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# Characterization on Nano-structures of Spin-on Mesoporous Low-k Dielectric Thin Films

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The relationship between structure and mechanical property of spin-on Low-k dielectric thin films has been investigated by measuring dielectric constant, Young's modulus and periodicity of pore structures. Nano-structures of these Low-k films have been characterized by TEM, SAXS and PALS method. Young's modulus of the films with periodic mesoporous structure is higher than the films with random pore structure at the same silica composition and the same film density. Experimental results indicated that the film density and the pore structure of these porous materials have paramount effect on the magnitude of k and mechanical property.

Key words: Low-k, MSQ, Young's modulus, dielectric constant, mesoporous.

## 1. INTRODUCTION

Ultra low dielectric constant (k) interlevel materials will be required for the future generation IC technologies. The reason is that for the short transistor gate length, so called RC delay occurs because of the present higher k value of k=4.2 for silicone dioxide ($SiO_2$) dielectric material.

Dielectric constant strongly depends on the hydrophobicity and the density of the material. Actually introducing some hydrophobic unit into the molecular structure enables to prepare the interconnect dielectrics (ILD) with k<3.5 such as FSG. However, for achieving k<3.0, it is indispensable to reduce the density of the materials. A common approach used to reduce the density is introducing porosity into the dielectric materials, but adding porosity decreases mechanical strength of the dielectric film, and has negative impacts on its integration performance as CMP process, leakage characteristics and thermo-mechanical stability depending on the pore structures. Understanding pore structures and their impacts on the mechanical property is essential for the material and the integration process developments. A number of porous dielectric materials with k of < 2.5 have been developed by a lot of fabrication method including CVD (Chemical Vapor Deposition) and SOD (Spin on Dielectric) low k dielectrics.

This report focused on the relationship between pore structure and mechanical property (Young's modulus) for the porous spin-on low dielectric thin film materials (hereafter denoted as Low-k film) prepared by the silica solution containing organic polymer as a porogen. In this process, porogen is removed from the film during the calcinations, giving nano-porous silica thin films.

## 2. EXPERIMENTAL

### 2.1. Film formation

The Low-k films used in this report are porous MSQ (methylsilsesquioxane) and are deposited through the processes of spin-on.[1,2] The solution for the spin-on consists of silica oligomers, polymer as a porogen and solution. Silica oligomers contain methyl unit for bringing hydrophobicity to the film. For the random pore structure, homo polymer is used as a porogen and for the periodic mesoporous structure, a tri-block copolymer that makes micelles in the solution is used. After spin-on, films are prebaked on a hot plate for 1min at 120℃ then cured in a furnace for 60 minutes at 400℃ under $N_2$.

### 2.2. Characterization of physical properties

The dielectric constant k of the films was measured at 1MHz with an Hg probe. The Young's modulus and hardness are determined by the nano-indentation measurement. The sample film thickness is 1um and contact stiffness for the surface detection is 200N/m for the nano-indentation measurement. Film thickness and refractive index were obtained by using Spectroscopic Ellipsometry.

### 2.3. Pore structure characterization

The pore structure has been studied with three commonly used techniques including transmission electron microscopy (TEM), X-ray reflectivity (XR) for density, grazing incidence small angle X-ray scattering (GISAXS) for periodicity.[3] Positron annihilation life time spectroscopy (PALS) is applied for the analysis of pore size and pore connectivity measurement.[4,5]

## 3. RESULTS AND DISCUSSION

One of the most required properties for Low-k films is the mechanical property such as Young's modulus and

Hardness. On the other hand, to achieve the lower k value, film density must be the lower as well. This situation makes a significant issue because the higher density is necessary to achieve the high modulus. This trade-off relationship between the mechanical property and low k value results in a typical contradiction and it makes difficult to use Low-k film in the chip process.

Figure 1 shows TEM image and SAXS pattern of a Low-k film with random pore structure made by spin-on process. This SAXS pattern shows that the pore structure of the film has no periodicity and pores are dispersed in the film randomly and homogeneously. The k value and Young's modulus of this film are 2.3 and 3GPa, respectively. Film density is $\rho$=0.97g/cm$^3$. The Young's modulus of 3GPa is very small but increasing density for achieving higher modulus also increases k value.

