and poor pore morphologies such as open pore structure because of their low compatibilities with matrix. Therefore, we synthesized chemically reactive porogens, which prevent the severe aggregation of pores. In order to investigate the effect of porogen size on the pore morphology and mechanical properties three reactive porogens were synthesized from  $\beta$ -cyclodextrin ( $\beta$ -CD), glucose (GC), xylitol (XT) by allylation and hydrosilylation. These reactive porogens went through condensation reaction between the trimethoxysilyl groups in reactive porogens and silanol (Si-OH) groups in matrix.

GI SAXS showed that the radii of pores were less than 2 nm for all the porogens and was 1.23 nm at porogen loading of 50 vol% for the TMSXT. In the case of TMSGC pore sizes were less than 1 nm upto 30 vol% and then it seemed to aggregate a little to 1.69 nm at 40 vol%. Independent on the size of porogens when the porogen loading was low. Consequently, we could prepare the nanoporous ultralow dielectrics ( $k < 2.3$ ) with desirable pore morphologies and remarkably higher mechanical strength ( $E > 8.0$  GPa,  $H > 1.1$  GPa). The smaller pores and well-organized pore morphology was responsible for the higher mechanical strengths compared to non-reactive porogen. In addition, the chemical structure of nanoporous ultralow  $k$  materials had been changed from T structure to Q structure during decomposition of reactive porogen, which was another reason for the improved mechanical properties of ultra nanoporous dielectrics. The change of chemical structures was investigated by solid-state  $^{29}\text{Si}$ -NMR.

**Keywords:** nanoporous ultralow dielectrics, reactive porogen, pore morphologies, mechanical properties.

## INTRODUCTION

The performance of integrated circuits improves by reducing the feature sizes. However, it results in RC delay

( $R$  = resistance,  $C$  = line capacitance) and cross talk noise between metal lines, which eliminate the benefits of high density devices. Thus, ultralow dielectric materials are key materials for the next generation semiconductor industries. Nevertheless, delayed development of ultralow  $k$  materials has caused outward revision of ITRS roadmap for the interlayer dielectrics every year. Therefore, one of the most promising approach is to incorporate pores ( $k = 1.0$ ) in the matrices in order to solve these problems. However, conventional porous low  $k$  materials have not satisfied the requirements of ultralow dielectrics because of open pore structure by pore aggregation at high porogen loading. This open pore structure deteriorates mechanical properties and dielectrical reliability. Thus, in order to solve this problem and to meet the industry requirements, it is critical to control pore morphologies such as pore size and pore structures. We studied the effect of reactivity and size of porogens on the properties of nanoporous ultralow dielectrics such as pore sizes, mechanical properties and dielectrical properties. Also we studied the chemical changes of Si structures during thermal processing to investigate its effect on the mechanical properties.

## EXPERIMENTAL SECTION

Organosilicate matrix was the copolymer of methyl trimethoxysilane (MTMS) with 25 mol% of bis-1,2-triethoxysilyl ethane (BTESE).

The reactive porogens based on  $\beta$ -CD, GC, XT were synthesized via allylation and hydrosilylation. The allylation of porogens was carried out by adding enough amount of allylbromide related to the porogens to the reaction mixture. The matrix and porogens were mixed together to make proper ratios of each porogen to the matrix from 0 to 50 vol%. Thickness and refractive indices of the nanoporous films were measured by a Filmetrics (F-20, Filmetrics, Inc.). The dielectric constants of the films were measured by using metal-insulator-semiconductor (MIS) configuration with HP 4294 LCR meter. Elastic modulus ( $E$ ) and surface hardness ( $H$ ) were measured by nanoindentation (MTS XP, MTS system Corp.) using the continuous stiffness measurement (CSM) technique. Pore sizes/distribution and morphologies of nanoporous ultralow  $k$  films were investigated by grazing-incident small angle x-ray scattering (GI-SAXS) measurements. The chemical

structure change of nanoporous ultralow k was determined by solid-state  $^{29}\text{Si}$ -NMR (unity INOVA, Varianan).

## DISCUSSION

The progress of hydrosilylation was confirmed by  $^1\text{H}$  NMR spectroscopy as shown in Figure 1. After the hydrosilylation, trimethoxysilyl peaks were observed at around 3.6 ppm. The  $\text{CH}_2\text{Si}$  and the  $\text{CH}_2\text{CH}_2\text{Si}$  resonances appeared at 0.6 ppm and 1.7 ppm as a triplet and a multiplet, respectively.

