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X-RAY REFLECTIVITY STUDY ON NANOPOROUS ORGANOSILICATES

A Thesis

Presented to

The Faculty of the Department of Materials Engineering

San Jose State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

By

Hsiao-Lin Wang

May 2005

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ABSTRACT

X-RAY REFLECTIVITY STUDY ON NANOPOROUS ORGANOSILICATES

by Hsiao-Lin Wang

Silicon dioxide with a dielectric constant of 4.0 is commonly used as a dielectric insulator for IC applications, i.e., interlayer dielectrics to separate metal interconnects. With the need for a smaller feature size, silicon dioxide no longer meets the requirements of a lower dielectric constant material. As such, ultra low-k organic-inorganic nanoporous materials such as organosilicates are one of the leading candidates for replacing silicon dioxide as interlayer dielectrics. In order to develop and optimize future ultra low-k interlayer dielectrics, characterization of material properties is important.

X-ray reflectivity has been recognized as a popular technique to characterize nanoporous thin films in terms of density, thickness, and coefficient of thermal expansion. This technique also provides insights into internal microstructures such as dominant orientation of pores. In this thesis, characterization of ultra low-k nanoporous thin films generated with two types of porogens has been studied using X-ray reflectivity technique.

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CHAPTER ONE INTRODUCTION

1.1 Interconnect Scaling

Over the past twenty years, feature sizes in integrated circuits (ICs) have continually shrunk. The feature size is the smallest dimension that the fabrication's equipment can etch onto the surface of a wafer, where a feature can be a wire, a transistor, or other circuit component. The numbers of transistors on a single chip, the transistor density, have been increased to improve the transistor performance. Figure 1 shows a typical chip cross section with eleven layers of metal copper interconnects. Each layer of copper interconnect wiring is separated by a dielectric insulator called interlayer dielectrics (ILD), normally silicon dioxide (SiO_2).

Figure 1. A typical cross section of a chip with eleven layers of copper interconnects [1].

As the minimum feature size in an IC device continues to shrink and approaches submicron regime (0.18 μ m), problems associated with metal interconnects become serious issues, i.e., crosstalk between adjacent conducting lines, power dissipation, and resistance-capacitance (RC) time delay. These issues can significantly limit the progress in IC technology. For example, RC delay degrades at a factor of 2 every technology generation assuming a constant metal aspect ratio and no change in conductors or dielectric materials [2] (Appendix A). Replacing ILD with a dielectric constant k lower than SiO₂ ($k \approx 4.0$) is necessary to reduce RC time delay.

Table 1 summarizes the dielectric constants required as Dynamic Random Access Memory (DRAM) metal half pitch decreases each year [1]. The technology node in Table 1 shows a 0.7 times scaling per technology node (per three years) according to Moore's Law with decreasing metal half pitch each year. The "node designation" is defined as DRAM half pitch, not the minimum feature size, by International Technology Roadmap for Semiconductors (ITRS) [1]. The metal half pitch is one half the width of a metal one pitch, as shown in Figure 1. The metal used to connect the transistors or other components in the chip is copper with an effective resistivity of 2.2 $\mu\Omega$ -cm. The last two rows in Table 1 show the dielectric constant required to fulfill ILD criteria. In 2004, DRAM half pitch has approached to 90 nm, and the number of metal levels is 10 with an effective dielectric constant of 3.1-3.6. It is projected that in 2007 DRAM half pitch is to reach 65 nm and the required dielectric constant falls between 2.7 and 3.0.

Table 1. Interconnect technology requirements for low-k materials [1].

Year of Production	2004	2005	2006	2007	2010	2013	2016
Technology Node	90			65	45	32	22
DRAM ½ Pitch (nm)	90	80	70	65	45	32	22
Number of Metal Levels	10	11	11	11	12	12	14
Metal Effective Resistivity ($\mu\Omega\text{-cm}$)	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Effective Dielectric Constant (k_e)	3.1-3.6	3.1-3.6	3.1-3.6	2.7-3.0	2.3-2.6	2.0-2.4	<2.0
Bulk Dielectric Constant (k)	<2.7	<2.7	<2.7	<2.4	<2.1	<1.9	<1.7

1.2 Low-k Interlayer Dielectric Materials

One of the challenges to improving performance and meeting dielectric constant requirements is to develop low dielectric constant (low-k) ILD materials with dielectric constants lower than SiO_2 ($k \approx 4.0$). The criteria for the replacement of ILD materials include good thermal stability in excess of 400°C , low coefficient of thermal expansion ($\text{CTE} < 50 \times 10^{-6}/^\circ\text{C}$), low moisture uptake, high mechanical strength with Young's modulus around 3 GPa, low reactivity with conductor metals at an elevated temperature, good adhesion to various substrates, high dielectric breakdown field ($> 2 \text{ MV/cm}$), high glass transition temperature (T_g) and so on, as summarized in APPENDIX B [3].

Not only is it important to obtain low dielectric constants in developing materials, but also maintain good thermal and mechanical stabilities [4]. There are several organic materials which have low dielectric constants ($k < 4.0$) due to their low densities (around 1 g/cm^3) and low individual bond polarizabilities [5]. Unfortunately, most organic materials decompose at subsequent processing temperatures ($> 400^\circ\text{C}$).

Another class of low-k materials is organic-inorganic hybrids built on an O-Si-O backbone with empirical formulas, such as organosilicates/silsesquioxanes ($\text{RSiO}_{1.5}$, where R can be hydrogen, alkyl, alkylene, aryl, arylene, or another organic group) [5]. These materials have low dielectric constants (2.6-2.8) and also maintain good thermal and mechanical properties at temperatures higher than 400°C.

In order to achieve an ultra low dielectric constant ($k < 2.2$) for future IC generations, air pockets in the form of pores will have to be introduced in the thin film (thickness less than 1 micron). This is due to the fact that air (pores) has a low dielectric constant of 1.0. Since dense organosilicates fulfill many of the desired low-k ILD properties, it is a good idea to introduce pores into these materials. Organosilicates, which are structurally similar to the common ILD material SiO_2 , possess advantages over other materials. Currently, research on porous organosilicates thin films is of great interest to future ILD materials.

1.3 Characterization Techniques

Apparently, decreasing the dielectric constant beyond current values ($k < 2.2$) for future interconnect technology requires the incorporation of pores into thin films. Since low-k thin films are generally less than 1000 Å thick and thin film properties can be different from bulk properties, the characterization techniques have to be capable of characterizing materials properties in the form of thin films. In addition, most materials cannot be prepared in a thickness of less than 1000 Å without cracking. Therefore, on-wafer characterization techniques of ultra low-k porous thin films are required.

Thin film properties, including density, thickness, and surface/interface roughness, as well as pore morphologies which include porosity, pore size, and pore distribution, are important parameters that can affect thin film dielectric constant, mechanical properties and so on. The capability of X-ray reflectivity in characterization of thin film properties has been studied and widely published [6, 7]. X-ray reflectivity is a nondestructive technique in which repetitive measurements on one specimen can be performed. Vacuum is not necessary during measurements by X-ray reflectivity. This technique also provides excellent spatial resolution down to 1.0 nm level. Due to its advantages, the interest in and use of the X-ray reflectivity technique have surged in recent years.

Since leading candidates of ultra low-k ILD are porous thin films, measurements and understanding the impact of pore morphologies, which are tightly coupled to the performance in modern ICs, are significant. Traditional techniques such as gas adsorption, mercury intrusion, and mass uptake are capable of characterizing pores smaller than 100 nm [8]. However, such techniques lack sensitivity to quantify porosity on such thin films ($<1000 \text{ \AA}$). Currently, there are a few techniques suitable for the characterization of ultra low-k thin film pore morphologies, such as positronium annihilation lifetime spectroscopy (PLAS), ellipsometric porosimetry (EP), and scattering-based techniques utilizing either neutrons or X-rays [8]. The strengths and weaknesses of these techniques are summarized in Table 2.