An alternative way is controlling the pore structure, i.e., by using periodic structure to increase the Young's modulus while keeping the film density at the same low value. The appropriateness of this concept is confirmed in figure 2. Figure 2 shows the silica network structure made by Coarse-Grained Molecular Dynamics (CGMD) simulation[6] under the periodic boundary condition. In this figure, film density is 1.2g/cm$^3$ for both figure 2a and 2b. However, figure 2a represents a random pore structure in which silica network is dispersed randomly and homogeneously in the material. In contrast to figure 2a, figure 2b represent an example of highly periodically organized. Calculated Young's moduli of these structures are 7.4GPa for figure 2a and 21GPa (average value of three direction) for figure 2b. This result clearly shows that high wall density with periodic pore structure makes the Young's modulus quite high even in the case of the same film density with random pore structure.

The structure of figure 2b is, however, rather unrealistic for the film formation as can be seen. Instead of that, periodic spherical pores are dispersed in silica framework in figure 3. The film density is the same value (1.2g/cm$^3$) with figure 2. In the CGMD simulation, periodic boundary condition is applied as well. Figure 3 shows that the Young's modulus of this structure is 15GPa, which is as twice as the random pore structure of figure 2a.

The pore structure such as shown in figure 3 can be made relatively easily by porogen type spin-on process. One of the common ways is to use tri-block copolymer (e.g., polyethyleneglycol (PEG) / polypropyleneglycol (PPG) / polyethyleneglycol (PEG)) as a porogen. This type of tri-block copolymer makes micelles and is dispersed periodically in the silica oligomer that works as a solvent. In other words, tri-block copolymer becomes spherical micelles in the silica framework during spin-on process even before prebaking.

Figure 4 shows a CGMD simulation indicating tri-block copolymer forms micelles in the silica oligomer. In this figure, silica oligomers are invisible to make it possible to see the spherical micelles. Fig. 4 clearly shows that the hydrophobic chains of the tri-block copolymer (PPG) coagulate each other and forms spherical region. The hydrophilic chains (PEG) are soluble with silica oligomer and distribute around the outside of the spherical region. It should be noted that

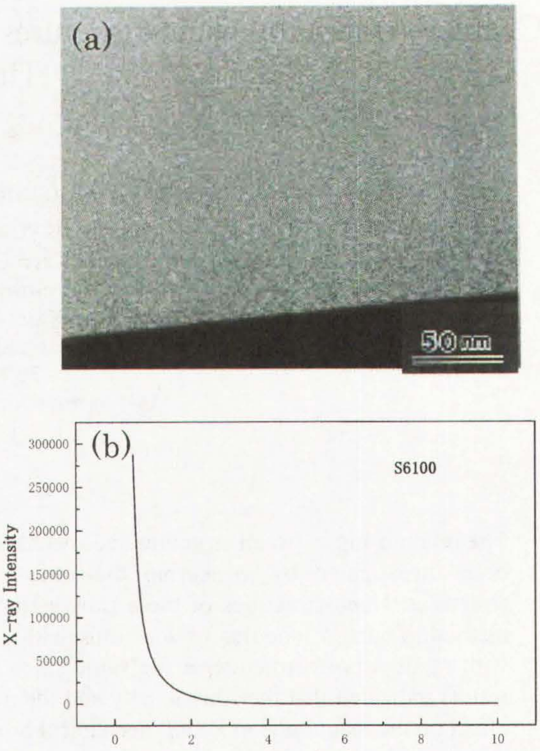

Fig. 1. Structure of random pore low k film with k=2.33, E=3GPa, $\rho$=0.97g/cm$^3$. (a) TEM image, (b) SAXS pattern.