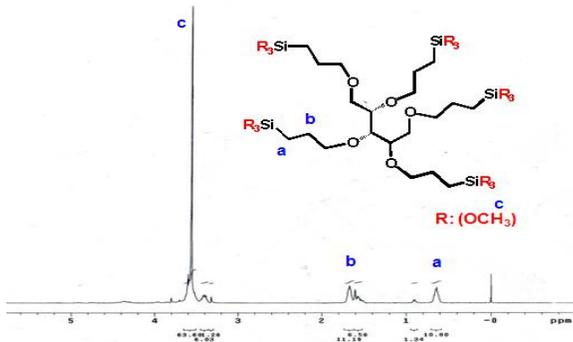


Figure 1:  $^1\text{H}$ -NMR spectra of reactive porogen (TMSXT)

Table 1 showed the pore sizes of nanoporous films prepared by TMSGC, TMSGD and TMSXT porogens by GI-SAXS techniques. The general trend in pore size is that the pore size and its distribution increased with increasing porogen loading. Despite of high porogen loadings upto 50 vol%, pore radius was less than 2 nm with narrower distributions were obtained in the case of reactive porogens. This result indicate that high compatibility/reactivity between the matrix and reactive porogen prohibited micro phase-separation and pore aggregation compared with non-reactive system. In the case of TMSGC, pore size was smallest by 30 vol% loading, but pore size increased at 40 vol% loading because of small degree of aggregation. In the case of TMSXT, radius size of the pore increased from 0.62 nm to 1.23 nm, which was the smallest. This result may suggest that the pore morphologies should be controlled by small and reactive porogens.

Porogen	Loading (vol%)	Avg. Pore radius (nm)
TMSGD	10	0.85
	30	$1.04 \pm 0.100$
	50	$1.29 \pm 0.127$

TMSGC	10	0.66
	30	0.60
	40	1.69
TMSXT	10	0.62
	30	$1.03 \pm 0.080$
	50	$1.23 \pm 0.231$

Table 1. Pore size and its distribution of reactive porogens.

Another advantage of reactive porogens is that they could induce the chemical structure change of the silicate matrix during the porogen decomposition. Figure 2 shows how the chemical structure of reactive porogen (TESGC) was changed by solid state  $^{29}\text{Si}$ -NMR. The Si-resonances of O-Si-O bond can be assigned as M, D, T and Q. M means silicon with one Si-O bond, D with two Si-O bonds, T with three Si-O bonds, and Q with four Si-O bonds. Fully densified silicate structure is denoted as  $\text{Q}^4$ .

Each sample was prepared by heating at the designated temperature for 2 hours under  $\text{N}_2$  atmosphere. At  $250^\circ\text{C}$ ,  $\text{T}^1$  and  $\text{T}^2$  of T species were observed around  $-43$  and  $-52$  ppm, which were caused by the condensation reaction of reactive porogen. When the temperature increased to  $300^\circ\text{C}$ , the intensity of Q species appeared between  $-90$  and  $-112$  ppm remarkably. The intensity of Q species increased further at  $430^\circ\text{C}$  and  $\text{Q}^4$  peak was observed with  $\text{T}^3$  peak. Therefore, it is obvious that the reactive porogens lead to the change of the chemical structure from T species to Q species during thermal decomposition.

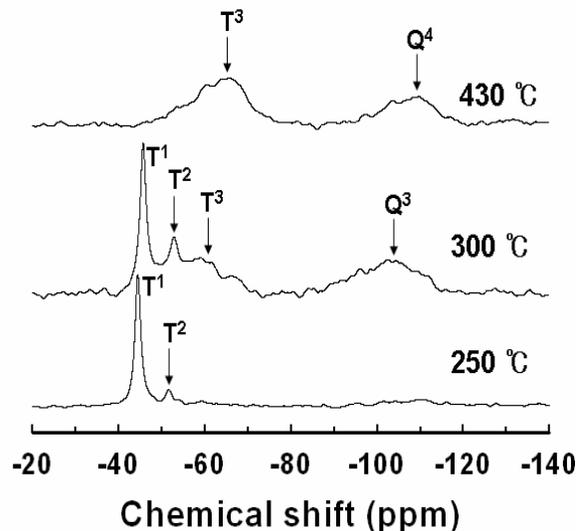


Figure 2:  $^{29}\text{Si}$ -NMR spectra of reactive porogen (TESGC) as a function of thermal treatment temperature.

The structural change in Si atoms also influenced the refractive index and  $k$  value of nanoporous film with improved mechanical properties. From the refractive index ( $n$ ), the porosity was estimated by Lorenzt-Lorentz (1) :

$$\frac{n_0^2 - 1}{n_0^2 + 1} (1 - P) = \frac{n^2 - 1}{n^2 + 1} \quad (1)$$

where  $n_0$  and  $n$  represented refractive indices of base matrix and nanoporous film, and  $P$  denoted volume fraction porosity. Figure 3 shows measured  $k$  values of the nanoporous film as a function of porogen loading. The dielectric constant was less than 2.2 even at high percentage (~ 25%) of porosity which corresponded to 50 vol%.