Table 2. The strengths and weaknesses of on-wafer characterization methods in ultra low-k porous thin films [8].

Technique	Strength	Weakness
PLAS	<ul style="list-style-type: none"> - Suitable for pore size of 2-20nm - Capable of quantifying closed pores 	<ul style="list-style-type: none"> - High vacuum - Non-trivial in terms of quantifying the total porosity
EP	<ul style="list-style-type: none"> - Powerful 	<ul style="list-style-type: none"> - Requires the index of refraction for the specimen
Scattering-based technique	<ul style="list-style-type: none"> - Neutron based is powerful 	<ul style="list-style-type: none"> - Limited by access to neutron scattering facilities

Given the weaknesses of the aforementioned techniques, X-ray porosimetry has been developed by the National Institute of Standards and Technology (NIST) as a powerful tool to characterize pore morphologies of ultra low-k porous thin films [8, 9-11]. The basic concept of X-ray porosimetry is to combine the capabilities of X-ray reflectivity with the mechanism of porosimetry to determine the mass uptake of probe molecules in porous thin films as a function of solvent vapor pressure. Structural properties including films density, pore-wall density, porosity, average pore size, and pore connectivity can be determined by means of X-ray porosimetry.

CHAPTER TWO LITERATURE REVIEW

2.1 Low-k Materials

There are two possible ways to reduce the dielectric constant of dielectric materials: decrease the dipole strength or decrease the number of dipoles [12]. In order to decrease the dipole strength, materials with chemical bonds of lower polarizability than Si-O bonds are to be used. The IC industry has replaced Si-O bonds with less polar Si-C bonds and nonpolar C-C or C-H bonds. Decreasing the number of dipoles means using materials with lower density. Reduction in density can be achieved by means of introducing pores into materials.

Low-k materials can be classified into two groups: organic and inorganic (from organic-inorganic hybrids) dielectric materials. Table 3 lists dielectric constants of current low-k ILD materials.

Table 3. Dielectric constants of current low-k ILD candidates [3].

Material	Dielectric constant
SiO ₂	3.9-4.5
Fluorosilicate glass (FSG)	3.2-4.0
Polyimides	3.1-3.4
Hydrogen silsesquioxane (HSSQ)	2.9-3.2
Diamond-like Carbon (DLC)	2.7-3.4
Black Diamond (SiCOH)	2.7-3.4
Parylene-N	2.7
B-staged Polymers (CYCLOTENE and SiLK)	2.6-2.7
Fluorinated Polyimides	2.5-2.9
Methyl Silsesquioxane (MSSQ)	2.6-2.8
Poly(arylene ether) (PAE)	2.6-2.8
Fluorinated DLC	2.4-2.8
Polytetrafluoroethylene (PTFE)	1.9

2.1.1 Organic Low-k Materials

Organic low-k materials such as polyimides, poly(arylene ether), B-stage polymers, etc. have low dielectric constants in the range of 2.5-3.4 that are due to the low polarizability of chemical bonds. However, they are not as thermally and mechanically stable as SiO₂ at temperatures above 400°C. Moisture uptake, low-thermal conductivity (4-5 times smaller than that of SiO₂, 1.1 W·m⁻¹·K⁻¹), and high CTE (>50×10⁻⁶/°C) still remain to be improved before implementation in the future ICs [5]. The challenge of organic low-k materials is to further reduce the dielectric constant to a value of less than 2.2. Although the dielectric constant of polytetrafluoroethylene (PTFE) is only 1.9, it has a low Young's modulus (0.5 GPa), a low decomposition temperature (<400°C), and a high CTE (>100×10⁻⁶/°C), failing to meet the criteria of ILD materials.

2.1.2 Organic-Inorganic Hybrids Low-k Materials

In comparison, organic-inorganic hybrids low-k materials, such as silsesquioxanes (or organosilicates), are structurally similar to inorganic silica, SiO₂ (common ILD materials), which have perceived advantages over organic polymers. These materials also have higher T_g and can maintain better thermal and mechanical stability. Silsesquioxanes can have cage, ladder, random structure, or the mixture of the three structures, in which the random structure has the lowest packing density and dielectric constant [5]. Figure 2 shows three different structures of silsesquioxanes with an organic functional group R.

Figure 2. The structures of silsesquioxanes, where (a) is cage structure, (b) is ladder structure, and (c) is random structure [5].

Hydrogen silsesquioxanes (HSSQ, where $R=H$) and methyl silsesquioxanes (MSSQ, where $R=CH_3$) have dielectric constants of 2.9-3.2 and 2.6-2.8, respectively. Hydrogen silsesquioxanes and methyl silsesquioxanes thin films also have high Young's modules of 6-8 GPa and low CTE around $20 \times 10^{-6}/^{\circ}C$ [5]. Due to the presence of the organic functional group, R, water absorption of silsesquioxanes is dramatically reduced which makes the material hydrophobic. In comparing HSSQ to MSSQ, the weak Si-H bonds in HSSQ oxidize at high temperatures and form Si-OH groups that can raise the dielectric constant. On the other hand, Si-C bonds in MSSQ are more robust than Si-H bonds in HSSQ and do not decompose at high temperatures ($>400^{\circ}C$). Methyl in MSSQ

is more hydrophobic than hydrogen in HSSQ. Thus, many companies and research groups are working on MSSQ thin films for the replacement of future ILD materials.

2.1.3 Ultra Low-k Nanoporous Materials

Unfortunately, none of the aforementioned dense materials has a dielectric constant less than 2.2 that can meet ILD criteria beyond 32 nm technology node, except for PTFE ($k=1.9$). An alternative way to further reduce the dielectric constant is to lower the density of a material by incorporation of nanometer-sized, closed pores into thin films since air has a dielectric constant of 1.0. Table 4 lists dielectric constants of ultra low-k nanoporous materials. As shown in Table 4, the dielectric constant can be reduced to ultra low-k regime ($k<2.2$) by introducing pores into thin films. For example, the dense HSSQ in Table 3 has a dielectric constant between 2.9 to 3.2. In Table 4, the dielectric constant is reduced to 1.7-2.2 as pores are introduced into HSSQ.

Table 4. Dielectric constants of low-k materials with nanometer-sized pores [3].

Material	Dielectric constant
Aerogels/Xerogels (porous silica)	1.1-2.2
Porous HSSQ	1.7-2.2
Porous SiLK	1.5-2.0
Porous MSSQ	1.8-2.2
Porous PAE	1.8-2.2

A model of the effect of porosity on the dielectric constant can be used to determine the effective dielectric constant, k_e , as shown in Equation 1 [3].

$$k_e = k_M \left(\frac{1 + 2A}{1 - A} \right) \quad \text{Equation 1}$$

where $A = f \left(\frac{k_p - k_M}{k_p + 2k_M} \right)$, f is the porosity, k_p is the dielectric constant of the pore ($k_p=1.0$),

and k_M is the dielectric constant of the matrix material. Using Equation 1, the porosity needed to reduce the dielectric constant depends on the dielectric constant of the matrix material, k_M . By starting with lower dielectric constant materials, lower porosity is needed to reduce the dielectric constant to the desired value.

Figure 3 compares the porosity required between SiO_2 and silsesquioxanes to lower the dielectric constant. Low-k materials, silsesquioxanes, require 40% porosity to achieve a dielectric constant of 2.0, whereas SiO_2 requires more than 60% porosity to achieve the same. The higher the porosity of a film, the weaker the mechanical strength that a film can withstand. Therefore, it is desirable to design a nanoporous thin film by starting with a matrix material with a lower dielectric constant so that less porosity is required to reduce the dielectric constant and hence less impact on the material's mechanical properties.