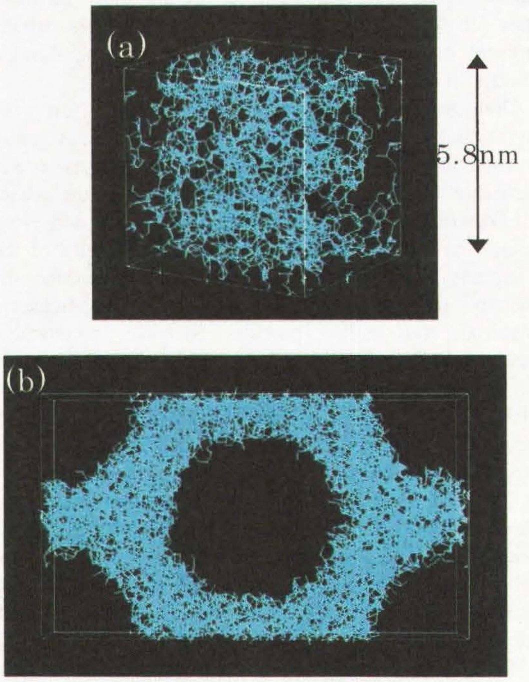

Fig. 2. CGMD Simulation of silica network for film density is 1.2g/cm$^3$. (a) random pore structure, (b) highly periodic pore structure. Calculated Young's modulus: (a) E=7.4GPa,( b) E=21GPa.

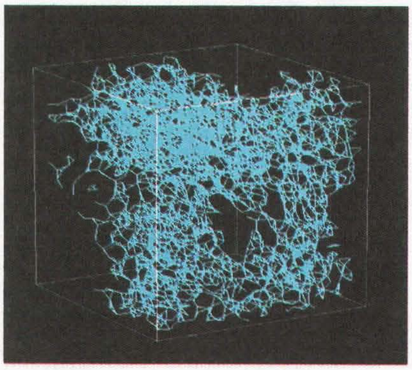

Fig. 3. CGMD Simulation of silica network with spherical periodic pore. Film density is 1.2g/cm$^3$. Calculated Young's modulus, E=15GPa.

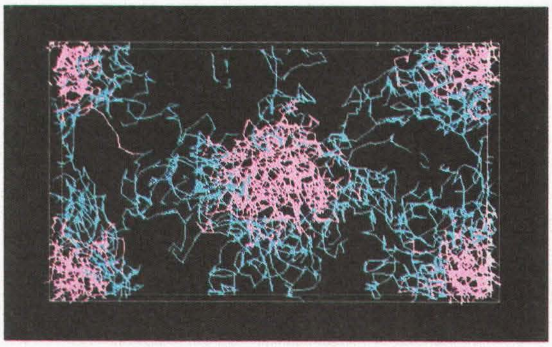

Fig. 4. CGMD Simulation of coagulated tri-block copolymer inside the silica oligomer. Blue line; PEG, pink line; PPG. The perpendicular size of the rectangular is 10nm.

the micelles of the tri-block copolymers are arranged periodically in the silica oligomers. This structure consisting of silica oligomer and tri-block copolymer is considered to be the nano-scale structure of the film on the silicon wafer after prebaking. After calcinations at 400℃ in $N_2$, tri-block copolymers are removed and the dielectric film with mesopores are obtained.

Dielectric constant k of thus obtained periodic mesoporous MSQ films is controlled by the weight ratio of porogen (organic polymer) and silica framework, P/S that is expressed as follow.

$$P/S = \frac{Polymer\ weight}{Silica\ framework\ weight}$$

The raw material of larger P/S value results in the lower density of the film after calcinations and gives smaller k value. And it is the case that the lower density also gives smaller Young' modulus. Table I shows the P/S dependence of k, Young's modulus, E and density, ρ of the mesoporous MSQ Low-k obtained by spin-on process using tri-block copolymer as porogen.

This table clearly shows that k, E and ρ decrease as P/S increases. It is noted that E of the mesoporous MSQ is as twice as that of random pore MSQ at the same k value, i.e., E=6.05GPa at k=2.34 for the mesoporous MSQ while E=3GPa at k=2.33 for the random pore MSQ. The density of both Low-k films are also the same (0.98 and 0.97g/cm$^3$). This result indicates that in the case of the same silica source of MSQ, the periodic mesoporous structure gives higher Young's modulus than the random pore structure even though the density is the same.

