

The Structural Evolution of Pore Formation in Low-k Dielectric Thin Films

Michael S. Silverstein¹, Barry J. Bauer², Hae-Jeong Lee², Ronald C. Hedden²,
Brian Landes³, John Lyons³, Brandon Kern³, Jason Niu³ and Tom Kalantar³

1. Department of Materials Engineering, Technion – Israel Institute of Technology, Haifa, Israel

2. Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD

3. Dow Chemical Company, Midland, MI

Abstract. Specular x-ray reflectivity and small angle neutron scattering were used to characterize changes in the porosity, pore size and pore size distribution on processing a polymeric low-k material filled with 21.6 volume percent of a deuterated porogen with an average radius of 56 Å. Processing yielded a decrease in porosity to about 11%, an increase in average pore radius to 83 Å, and a narrower pore size distribution. A sample with an unusual pore structure could be easily identified.

INTRODUCTION

The demand for increased signal transmission speed and device density in the next generation of multilevel integrated circuits has placed stringent demands on materials performance. A suitable low k dielectric for the next device generation should have a permittivity of less than 2.5, and there is already a plan for permittivities lower than 2.0. Nanometer scale porosity is being introduced into low k dielectrics in an attempt to achieve such low permittivities. It has proved extremely difficult to describe the mechanism of pore formation and to characterize the porous structure (porosity, pore size, pore size distribution) owing to the nanometer size scale of the pores. This research investigates pore formation and characterizes porous polymeric low k dielectrics.

EXPERIMENTAL

The materials investigated in this research are a porous organic based on a developmental version (V7) of Dow Chemical's SiLK* (polyphenylene precursor) specially prepared for this research whose oligomer contained a deuterated porogen. The mass fractions of the oligomer, polymer, porogen and an 80/20 mass ratio (78.4/21.6 volume ratio) oligomer/porogen mix are

listed in Table 1. The densities of the polymer and porogen are (1.18 and 1.07) g/cc, respectively. The basic film is a spin-cast porogen-containing oligomer that underwent a bake at 150°C. Films at various stages of pore formation were investigated including films heated to 400°C (partial formation) and films heated to 430°C (complete formation). The sample names in Table 2 reflect the processing. Two sets of samples were prepared, sets A and B.

Specular x-ray reflectivity measurements (XRR) were performed using a modified Philips high resolution x-ray diffractometer in vacuum and in the presence of saturated solvent vapors which can spontaneously condense in the pores. Both methanol and toluene were used since previous results have indicated that toluene might swell the film. The data was plotted as the log of the relative intensity (reflected beam intensity, I , divided by the incident beam intensity, I_0) versus q (where q is related to the scattering angle θ and the wavelength, λ , by $q = 4\pi \sin \theta / \lambda$). Small angle neutron scattering (SANS) was performed on the 8th and 30th lines at the National Institute of Standards and Technology (NIST) Center for Neutron Research. The high q range SANS data was taken on the 8th SANS using a wavelength of 6 Å, the mid-range data was taken on the 8th SANS using a wavelength of 12 Å and the low-range data was taken on the 30th SANS using a wavelength of 6 Å. The data is plotted as intensity versus q on a log-log scale.

The uncertainties of the data presented are estimated as the standard deviation of the mean. In cases where the limits are smaller than the plotted symbols, the

* Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

limits are left out for clarity. All temperatures reported are within $\pm 1^\circ\text{C}$, thicknesses are within $\pm 1\text{ }\mu\text{m}$, q_c^2 within ± 0.005 , and densities and porosities within $\pm 0.5\%$, as determined by previous experience of repeated measurements. The standard deviations from the fits of the SANS data using a polydisperse sphere model were less than: $\pm 0.5\%$ for radius, $\pm 0.5\%$ for polydispersity and $\pm 0.5\%$ for scattering contrast.

TABLE 1. Composition (mass fractions).