Figure 3. The porosity effect on dielectric constants for SiO₂ and silsesquioxanes [5].

There are three methods to generate pores into thin films: sol-gel chemistry [13], solvent extraction using supercritical CO₂ [14], and sacrificial templates [15]. In the sol-gel process, pores are formed in the gel, followed by supercritical drying or slow evaporation. In the solvent extraction method, supercritical fluid CO₂ is applied to a film to extract low molecular weight or CO₂ species to introduce pores.

In another approach, sacrificial templates, parts of materials are selectively removed in order to leave pores inside the materials. Thin films can be prepared by spin-coating a solution containing thermally labile organic templates, called porogens, and resin such as organosilicates onto a silicon substrate. The matrix is first subjected to a moderate thermal treatment (around 100-150°C) to promote vitrification, followed by a higher temperature treatment (>400°C) to thermally decompose the porogens. The high temperature treatment leaves voids in films forming nanoporous thin films. Because pore

morphologies can be highly controlled, researchers are aiming at using this approach to generate ultra low-k nanoporous thin films.

2.2 Fundamentals of X-Ray Reflectivity

New low-k or ultra low-k ILD materials are highly desired to address the problems of metal interconnects such as crosstalk between interconnects, power consumption, and RC delay. One avenue to reduce the dielectric constant is to introduce nanometer-sized pores into thin films. However, one must note that physical properties and pore structures of low-k thin films can significantly affect material properties, including CTE, mechanical strength, moisture uptake and so on, other than the dielectric constant. On-wafer measurements of thin film properties and pore morphologies are very important in order to develop and optimize future low-k and ultra low-k ILD materials.

X-ray reflectivity (XR) has been reported as a powerful technique for characterizing thin films with a thickness of less than 1000Å [6, 7]. X-ray reflectivity can be used to determine thin film density, density profile perpendicular to film surfaces, and thickness and roughness of thin films [16].

When X-rays are emitted from air onto a specimen with an incident angle θ , the specularly reflected X-rays leave the specimen with the same angle, as illustrated in Figure 4. The detector measures the intensity of specularly reflected X-rays, which strongly depends on the surface and near-surface electron density [17], as a function of incident angle.

Figure 4. A schematic representation of a reflectivity experiment where the incident angle and the reflected angle are the same [18].

If X-rays are incident from air onto a perfectly flat surface, they obey the Fresnel law of optics (see Section 2.2.1). In reality, interfaces are not infinitely perfect; instead, there always exists some roughness. Therefore, the reflectivity will depart from the Fresnel law, and the first Born approximation (see Section 2.2.2) is used to calculate the reflectivity.

2.2.1 Fresnel Equation

The index of refraction, n , for X-rays in matter is less than unity and is given by Equation 2 [6, 18].

$$n = 1 - \delta - i\beta \quad \text{Equation 2}$$

$$\text{where } \delta = \frac{e^2 \lambda^2}{2\pi m c^2} N_0 \frac{\rho_m (Z + f')}{A} = 2.70 \times 10^{-6} \left(\frac{Z + f'}{A} \right) \rho_m \lambda^2 \text{ and } \beta = \frac{\lambda \mu}{4\pi}.$$

Both δ and β represent the dispersion and absorption factor, respectively. N_0 is Avogadro's number, Z is the atomic number, A is the average atomic mass, m is the electron mass (0.000549 amu), c is the speed of light, ρ_m is the mass density (in g/cc),

f' is the average of the real part of the anomalous scattering factor, μ is the linear absorption coefficient, and λ is the X-ray wavelength (in Å).

Figure 5 shows that X-rays are incident from a medium with the refractive index of n_0 onto another medium with the refractive index of n_1 . The ratio of two refractive indices determines the angle at which radiation is refracted (θ_1) in comparison to the grazing incident angle (θ_0) by using Snell's law [16], as expressed in Equation 3.

$$n_0 \cos \theta_0 = n_1 \cos \theta_1 \quad \text{Equation 3}$$

If the interface between air and solid or liquid surface is of interest, then n_0 is equal to 1 ($\delta_0=0$ and $\beta_0=0$). As such, Equation 3 can be rewritten as Equation 4.

$$\cos \theta_1 = \frac{1}{n_1} \cos \theta_0 \quad \text{Equation 4}$$

Since the index of refraction for X-rays in matter is less than one ($n_1 < 1$), then θ_1 is less than θ_0 . Therefore, X-ray refraction occurs only when θ_0 is larger than the critical angle θ_c . The critical angle θ_c is the maximum angle at which total external reflection can take place and can be approximated by Equation 5 [18].

$$\theta_c = \sqrt{2(\delta_1 - \delta_0)} = \sqrt{2\delta_1} = \sqrt{\frac{e^2 \lambda^2}{\pi m c^2} N_0 \frac{\rho_m (Z + f')}{A}} \quad \text{Equation 5}$$

where δ_0 and δ_1 are dispersions in air and in the medium, respectively. From Equation 5, the critical angle depends on the wavelength of the radiation and the mass density of the medium. If the wavelength of X-ray is fixed, the mass density of the medium can be determined from the critical angle. In Equation 5, the critical angle θ_c is proportional

to $\sqrt{\rho_m}$. It can also be expressed in terms of the electron density of the medium, as given in Equation 6.

$$\theta_c = \lambda \sqrt{\frac{\rho_e r_e}{\pi}} \quad \text{Equation 6}$$

where ρ_e is the electron density and r_e is the classical electron radius

$$(r_e = \frac{e^2}{mc^2} = 2.818 \times 10^{-13} \text{ cm}) [9].$$

Figure 5. Schematic illustration of reflection and refraction of X-rays onto an interface between two materials [18].

In Figure 5, k_i and k_s are the incident and the scattered wavevectors, respectively.

The variable q is the scattering vector (momentum transfer vector) that equals to $k_s - k_i$.

For the specular reflection, q is perpendicular to the surface and has a magnitude of

$$\frac{4\pi}{\lambda} \times \sin \theta_0 [18]. \text{ The corresponding } q \text{ at critical angle } \theta_c \text{ is defined as } q_c. \text{ The electron}$$

density ρ_e can be rewritten in terms of the critical scattering vector q_c , as expressed in

Equation 7.

$$q_c^2 = 16\pi\rho_e \quad \text{Equation 7}$$

As illustrated in Figure 5 with a perfectly flat interface, the specular reflectivity R , ratio of X-rays reflected intensity to incident intensity, can be expressed by using the Fresnel equation shown as Equation 8.

$$R = R_F = |r_F|^2 \quad \text{Equation 8}$$

where R_F is the Fresnel reflectivity and r_F is the Fresnel reflection amplitude. For a small incident angle, the Fresnel reflection amplitude r_F can be calculated by using Equation 9 [18].

$$r_F = \frac{\theta_0 - \theta_1}{\theta_0 + \theta_1} = \frac{\theta_0 - [\theta_0^2 - \theta_c^2 - i(\beta_1 - \beta_0)]^{1/2}}{\theta_0 + [\theta_0^2 - \theta_c^2 - i(\beta_1 - \beta_0)]^{1/2}} \quad \text{Equation 9}$$

If the incident angle, θ_0 , is smaller than θ_c , the Fresnel reflectivity R_F is close to one and the X-rays are totally reflected [6, 18]. When θ_0 is at θ_c , the Fresnel reflectivity R_F drops sharply. When θ_0 is much larger than θ_c , the effect of β can be neglected [19]. As a result, the Fresnel reflectivity R_F can be approximated by using Equation 10.

$$R_F \approx \left(\frac{\theta_c}{2\theta_0}\right)^4 \quad \text{Equation 10}$$

When the incident angle increases, the reflectivity R_F decreases very rapidly with an exponential function of $(\theta_0)^{-4}$.