Table I. P/S dependence on k, E, and ρ for mesoporous MSQ low-k film.

| P/S | k | E /GPa | ρ / g/ml$^3$ |
|---|---|---|---|
| 0.5 | 2.34 | 6.05 | 0.98 |
| 0.7 | 2.20 | 5.06 | 0.86 |
| 0.8 | 2.02 | 3.62 | 0.8 |
| 1.0 | 1.95 | 2.99 | 0.72 |

Figure 5 shows the relationship between E and k for Low-k films of random porous MSQ and mesoporous MSQ. This figure clearly shows that Young's modulus decreases linearly as dielectric constant decreases. At the same time, this figure also shows that E of the mesoporous MSQ film is significantly higher than that of random pore MSQ film.

Figures 6 and 7 show the TEM images of the mesoporous MSQ Low-k films. The clear difference of the structure between random pore film (Fig. 1) and periodic mesoporous films are confirmed by these figures evidently.

Figure 6 indicates that for P/S=0.5, pore shapes are rather spherical like and for P/S=0.7, pore shapes become cylindrical. It means that for higher porogen ratio, micelles formed by tri-block copolymers tend to contact each other and resultant pore shape in the film changes from spherical to cylindrical.

Figure 7 shows the TEM image for P/S=1.0 and the figure clearly shows the anisotropy of the cylindrical pore. From the radial view that is the same direction with solution flow in the spin coating on the wafer, pores are arranged in the way of highly periodic hexagonal structure. On the other hand, from the circumference view, pores are clear cylindrical shape. This result indicate that in the MSQ film from P/S=1.0, cylindrical pores are assembled toward the direction of

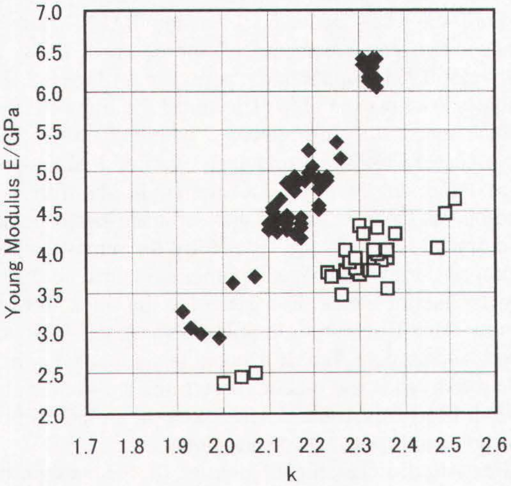

Fig. 5. Young's modulus E vs. dielectric constant k for low-k films. □ random pore MSQ, ◆ mesoporous MSQ.

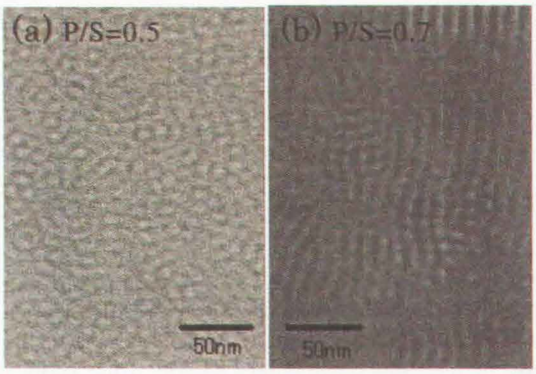

Fig. 6. TEM image of mesoporous MSQ Low-k film. (a) P/S=0.5, (b) P/S=0.7.

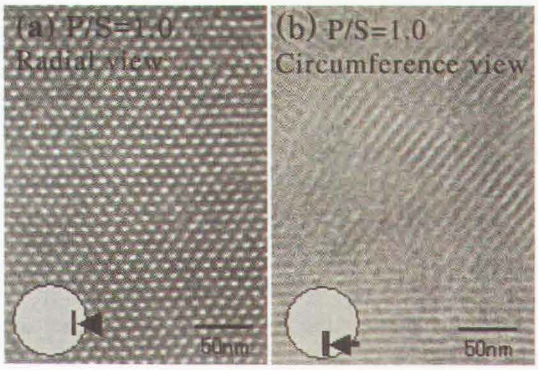

Fig. 7. TEM image of mesoporous MSQ Low-k film for P/S=1.0. (a) P/S=radial view, (b) circumference view.

the solution flow during spin coating and they are also arranged in the hexagonal structure.