	C	H	D	O
Oligomer	0.9316	0.0504	0	0.0180
Polymer	0.9348	0.0507	0	0.0145
Porogen	0.8634	0.0073	0.1292	0
80/20	0.9180	0.0418	0.0258	0.0144
Oligomer/Porogen				

TABLE 2. Film processing.

Sample Name	Bake, $^\circ\text{C}$	Cure, $^\circ\text{C}$	Hold, min	Thickness, μm
150	150	None	0	1.215
330	150	330	0	1.210
400	150	400	0	1.095
430	150	430	0	0.995
43040	150	430	40	0.935

RESULTS AND DISCUSSION

XRR in vacuum for the porogen-filled oligomer (150A) for a partially processed sample (400A) and for a fully processed sample (43040A) are seen in Fig. 1. The critical edge, q_c , is the sharp drop in $\log(I/I_0)$ from the initially flat reflectivity curve. The data were fit to find q_c^2 , which is used to calculate the electron density and, for the samples whose wall molecular structure is known (150, 430, 43040), the effective mass density, d_{eff} [1,2,3]. The porosity, p , was then calculated for the samples whose wall density, d , is known ($d_{\text{eff}} = d(1-p)$), as seen in Table 3. The critical edge decreases with increasing processing temperature, indicating a decrease in film density. The density of 1.120 g/cc calculated for 150 is close to the density of 1.156 g/cc calculated for an 80/20 oligomer/porogen mixture. The decrease in effective density for films processed at (400 and 430) $^\circ\text{C}$ indicate pore formation. The effective density for sample 430A was unusually large, and, therefore the results from 430B are also presented. Assuming a density of 1.18 g/cc for the materials processed at 430°C yields a porosity of approximately 13% , far below the 20% expected from the amount of porogen added. The porosity of 430A was less than those of 430B and 43040A. The porosity of 400A could not be calculated from d_{eff} since its wall density is unknown. However, the porosity of 400A was calculated using XRR porosimetry.

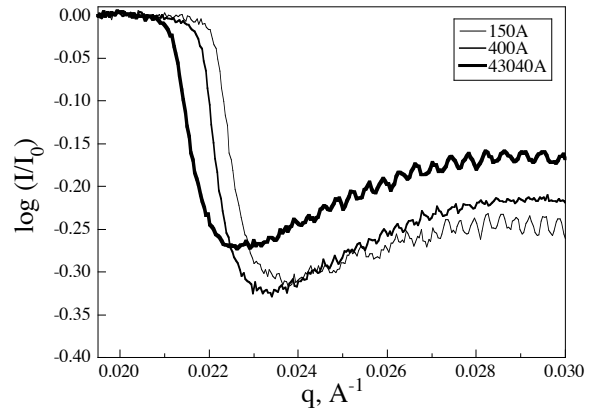


FIGURE 1. Variation of XRR in vacuum with processing conditions.

TABLE 3. Porosity from effective density.

Sample	$q_c^2, \text{\AA}^{-2}$	$d_{\text{eff}}, \text{g/cc}$	Porosity, %
43040A	4.57 E-4	1.019	13.6
430A	4.75 E-4	1.060	10.2
430B	4.60 E-4	1.026	13.1
400A	4.85 E-4	1.082	NA
150A	4.98 E-4	1.120	NA

The porosity was also calculated from the change in q_c^2 on filling the pores with a known solvent with no knowledge of wall density (1,2,3). There is an increase in q_c^2 on exposure of 43040A to methanol and toluene, as seen in Fig. 2. All the results in vacuum, before and after exposure to methanol or toluene, fall on the same curve. Samples 430A and 400A exhibit similar behavior. The porosities and wall densities calculated from XRR porosimetry are listed in Table 4. The measured porosities are somewhat smaller than those in Table 3 and, therefore, the measured wall density is somewhat less than 1.18 g/cc . The results from methanol and toluene porosimetry are similar, indicating that in both cases the solvent vapor has condensed in the pores. The porosity for 43040A is about 11% and that of 430B is about 10.5% . The porosity of 430A is about 7.7% , again lower than expected. The porosity of 400A is about 5.4% , half the porosity of the samples exposed to 430°C . This indicates that about half of the porogen has degraded at 400°C . XRR porosimetry allows the porosity and wall density of an unknown porous material to be determined. Sample 150A exhibited no significant changes in critical edge on exposure to methanol or toluene, demonstrating, as expected, that it is not porous.