2.2.2 Born Approximation

Real interfaces have some roughness and a gradual change in the electron density. In order to calculate the reflectivity, the average of the electron densities over the specimen surface is taken into account using the Born approximation [18, 19]. The Born

approximation is only valid when the reflectivity is small, that is when θ_0 is much larger than θ_c . When reflectivity is small, the reflection amplitude, r , can be expressed as Equation 11.

$$r = r_F \int_{-\infty}^{\infty} \left(\frac{-1}{\rho_{-\infty}} \frac{d\rho(z)}{dz} \right) e^{-iqz} dz \quad \text{Equation 11}$$

where $\rho_{-\infty}$ is the electron density deep into the substrate, $\rho(z)$ is the average electron density, and q is the scattering vector [18]. By using an error function model, Equation 11 can be written as Equation 12.

$$r = r_F \exp\left[-\frac{1}{2}(\sigma \times q)^2\right] \quad \text{Equation 12}$$

where σ is the root-mean-square average of the interfacial width resulting from the microscopic roughness [18, 19].

Equation 12 is only valid when the Born approximation holds, which means the reflectivity is small, i.e., $\theta_0 \gg \theta_c$. When the reflectivity is approaching one, the reflection amplitude does no longer follow Equation 12. Equation 13 is then used to calculate the roughness in this situation.

$$r = r_F \exp\left[-\frac{1}{2} \times \sigma^2 \times q \times q_1\right] \quad \text{Equation 13}$$

where q_1 is the scattering vector in the material with the index of refraction n_1 and q_1 is equal to $\frac{4\pi}{\lambda} \times \sin \theta_1$ [18, 19].

The roughness effect can significantly decrease reflectivity, especially at high q regimes [8]. Figure 6 illustrates that increased roughness reduces reflectivity from silicon

surfaces with different surface roughness. The solid line and dash line in Figure 6 correspond to silicon root-mean-square roughness values of $1\text{\AA}$ and $10\text{\AA}$, respectively. As seen in Figure 6, reflectivity diminishes faster in silicon with larger root-mean-square roughness ($10\text{\AA}$) compared to that with a smoother surface ($1\text{\AA}$).

Figure 6. Logarithm (I/I_0) versus q of silicon substrates with different surface roughness [8].

2.2.3 Reflection from Several Stratified Layers

When X-rays are incident onto a specimen (thin film) of different material residing on the top of a substrate, there are two contributing factors to the reflectivity [6, 16 and 18]. One is from the thin film's external surface, while the other is from the interface between the film and the inner substrate. Figure 7 illustrates a specimen with thickness t (medium 1) on a substrate (medium 2) in contact with air (medium 0).

Figure 7. The schematic illustration of the beam path in a specimen with thickness, t , on a substrate [16].

The X-rays reflected from these two interfaces can interfere with each other. The reflectivity R can be expressed in Equation 14.

$$R = \left| \frac{r_{0,1} + r_{1,2} e^{-iq_1 t}}{1 + r_{0,1} r_{1,2} e^{-iq_1 t}} \right| \quad \text{Equation 14}$$

where $r_{0,1}$ and $r_{1,2}$ are the reflection amplitudes at the surface and interface, and t is thickness of the thin film.

Due to the difference in pathlength between the reflections at two interfaces, there is a modulation of the reflectivity, shown in Equation 14, directly related to the film thickness. The difference of pathlength results in interference fringes (constructive and destructive interference patterns) which cause oscillations in the reflectometry plot (logarithm reflectivity versus q or logarithm reflectivity versus θ_0). The oscillatory behavior is known as Kiessig fringes [8]. The thickness t is inversely proportional to the fringe periodicity (Δq) and can be determined by using Equation 15 [8, 16].

$$t = \frac{2\pi}{\Delta q} \quad \text{Equation 15}$$

Thickness can also be determined by using Fourier transform to convert the characteristic frequency of the Kiessig fringes [7, 20]. Surface/interface roughness can be calculated from Equation 12 or Equation 13 depending on whether the reflection amplitude is known. In addition, the reflection from the interface between the film and the substrate results in a second critical angle, which is the indication of substrate density (in most cases, silicon is chosen as the substrate).

To calculate the reflectivity for stratified materials consisting of several layers with different thickness, interfacial roughness, and electron densities, the recursive approach from classical optics can be used. This is a much more complicated situation, which will not be considered in this research. However, it has been described in detail elsewhere [17, 21] and is incorporated in the software such as the Philips X-Ray Reflectivity.

2.3 X-Ray Reflectivity Measurements of Thin Films

Figure 8 shows a typical XR curve, logarithm reflectivity versus incident angle, with indications of critical angle, second critical angle, slope (amplitude), and periodicity of fringes. The critical angle in Figure 8 is used to calculate the density of the thin film (Equation 5 or Equation 6), and the second critical angle is related to the substrate density. The thin film roughness can be determined from the slope or amplitude of Kiessig fringes (Equation 12 or Equation 13) and the fringe periodicity Δq can be used to calculate the thin film thickness (Equation 15).

Figure 8. A typical X-ray reflectivity curve, logarithm reflectivity versus incident angle [22].

2.3.1 Measurements of Thin Film Density

Figure 9 shows one example of X-ray reflectivity curve for a porous HSSQ thin film published by Wu et al. [7]. Notice that there were two sharp drops of reflectivity in Figure 9. The first drop occurred near $q=0.0155\pm0.0003 \text{ \AA}^{-1}$, and the second drop occurred near $q=0.0320\pm0.0006 \text{ \AA}^{-1}$. The second drop, $q=0.0320 \text{ \AA}^{-1}$, corresponded to the q_c of the Si substrate, while the first drop corresponded to that of the porous HSSQ thin film. The critical scattering vector q_c of the porous HSSQ thin film was smaller than that of Si, which was due to the lower ρ_e or ρ_m of the porous HSSQ thin film. By using Equation 7, the electron density ρ_e of the porous HSSQ thin film was calculated to be

$$1.693 \times 10^{23} / \text{cm}^3 \left(\rho_e = \frac{q_c^2}{16\pi r_e} = \frac{(0.0155 \times 10^8 \text{ cm}^{-1})^2}{16 \times \pi \times 2.818 \times 10^{-13} \text{ cm}} \right). \text{ Given the chemical}$$

composition of the film, the mass density ρ_m was able to be calculated since ρ_e is equal to $N_0 \rho_m \frac{Z}{A}$. Hence, the mass density ρ_m was calculated to be $0.55 \pm 0.01 \text{ g/cm}^3$.

Figure 9. X-ray reflectivity data showing the logarithm reflectivity as a function of q for a porous HSSQ thin film supported on a Si substrate [7].

2.3.2 Measurements of Thin Film Thickness

Instead of using Equation 15 to calculate thickness, Wu et al. [7] used Fourier transform to determine thin film thickness. Fourier transform can be performed by the software such as Microsoft Excel or Origins. Figure 10 shows Fourier transform of an XR curve for data in Figure 9 greater than $q = 0.035 \text{ \AA}^{-1}$. When q was larger than q_c of silicon ($q_c = 0.032 \text{ \AA}^{-1}$), the oscillations of fringes were resulting from the interferences between air/film and film/substrate interfaces. At lower q region ($q > 0.032 \text{ \AA}^{-1}$), the oscillations were not simply related to the thickness of the thin film due to the existence

of multiple scattering. Hence it was the best to determine thickness at higher q region, $q > 0.035 \text{ \AA}^{-1}$ in this example. The abscissa in Figure 10 is the frequency ($1/q$) in the transform, while the ordinate shows the strength of the period. The thickness (in $\text{\AA}$) of the porous HSSQ thin film was calculated by multiplying the period value at the peak ($f = 1488$) by 2π .