The periodic structures of the mesoporous MSQ Low-k films by the SAXS measurement are shown in Figure 8. Figure 8 shows that distance from pore to pore indicates the constant value of 9.5nm regardless of the P/S. It also shows that the periodicity of the structure becomes the higher for the higher P/S value.

Pore size was evaluated by using PALS. Table II shows the pore diameter of mesoporous films for P/S=0.5, 0.7, 1.0 and random pore film for P/S=0.5. The table also shows the pore diameter of the film of P/S=0, which means the film calcined without porogen, i.e., spin coated only silica oligomer solution. PALS shows that there are two types of pores in the film i.e., mesopores larger than 1nm and sub-nano pores smaller the 1nm. Mesopores are formed by the removal of the porogen during calcinations. Sub-nano pores are caused by the intermolecular distance inside the silica network. From Table II, mesoporous films have larger mesopore than random pore film. It is noted that sub-nano pore of the mesoporous and random pore films are smaller than P/S=0 film. This result indicates that the wall density of the porogen type film becomes higher.

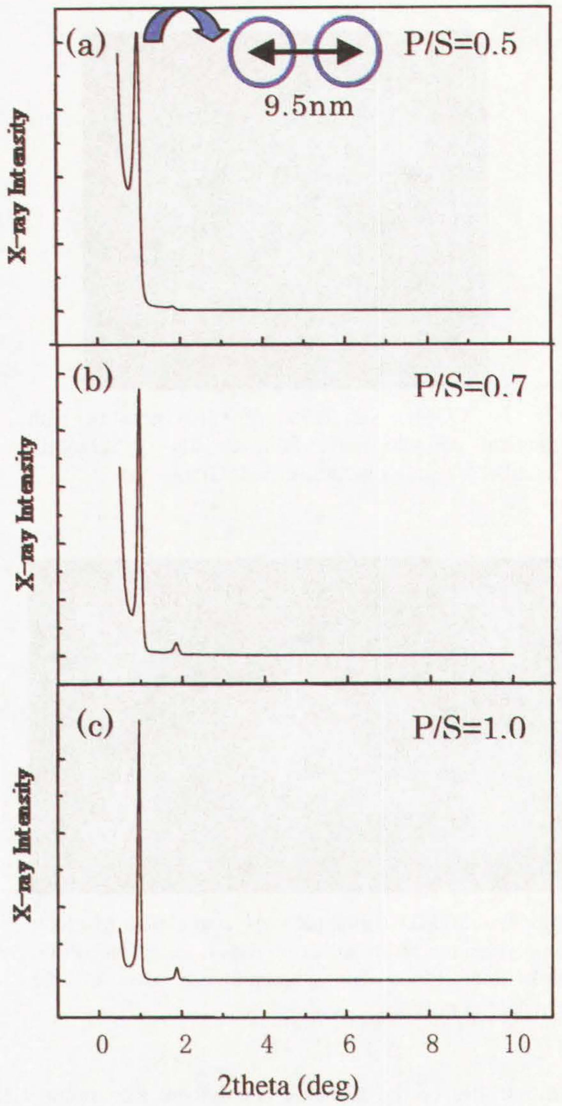

Fig. 8. SAXS patterns of mesoporous MSQ Low-k films. (a) P/S=1.0, (b) P/S=0.7, (c) P/S=1.0. Pore to pore distance is 9.5nm.

Table II. Pore diameters obtained by PALS.

| Structure | P/S | Mesopore | Sub-nano pore |
|---|---|---|---|
| | 0 | - | 0.8nm |
| Periodic | 0.5 | 5nm | 0.6nm |
| | 0.7 | 6nm | 0.6nm |
| | 1.0 | 6nm | 0.6nm |
| Random | 0.5 | 2.4nm | 0.6nm |

Regarding of the higher density of the mesoporous MSQ, it is considered that the separation of the mesopore part and wall part is more evident in periodic mesoporous MSQ than in random pore MSQ, and larger part of the silica network in random pore MSQ has lower density than the wall. On the other hand, in the periodic mesoporous MSQ, relatively larger part of the silica network behaves as the wall. The higher Young's modulus of the periodic mesoporous MSQ is presumed to be attributed to the large amount of wall with high density.