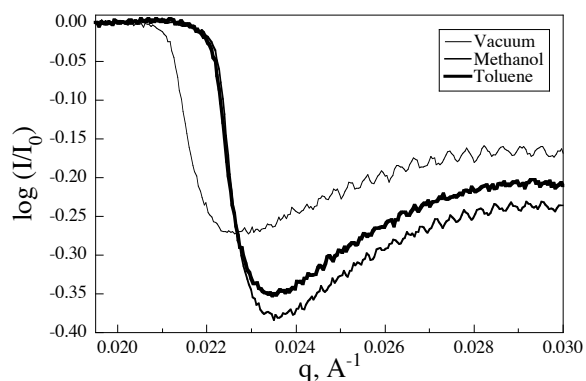


FIGURE 2. XRR for 43040A: vacuum, methanol or toluene.

TABLE 4. Porosity and wall density (XRR porosimetry).

Sample	Solvent	d , g/cc	Porosity, %
43040A	Methanol	1.16	12.1
43040A	Toluene	1.13	9.9
430A	Methanol	1.15	7.9
430A	Toluene	1.15	7.5
430B	Methanol	1.15	11.1
430B	Toluene	1.14	9.9
400A	Methanol	1.14	5.5
400A	Toluene	1.14	5.2

In Fig. 3 the neutron scattering decreases, from 150B to 400B to 430B, as the porogen degrades and pores are formed. This decrease in scattering reflects the differences in scattering contrast. The contrast between the deuterated porogen and the matrix (150B) is larger than the contrast between the pores and the matrix (430B). All the SANS curves from sample set B and all from set A except 430A have a similar shape, a plateau below $q \approx 0.01$ and q^{-4} behavior above $q \approx 0.02$. Sample 430A exhibits less scattering below $q \approx 0.01$ and q^{-3} behavior above $q \approx 0.02$. A comparison of 430A with the other samples processed at 430°C can be seen in Fig. 4.

The pore size was estimated by fitting the mid-range SANS data to a NIST structural model for the scattered intensity from a population of polydisperse spheres that includes hard sphere interactions between the particles and uses a Schultz distribution to describe the polydispersity of the radius. The fit to the mid-range data for 150A and 43040A, as well as the data in the low and high ranges can be seen in Fig. 5. The results for set A are listed in Table 5. The volume fraction of the scattering moiety, v_s , was set at 0.2 for 150 and 330, and at 0.1 for 400, 430 and 43040, reflecting the known compositions and the XRR results. The background (scattering at high q), B , was set using the experimental data. The average pore radius, R , the polydispersity, PD , and the scattering contrast, SC , were allowed to vary. The scattering contrast of about $3 \times 10^{-6} \text{Å}^{-2}$ from

the fits for the films containing deuterated porogen (150, 330 and 400) is significantly larger than the $2 \times 10^{-6} \text{Å}^{-2}$ from the fits for the films containing no porogen (430, 43040). These scattering contrasts are similar to those calculated from the molecular structure, $3.2 \times 10^{-6} \text{Å}^{-2}$ for oligomer/porogen and $2.4 \times 10^{-6} \text{Å}^{-2}$ for polymer/pore. PD ($PD = s/R$, where s^2 is the variance) for the fits ranges between 0.57 and 0.29 and seems to decrease with increasing processing temperature. The average radius of the porogen domains is about 56Å . The average radius increases with processing temperature, reaching 83Å for 43040. Sample 430A exhibits a lower R and is more difficult to fit using model. R for 430B, however, is similar to that of 43040A.