Figure 10. Fourier transform of an X-ray reflectivity curve for data in Figure 9 greater than $q = 0.035 \text{ \AA}^{-1}$ [7].

2.3.3 Measurements of Thin Film Roughness

The calculation of thin film roughness is much more complicated than density and thickness calculations. Fortunately, X'Pert Reflectivity provides a fitting program in which the roughness can be determined by fitting the XR curve [23].

2.3.4 Other Applications of X-Ray Reflectivity

The coefficient of thermal expansion (CTE) is defined as the ratio of change in thickness for a given unit change of temperature. The CTE, α , is defined by Equation 16.

$$\Delta t = \alpha \times t_1 \times \Delta T \quad \text{Equation 16}$$

where Δt is the thickness change due to the change of temperature ΔT , and t_1 is the reference thickness at the temperature T_1 .

Since XR is capable of calculating thickness of thin films from the fringe periodicity, thicknesses of thin films at different temperatures can also be determined by changing the experimental temperature [7, 20]. Hence, by plotting $\frac{\Delta t}{t_1}$ versus ΔT , the CTE can be determined from the linear regression fit of data.

Wu et al. [7] used Fourier transform to determine the thickness of the porous HSSQ thin film as a function of temperature. Before each measurement, the specimen was held at each temperature for at least an hour to reach equilibrium. The thickness determined at each temperature was plotted in Figure 11. There were two runs of measurements on the same specimen, as indicated in Figure 11 solid and open circles. The range of error bars in Figure 11 was unknown. The CTE of the porous HSSQ thin film was determined to be $(60 \pm 20) \times 10^{-6}/^\circ\text{C}$. However, $\frac{\Delta t}{t_1}$ versus ΔT plot was not provided.

Figure 11. Film thickness, taken from the position of the Fourier transform peak, versus temperature [7].

Not only is XR capable of measuring thin film density, thickness and surface/interface roughness, but it is also capable of characterizing multilayer (lamellar) structures of thin films from the observation of Bragg peaks [24]. Due to the interferences of constructive and destructive X-ray beams reflected from each layer within thin films, the Bragg peaks can be used to determine the thickness of the layer.

2.4 X-Ray Porosimetry

Pore morphologies including porosity, pore size, and pore distribution of nanoporous thin films are also important parameters that need to be characterized. Due to the capabilities of XR in determining thin film properties, porosimetry can work in conjunction with XR to characterize pore morphologies.

2.4.1 Theories of Porosimetry

Porosimetry is based on the amount of surface adsorption and/or condensation of vapor inside the porous media. The porous specimen is first sealed in a vessel of fixed volume. The vessel is then filled with a known quantity of vapor. Given the fixed volume of the vessel and the known volume of vapor, the partial pressure of vapor can be defined. When the partial pressure is increased up to certain values, after a few monolayers of gas are adsorbed onto the pore walls, the vapor starts to condense inside the smallest pores. This effect was first described by Zsigmondy, using the concept of capillary condensation proposed by Thompson [8].

Capillary condensation can be analyzed by the Kelvin equation, known as Equation 17. The Kelvin equation relates the critical pore radius to capillary condensation, r_k , to partial pressure P , equilibrium vapor pressure P_0 , liquid surface tension γ and molar volume of the liquid V_m over a flat liquid surface at temperature T (absolute temperature) [9].

$$r_k = \frac{2V_m\gamma}{-RT \ln(P/P_0)} \quad \text{Equation 17}$$

where R is an ideal gas constant.

The International Union of Pure and Applied Chemistry (IUPAC) has proposed classifying pore sizes and gas adsorption isotherms, which reflect the relationship between pore sizes and adsorption [25]. Pores are classified into three groups according to the pores' diameter: micropores, mesopores, and macropores. Micropores have diameters less than 2 nm, mesopores have diameters between 2 and 50nm, and

macropores have diameters larger than 50 nm. IUPAC has also classified adsorption isotherms into six types, as illustrated in Figure 12. The vertical axes, q_{ads} , in Figure 12 are the amount of vapor being adsorbed, while the horizontal axes, P/P_0 , are the relative pressure.

Figure 12. Illustration of the six types of gas adsorption isotherms that classified by IUPAC [25].

In Figure 12, a sharp increase in adsorption during a low partial pressure, like type I, II, IV, and VI, is usually an indication of enhanced or favorable interactions between adsorbent and adsorbate, as opposed to type III and V where the interactions are weak. The six types of adsorption isotherms represent the characteristic of adsorbents. Type I exhibits the characteristic of micropore filling, type II, III, and VI exhibit the

characteristic of macropore filling, and type IV and V exhibit mesopore filling. The hysteresis loops in type IV and V are a signature of capillary condensation in the mesopores. Type VI isotherm is discrete in steps that represent a stepwise multilayer adsorption on macropores.

2.4.2 Concept of X-Ray Porosimetry

X-ray porosimetry (XRP) is a technique which combines XR measurements with the mechanism of porosimetry so that the vapor uptake as a function of partial pressure can be monitored. The density changes in porous thin films due to vapor uptake can be measured via XR. Capillary condensation of the solvent vapor introduced into a vessel results in an increase in porous thin film density. The porosity can thus be defined as those pores filled by the solvent [10]. The average density of a thin film ρ_{ave} , which is related to the porosity and matrix density, can be calculated by Equation 18 and Equation 19 [10].

$$\rho_{ave} = \rho_w \times (1 - P) \quad \text{Equation 18}$$

$$\rho_{ave, solvent} = \rho_w \times (1 - P) + \rho_{solvent} \times P \quad \text{Equation 19}$$

where ρ_w , P , $\rho_{ave, solvent}$, and $\rho_{solvent}$ denote the density of the wall material between the pores, porosity, average mass density of a porous thin film saturated under solvent vapor, and average mass density of the solvent, respectively. The wall density (ρ_w) calculated from Equation 18 and Equation 19 is an average of the wall material and any unfilled pores such as closed pores or pores smaller than the solvent molecules.

X-ray porosimetry has been widely used to study density changes as a function of partial pressure of low-k nanoporous thin films [8-11]. Lee et al. [11] have been using XRP to characterize ultra low-k nanoporous thin films. Figure 13 shows a series of XR data as a function of toluene partial pressure for an ultra low-k nanoporous HSSQ thin film. As shown in Figure 13, the critical scattering vector q_c shifted to higher angles as partial pressure increased, which indicated an increased average film density as toluene condensed progressively into larger pores. From the differences of measured critical angles between vacuum ($P/P_0=0.00$) and saturated ($P/P_0=1.00$) curves, the porosity was calculated to be 46%. The wall density, ρ_w , was determined to be 0.98g/cm^3 .

Figure 13. X-ray porosimetry curves of a nanoporous HSSQ thin film at varying toluene partial pressure [11].

2.5 Summary

In order to replace interlayer dielectrics (ILD) with ultra low-k materials, nanoporous thin films are necessary. Nanoporous silsesquioxane thin films are promising

candidates that meet criteria of ILD materials with expected dielectric constants around 1.7-2.2.

X-ray reflectivity (XR) is a powerful nondestructive technique, which is able to determine thin film density, thickness, and surface/interface roughness with excellent accuracy. It also allows on-wafer measurements to be performed. Because of high accuracy on thickness measurements, X-ray reflectivity is proven to be capable of determining CTE of nanoporous thin films. Multilayer structures within thin films can also be characterized from the observation of Bragg peaks. Pore morphologies including porosity, pore size, and pore distribution can further be determined using XR with the porosimetry mechanism (i.e., XRP) by means of solvent adsorption.