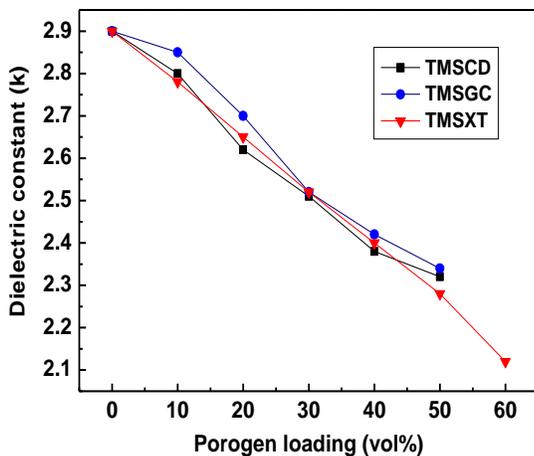


Figure 3: Dielectric constant of nanoporous ultralow dielectric films as a function of porogen loading.

The mechanical properties of nanoporous thin films were obtained by nanoindentation technique. The elastic modulus ( $E$ ) values decreased with increasing porogen loading due to the increasing porosity. However, The reactive porogen system produced ultralow dielectrics ( $k < 2.3$ ) with superior mechanical strengths ( $E > 8.0$  GPa and  $H > 1.1$  GPa). Especially, TMSXT was quite effective in obtaining nanoporous ultralow dielectrics with greatly enhanced mechanical properties and lowest dielectric constant ( $E > 9.0$  GPa,  $H > 1.5$  GPa and  $k = 2.12$ ) at 60 vol% of porogen loading. This result was closely related to the smallest pore sizes at the given porosity over 40 vol% of porogen loading.

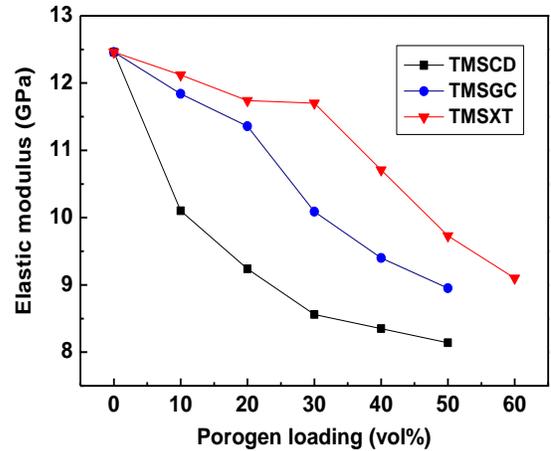


Figure 4: Elastic modulus of nanoporous ultralow dielectric films as a function of porogen loading.

## CONCLUSION

We specially designed reactive porogens which could react chemically with silanol (Si-OH) groups in matrix during their thermal curing. These reactive porogens prevented their aggregation during sol-gel process or cross-linking. Therefore, They resulted in desirable pore and remarkably enhanced mechanical properties of nanoporous ultralow dielectrics. In particular, TMSXT resulted in the highest elastic modulus of 9.1 GPa even at dielectric constant of 2.12 (at porogen loading 60 vol%). These results were good enough to withstand CMP-processing ( $E > 6$  GPa) for the interlayer SOD.

The pore size of TMSXT was smallest above 40 vol% of porogen loading. Therefore, the excellent mechanical properties was related to the smallest and closed pores. Therefore, this study indicate that we could develop superior ultralow dielectrics by controlling the pore size and structures of chemical structures of the matrix by specially designed porogens.

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## REFERENCES

- [1] C.V. Nguyen, K.R. Carter, C.J. Hawker, J.L. Hedrick, R.D. Miller, H.W. Rhee and D.Y. Yoon, *Chem. Mater.*, 11(11), 3080 (1999).
- [2] L. Hedrick, T. Magbitang, E.F. Connor, T. Glauser, W. Volkson, C.J. Hawker, V.Y. Lee and R.D. Miller, *Chem. Eur. J.*, 8(15), 3309 (2002).
- [3] Q. R. Haung, H. C. Kim, E. Huang, D. Mecerreyes, J. L. Hedrick, W. Volksen, C. W. Frank, and R. D. Miller, *macromolecules*, 36, 7661 (2003).
- [4] Y. Toivola, S. Kim, R.F. Cook, K. Char, J.K. Lee, D.Y. Yoon, H.W. Rhee, S.Y. Kim, and M.Y. Jin, *Journal of The Electrochemical Society*, 151(3), F45 (2004).
- [5] M. D. Ong, W. Volksen, G. Dubois, V. Lee, P. J. Brock, V. R. Deline, R. D. Miller, and R. H. Dauskardt, *Adv. Mater.*, 20, 3159 (2008).