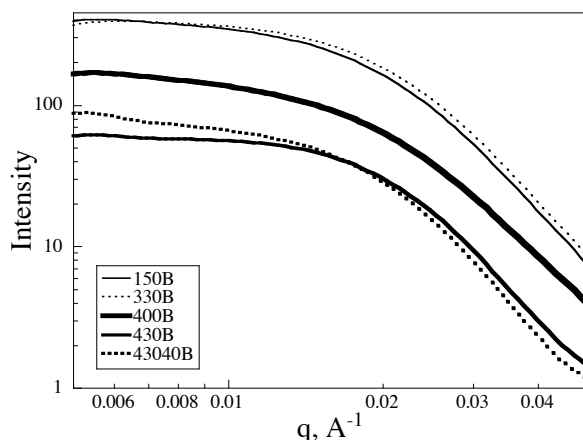


FIGURE 3. Variation of SANS scattering with processing conditions (mid range).

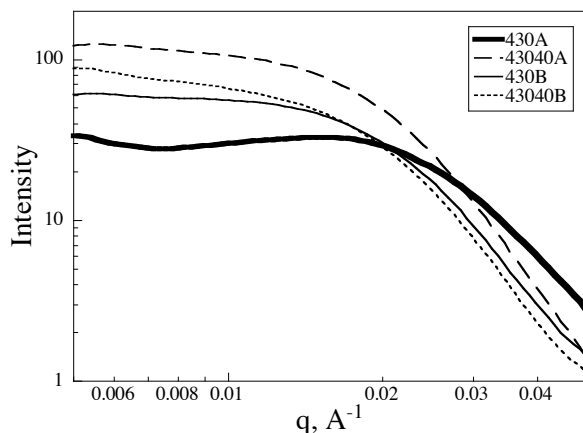


FIGURE 4. SANS scattering from 430A and other films processed at 430°C.

There is a large degree of overlap between the 3 data ranges in Fig. 5 and the match in the data is extraordinarily good. The fits describe the mid and high range data accurately. However, the low-range data

exhibits an upturn that is not described by the model and thus reflects a structure unrelated to polydisperse spheres that may originate in the wall material. The contrast-match SANS technique developed at NIST, using solutions of methanol and deuterated methanol, is being used to eliminate the scattering from the pores in order to isolate this additional scattering and determine its source.

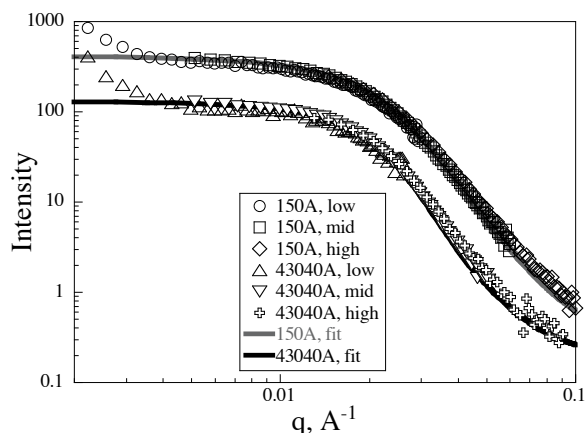


FIGURE 5. Fit to SANS scattering from mid q range.

TABLE 5. The size of the scattering domains from set A.

Sample	R , Å	PD	v_2	SC , Å ⁻²	B , cm ⁻¹
150A	56	0.57	0.2	2.8 E-6	0.3
330A	69	0.46	0.2	3.0 E-6	0.3
400A	66	0.42	0.1	3.3 E-6	0.5
430A	43	0.52	0.1	1.9 E-6	0.3
430B	85	0.29	0.1	1.4 E-6	0.35
43040A	83	0.35	0.1	1.8 E-6	0.2

CONCLUSIONS

A combination of XRR and SANS provide a description of porosity, pore size, and pore size distribution. The 83Å pores were larger than the 56Å porogen, the 11% porosity was about half the amount of porogen, and the pore size distribution was narrower than the distribution of the porogen domains. A sample with an unusual structure was easily identified.

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