CHAPTER THREE RESEARCH HYPOTHESES

3.1 Research Hypotheses

The hypotheses of this thesis are: First, X-ray reflectivity, XR, is capable of determining nanoporous thin film (thickness less than 1000Å) properties, including density, thickness and coefficient of thermal expansion (CTE). Second, X-ray reflectivity can confirm a lamellar structure within a nanoporous thin film, such as a perforated lamellar structure, based on the observed Bragg peaks. Third, with a higher weight percentage porogen loading of a nanoporous thin film, the critical angle (or the critical scattering vector) shifts to a lower angle (or a lower scattering vector) region. Fourth, a higher weight percentage porogen loading will result in a higher volume fraction of pores, which leads to a lower density of a nanoporous thin film.

3.2 Research Objectives

The primary objectives of this research are to employ Philips X'Pert diffractometer to characterize nanoporous thin film properties, including density and thickness, and demonstrate the equipment capability of determining CTE of thin films. Thin films being characterized are nanoporous organosilicates generated by removing organic components from organic-inorganic phase separation. The secondary objective is to characterize nanoporous thin films with lamellar structures (porous layer between organosilicates layers oriented parallel to the surface) by X-ray reflectivity. The thickness of the layers is determined based on the observation of Bragg peaks. Finally,

nanoporous thin films prepared from the same porogen but with different weight percent loading are characterized in order to link thin film properties to the weight percentage porogen loading.

CHAPTER FOUR RESEARCH APPROACH

4.1 Specimen Preparations

All specimens were custom made at IBM Almaden Research Center, San José, California. Two copolymers, linear-dendritic and linear-linear diblock copolymers, were used as porogens and mixed with organosilicates to create nanoporous thin films.

4.1.1 Porogen Preparations

Structure-directing agents, amphiphilic linear-dendritic copolymers based on polyethylene oxide (PEO) and 2,2'-bis(hydroxymethyl) propionic acid (bis MPA), were used for organosilicates to generate a unique perforated porous lamellar structure. Polyethylene oxide hydroxyl functional oligomers (molecular weight 4800 and 9800 g/mol with polydispersity of 1.03 and 1.05, respectively) were chosen as the linear component of the copolymer, whereas dendrons were derived from bis MPA. The higher the generation of bis MPA dendrons (longer block length and higher molecular weight), the bigger the molecules are and the bigger the size of the pores that are generated. Polyethylene oxide had been shown to be miscible with the organosilicate prepolymer over a wide compositional and molecular weight range, while bis MPA decomposed cleanly and quantitatively upon thermolysis and left porous structures.

Hydroxy terminated PEOs were used as scaffolds for the divergent growth of dendrons using acetonide-protected bis MPA anhydride. Acetonide-protected bis MPA anhydride was generated from the self-condensation of the acetonide protected bis MPA

using N,N'-dicyclohexylcarbodiimide (DCC) (0.25 mol% with respect to anhydride), in the presence to dimethyl amino pyridine (DMAP) in CH₂CCl₂/pyridine solvent mixture (90/10). The reaction was performed at room temperature for approximately 15 to 18 hours under a nitrogen atmosphere. Deprotection of the acetonide groups was accomplished using DOWEX 50W-X2 in methanol at 50°C for 5 hours. The deprotection procedure created the 1st generation of bis MPA dendrons “block length” and it was repeated for each generation. For both PEO molecular weights 4800 and 9800 g/mol, up to the 5th generation of bis MPA dendrons “block length” in the copolymers were produced. The 4th and 5th generations showed interesting structures when they were mixed with organosilicates to generate nanoporous thin films. Figure 14 shows the chemical structure of the 4th generation linear-dendritic copolymers. The 1st to 4th generations are indicated as G1, G2, G3, and G4.

Figure 14. Chemical structure of the 4th generation PEO-bis MPA (linear-dendritic) copolymer.

Another structure-directing agent, amphiphilic linear-linear diblock copolymer, based on polystyrene-block-polyethylene oxide (PS-b-PEO) was used. The PS-b-PEO copolymer was commercially available. Their molecular weights were set at 20,000 (20K) g/mol. Figure 15 shows the chemical structure of a linear-linear diblock copolymer PS-b-PEO.

Figure 15. Chemical structure of a linear-linear diblock PS-b-PEO copolymer.

4.1.2 Nanoporous Thin Films Prepared by Sacrificial Templates

The amphiphilic copolymers PEO-bis MPA and PS-b-PEO were each dissolved in a solution containing methyl silsesquioxanes (MSSQ) prepolymer (commercially available) in propylene glycol monomethyl ether. The resulting solution was spun on a 1 inch diameter silicon wafer with a spin rate of 3000 rpm for 30 seconds to produce thin films. Then the thin films (along with the wafers) were placed onto a 50°C hot plate under argon environment. The temperature was increased to 430°C at a rate of 5°C/min and held at 430°C for 2 hours followed by cooling. The thin films were cured at 430°C to effect network formation of the MSSQ and to decompose the sacrificial copolymer template that created nanoporous thin films.

The nanoporous thin films prepared from linear-dendritic copolymers, including PEO (4800 g/mol) with bis MPA (G4) and bis MPA (G5) and PEO (9800g/mol) with bis MPA (G4) and bis MPA (G5), are summarized in Table 5. Table 5 summarizes the names of nanoporous thin films that were generated by different combinations of PEO molecular weight (4800 and 9800 g/mol) and dendron generation (4th and 5th). The weight percentage of prepolymer and porogen loadings is also included in Table 5. The weight percentage of PS-b-PEO porogen loading was 20% with respect to MSSQ prepolymer. The nanoporous thin film prepared from PS-b-PEO copolymer was marked as MSSQ/PS-b-PEO (80/20).

Table 5. The characteristics of nanoporous thin films used in the experiments.

Name	Prepolymer/ Wt. % Loading	Porogen ID/ Wt. % Loading	PEO Mn (g/mol)	Dendron Generation/ Mn (g/mol)
MSSQ/PEO5K_G4 (90/10)	MSSQ/ 90%	PEO5K_G4/ 10%	4800 (5K)	4/ 4030
MSSQ/PEO5K_G4 (60/40)	MSSQ/ 60%	PEO5K_G4/ 40%	4800 (5K)	4/ 4030
MSSQ/PEO5K_G4 (40/60)	MSSQ/ 40%	PEO5K_G4/6 0%	4800 (5K)	4/ 4030
MSSQ/PEO5K_G5 (80/20)	MSSQ/ 80%	PEO5K_G5/ 20%	4800 (5K)	5/ 8200
MSSQ/PEO5K_G5 (60/40)	MSSQ/ 60%	PEO5K_G5/ 40%	4800 (5K)	5/ 8200
MSSQ/PEO10K_G4 (60/40)	MSSQ/ 60%	PEO10K_G4/ 40%	9800 (10K)	4 /4030
MSSQ/PEO10K_G5 (60/40)	MSSQ/ 60%	PEO10K_G5/ 40%	9800 (10K)	5/ 8200

4.2 X-Ray Reflectometer Operation Procedures

The experiments were conducted using the Philips X'Pert diffractometer, which functioned as a reflectometer, located at the IBM Almaden Research Center, San José, California.

4.2.1 Apparatus Configurations

X-ray reflectivity measurements were performed in a θ - 2θ configuration with a fine focus copper X-ray tube. The X-rays were generated by bombarding a copper target with 40 keV electrons. The emitted X-ray ($\text{Cu-K}\alpha_1$) with wavelength of $1.54 \text{ \AA}$ was used.