In the pore connectivity viewpoint, TEM results suggest that the film of P/S=0.5 has close pore and the

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film of P/S=0.7 has open pore. In other words, pores of former film are isolated inside silica network and those of latter film are penetrated to the surface.

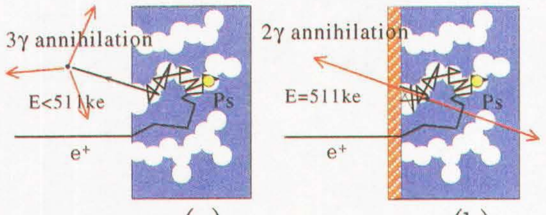
PALS is the appropriate method to elucidate the pore connectivity. Positron injected into the film changes to positronium (Ps). Ps is reflected on the inside surface of the pore and has finite lifetime. If the pore is isolated in the silica network, Ps is locked inside the pore and the annihilation occurs on the inside surface of the pore. In this case, spectrum of the emitted γ-ray in the annihilation has a peak at 511keV range (2γ annihilation). On the contrast, if the pore is open, Ps comes out from the film and annihilation occurs outside, and spectrum of the emitted γ-ray has no peak (3γ annihilation). This phenomenon is the principle of the elucidation of pore connectivity by PALS.

Figure 9 shows the schematic representation of the Ps annihilation in the PALS measurement of the open pore film. Without cap layer, Ps comes out to the outside of the film and 3γ annihilation occurs. When cap layer is deposited on the film surface, no Ps is able to come out from the film and 2γ annihilation occurs. It means that for the open pore film, emitted γ-ray spectrum is different between with and without cap layer. However, for the close pore film, γ-ray spectrum is the same regardless of the cap layer.

Figure 10 shows the γ-ray spectra emitted from the Ps annihilation in the PALS measurement of mesoporous film. In this figure, red line denotes the spectra of the cap film and blue line denotes that of the no cap film. Figure 10a shows that the spectra of the film of P/S=0.5 have no difference between cap and no cap samples. This result means that the pores of the mesoporous film of P/S=0.5 are close. On the contrast, as Figure 10b shows, spectra of the film of P/S=0.7 are clearly different between cap and no cap samples, i.e., the pores of this film are open.

## 4. CONCLUSIONS

The Low-k dielectric thin film of high Young's modulus is obtained by introducing the periodic mesoporous structure into the silica network of the MSQ Low-k thin. The periodicity of the film becomes higher for the higher amount of tri-block copolymer as a porogen. As for the pore connectivity, the periodic mesoporous film of P/S=0.5 has close pore by the PALS measurement. But P/S=0.7 film has open pore.



(a) (b)

Fig. 9. Schematic representation of the Ps annihilation. (a) without cap, (b) with cap layer

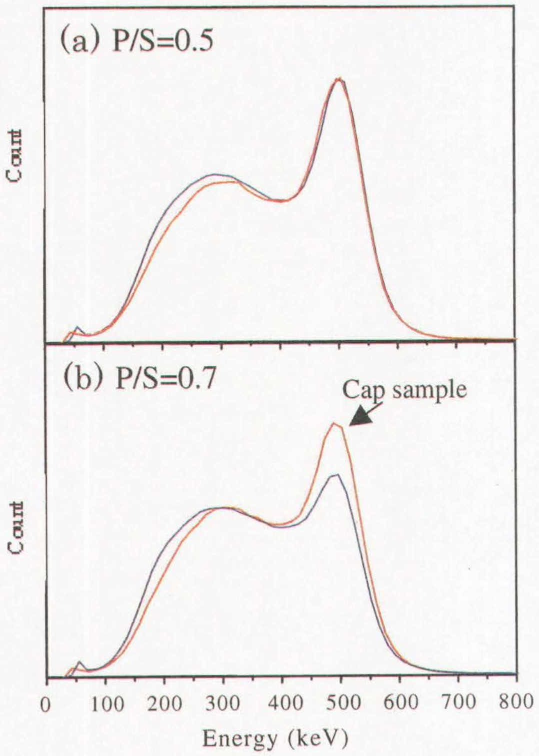


Fig. 10. γ-ray spectra of the mesoporous MSQ in the PALS measurement. (a) P/S=0.5, (b) P/S=0.7. Red line; cap sample, blue line; no cap sample.

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