In the θ - 2θ configuration, the specular condition was maintained by rotating the specimen at an angle of θ ($=\omega$) while the detector simultaneously moved 2θ with respect to the X-ray source, as illustrated in Figure 16. In Figure 16, capital S and D represent the X-ray source and the detector.

Figure 16. The illustration of specular reflection where the incident angle $\omega = (2\theta/2) = \theta$ = reflected angle.

X-ray reflectivity data were collected at grazing incident angles ranging from 0.05° to 1.5° with a minimum step size of 0.0001° in θ . The operating temperature was $(25 \pm 1)^\circ\text{C}$.

4.2.2 Procedures for Specimen Alignment

Once the specimen was mounted into the X-ray reflectometer, X-ray optics needed to be aligned. The first step was to determine the $2\theta=0^\circ$ position where the X-ray source was focused directly at the detector. The position was defined by scanning the range of 2θ values to find the peak position of the direct X-ray beam. The $2\theta=0^\circ$ position was calibrated to coincide with the peak position of the direct beam. The peak intensity was marked as I_p . There should be nothing obstructing the beam path of X-rays toward the detector.

The second step was to adjust the specimen height (z direction) until the beam intensity was equal to $I_p/2$. This step moved the specimen to bisect the X-ray beam.

The third step was to scan the ω position to align the sample to the X-ray source and the detector. The $\omega=0^\circ$ position was defined at the peak position of ω scan. The peak intensity (I_m) should be roughly equal to $I_p/2$.

To fine-tune the alignment, the second and third steps needed to be repeated 2 to 3 times in order to ensure the X-ray source, the specimen, and the detector were aligned along the same line. The specimen should bisect the X-ray beam.

4.2.3 Aligning Procedures for Changing Experimental Temperature

Once the specimen was mounted on the sample stage, a dome made of PEEK (a synthetic material based on polyetheretherketone resin) was used to cover the specimen; thereby, the temperature inside the dome could be maintained. Inside the dome, inert gas nitrogen was supplied to avoid specimen oxidation and any other chemical reactions that occurred at high temperatures. The specimen had to be fully sealed inside the dome. In order to avoid over heating the dome, cooling gas (dry air) was required, especially at temperatures higher than 200°C. The specimen was finally set at the desired temperature and kept for 10 minutes until the state of equilibrium was reached. The specimen was aligned after 10 minutes. The objective of the aligning procedures was the same as described in section 4.2.2.

The nanoporous thin film, MSSQ/PS-b-PEO (80/20) was heated from 40°C to 260°C and the XR data were collected every 20°C. The specimen had to be aligned before each measurement was started. The CTE measurements were determined as per heat treatment of MSSQ/PS-b-PEO (80/20) with respect to the temperature gradient, such as 40°C, 60°C, and 80°C.

CHAPTER FIVE EXPERIMENTAL RESULTS

5.1 X-Ray Reflectivity Measurements

Figure 17 shows logarithm (Reflectivity), $\log(R)$, versus scattering vector (q) curves of nanoporous thin films generated by different PEG block lengths (4800 and 9800) and different generation of dendrons (the 4th and 5th generation). The weight percentage porogen loadings were 40%. The critical scattering vectors, q_c s, were determined from the position where the reflectivity started to drop sharply. The critical scattering vectors were determined to be 0.01995 $\text{\AA}^{-1}$, 0.01868 $\text{\AA}^{-1}$, 0.01861 $\text{\AA}^{-1}$, and 0.01829 $\text{\AA}^{-1}$ for nanoporous thin films MSSQ/PEO5K_G5 (60/40), MSSQ/PEO10K_G5 (60/40), MSSQ/PEO5K_G4 (60/40), and MSSQ/PEO10K_G4 (60/40), which corresponded to densities of 0.91957 g/cm^3 , 0.80622 g/cm^3 , 0.80019 g/cm^3 , and 0.77291 g/cm^3 , respectively. In Figure 17, the reflectivity curves of MSSQ/PEO10K_G5 (60/40), MSSQ/PEO5K_G4 (60/40) and MSSQ/PEO10K_G4 (60/40) at high q regions ($q > 0.1 \text{\AA}^{-1}$) were cut off. The reason was due to the fact that the intensity of reflected X-rays was too low. In order to increase the intensity of reflected X-rays, the exposure time has to be increased.

Figure 17. Log (R) versus q reflectivity curves of nanoporous thin films prepared from different linear-dendritic porogens with 40% loading.

The specimens prepared with porogens of the 5th generation dendrons showed Bragg peaks in Figure 17, which indicated dominant orientation of pores parallel to the surface. For MSSQ/PEO5K_G5 (60/40) and MSSQ/PEO10K_G5 (60/40), the spacing determined from the first Bragg peaks ($q=0.05865 \text{ \AA}^{-1}$ and $0.04897 \text{ \AA}^{-1}$, respectively) was around 10 nm and 13 nm ($2\pi/q$), respectively. Analysis of higher order peaks suggested the specimens prepared with PEO5K_G5 and PEO10K_G5 had layers of MSSQ with a thickness of approximately 6 nm and 9 nm, respectively, and layers of pores with a thickness of 4 nm for both specimens. However, there were no Bragg peaks shown for specimens generated from porogens with the 4th generation dendrons, MSSQ/PEO5K_G4 (60/40) and MSSQ/PEO10K_G4 (60/40).

Figure 18 shows log (R) versus q curves of MSSQ/PEO5K_G4 specimens with three different porogen loadings, 10%, 40%, and 60%. As seen in Figure 18, the critical scattering vector shifted to a lower q region when the weight percentage porogen loading increased. The densities determined from the critical scattering vectors ($0.02265 \text{ \AA}^{-1}$, $0.01861 \text{ \AA}^{-1}$, and $0.01542 \text{ \AA}^{-1}$) were 1.18532 g/cm^3 , 0.80019 g/cm^3 , and 0.54938 g/cm^3 for specimens with 10%, 40%, and 60% porogen loadings, respectively. For this porogen, 40% loading showed a secondary structure within the thin film, as shown by the broad peak around $q=0.06 \text{ \AA}^{-1}$. However, the structure was not well defined compared to that of the porogens with the 5th generation dendrons. Due to the roughness on the surface of MSSQ/PEO5K_G4 (40/60), the fringes were unclear, shown as the green curve in Figure 18, and the thickness could not be determined.

Figure 18. Log (R) versus q reflectivity curves of MSSQ/PEO5K_G4 (90/10), (60/40), and (40/60) nanoporous thin films.

Figure 19 shows log (R) versus q curves of MSSQ/PEO5K_G5 specimens with two different weight percentage porogen loadings, 20% and 40%. In Figure 19, the critical scattering vector shifted to the lower q region as weight percentage porogen loading increased from 20% to 40%. The critical scattering vectors were determined to be $0.02117 \text{ \AA}^{-1}$ and $0.01995 \text{ \AA}^{-1}$, which corresponded to densities of 1.03548 g/cm^3 and 0.91957 g/cm^3 , for specimens with 20% and 40% porogen loadings, respectively.

Figure 19. Log (R) versus q reflectivity curves of MSSQ/PEO5K_G5 (80/20) and (60/40) nanoporous thin films.

Thin film properties including critical angles, critical scattering vectors, thicknesses and densities of nanoporous thin films generated by linear-dendritic copolymers are summarized in Table 6.

Table 6. Material properties of nanoporous thin films prepared from linear-dendritic porogens.

Name	θ_c (°)	q_c ($\text{\AA}^{-1}$)	t (nm)	ρ_m (g/cm ³)
MSSQ/PEO5K_G4 (90/10)	0.15904	0.02265	206.75	1.18532
MSSQ/PEO5K_G4 (60/40)	0.13067	0.01861	188.01	0.80019
MSSQ/PEO5K_G4 (40/60)	0.10827	0.01542	N/A	0.54938
MSSQ/PEO5K_G5 (80/20)	0.14865	0.02117	836.64	1.03548
MSSQ/PEO5K_G5 (60/40)	0.14008	0.01995	587.21	0.91957
MSSQ/PEO10K_G4 (60/40)	0.12842	0.01829	224.00	0.77291
MSSQ/PEO10K_G5 (60/40)	0.13116	0.01868	209.21	0.80622

5.2 Coefficient of Thermal Expansion Determined by X-Ray Reflectivity

The X-ray reflectivity data were collected every 20°C from 40°C to 260°C on the MSSQ/PS-b-PEO (80/20) nanoporous thin film. The X-ray reflectivity curves, known as log (R) versus q curves, at each temperature are shown in Figure 20. As seen in Figure 20, Kiessig fringes shift to a lower q region as the temperature increases.

Figure 20. Log (R) versus q reflectivity curves of MSSQ/PS-b-PEO (80/20) collected at different temperatures, from 40°C to 260°C.

The thicknesses determined at each temperature are tabulated in Table 7. At 40°C, the thickness was calculated to be 86.47 nm, while at 260°C, the thickness was 87.47 nm. The thicknesses at each temperature was determined by averaging three fringe periodicities ranging from $q=0.04 \text{ \AA}^{-1}$ to $0.07 \text{ \AA}^{-1}$ ($2\pi/\Delta q$). The thickness changes associated with the temperature treatment can be seen in Table 7.

Table 7. The thicknesses of MSSQ/PS-b-PEO (80/20) at different temperatures determined by XR.

Temperature (°C)	Thickness (nm)	Temperature (°C)	Thickness (nm)
40	86.47	160	87.15
60	87.31	180	87.02
80	87.51	200	87.35
100	87.06	220	87.88
120	87.71	240	87.59
140	87.31	260	87.47

Figure 21 shows the fractional thickness change versus the temperature gradient of the MSSQ/PS-b-PEO (80/20) nanoporous thin film. The subscript 2 in Figure 21 represents the thickness determined at various temperatures (from 40°C, 60°C, 80°C... to 260°C) and the subscript 1 represents the thickness measured at the starting temperature, 40°C. The red line in Figure 21 is the linear regression fit of the fractional thickness change per temperature gradient, which represents the CTE of the specimen. The CTE of MSSQ/PS-b-PEO (80/20) was determined to be around $31 \times 10^{-6}/^{\circ}\text{C}$.

Figure 21. The fractional thickness change versus the temperature gradient of the MSSQ/PS-b-PEO (80/20) nanoporous thin film where the slope is the linear regression fit and gives the CTE of $31 \times 10^{-6}/^{\circ}\text{C}$.

CHAPTER SIX DISCUSSION

6.1 Effect of Molecular Weight

Bragg peaks were only observed for the copolymer having the 5th generation dendrons, irrespective of PEO molecular weights (4800 g/mol or 9800 g/mol). As seen in Figure 17, Bragg peaks were only observed for nanoporous thin films generated by porogens PEO5K_G5 and PEO10K_G5, whereas no Bragg peaks were observed in porogens PEO5K_G4 and PEO10K_G4.

Figure 22 (a) and (b) are schematic representations of internal structures of MSSQ/PEO5K_G5 (60/40) and MSSQ/PEO10K_G5 (60/40), respectively. In Figure 22 (a), the thicknesses of the MSSQ and the porous layers were around 6 nm and 4 nm, which were determined from the second and third order Bragg peaks, with a total thickness of approximately 10 nm (as determined from the first order Bragg peak). In Figure 22 (b), the thickness of the MSSQ layer in MSSQ/PEO10K_G5 (60/40) was about 9 nm (determined from the second order Bragg peak), which was thicker than that in MSSQ/PEO5K_G5 (60/40) (about 6 nm). From the first order Bragg peak of MSSQ/PEO10K_G5 (60/40), the combined thickness of the MSSQ layer and the porous layer was approximately 13 nm. Without higher order (third) Bragg peaks observation, the thickness of the porous layer was predicted to be 4 nm ($13\text{nm} - 9\text{nm} = 4\text{nm}$).

Figure 22. Schematic representations of porous MSSQ layers oriented parallel to the surface, where (a) represents MSSQ/PEO5K_G5 (60/40) and (b) represents MSSQ/PEO10K_G5 (60/40).

The specimen prepared from the higher PEO molecular weight (PEO10K) porogen resulted in a thicker MSSQ layer, which was proved from the shift of second order Bragg peak (from $0.11226 \text{ \AA}^{-1}$ to $0.09343 \text{ \AA}^{-1}$). On the other hand, the specimens MSSQ/PEO5K_G5 (60/40) and MSSQ/PEO10K_G5 (60/40) were prepared with the same generation dendron (G5). Hence, the thicknesses of the porous layers were the same (around 4 nm).

Transmission electron microscopy (TEM) micrographs of nanoporous thin films MSSQ/PEO5K_G5 (80/20) and (60/40) are shown in Figure 23 (a) and (b). The reference length in Figure 23 (a) is equal to 50 nm, while that in Figure 23 (b) is equal to 20 nm. The lamellar structure was clearly seen in Figure 23 (b) that porous layers (white colored layers) and MSSQ layers (gray colored layers) were oriented parallel to the surface. The observation of layered structure highly corresponded to a Bragg's condition characterized by XR. The thickness calculation based on Bragg peaks was consistent with thickness measured in Figure 23 (b). In Figure 23 (a), instead of seeing the porous

lamellar structure, pores were randomly distributed within the MSSQ matrix. Therefore, there were no Bragg peaks revealed on the XR plot for MSSQ/PEO5K_G5 (80/20).

Figure 23. TEM micrographs of MSSQ/PEO5K_G5 nanoporous thin films with (a) 20% and (b) 40% porogen loadings.

6.2 Effect of Porogen Amount

Nanoporous thin films generated from the same porogen with different weight percentage loadings resulted in different material properties. The more weight percentage porogen loading of a thin film, the lower the critical angle (θ_c) or the critical scattering vector (q_c) was obtained by XR.

6.2.1 Linear-Dendritic Copolymer with the 4th Generation Dendron

The weight percentage porogen loadings of PEO5K_G4 were 10%, 40%, and 60%. The nanoporous thin film MSSQ/PEO5K_G4 with 60% porogen loading had the smallest q_c value. The densities of specimens with 10%, 40%, and 60% porogen loadings were determined to be 1.18532 g/cm³, 0.80019 g/cm³, and 0.54938 g/cm³, respectively. The more weight percentage porogen loading, the higher volume fraction of pores. As a result, a less dense nanoporous thin film was measured.

The thickness of MSSQ/PEO5K_G4 (40/60) was unable to be calculated. The reason was due to the surface roughness. With 60% porogen loading, the porosity might be too high that the thin film could not withstand the mechanical strength resulting in cracks on the surface. This could significantly increase root-mean-square surface roughness and further reduce the intensity of reflected X-rays. Therefore, the periodic fringes were not obtained from the XR curve.

6.2.2 Linear-Dendritic Copolymer with the 5th Generation Dendron

The weight percentage of the porogen PEO5K_G5 loadings were 20% and 40%. The critical scattering vector, q_c , of MSSQ/PEO5K_G5 (80/20) was 0.02117 Å⁻¹, and it shifted to a lower q region (q_c = 0.01995 Å⁻¹) as the weight percentage porogen loading increased to 40%. The density of MSSQ/PEO5K_G5 (60/40) was less dense than MSSQ/PEO5K_G5 (80/20), and the respective densities were 0.91957 g/cm³ and 1.03548 g/cm³.

For 40% porogen loading, strong peaks satisfying Bragg's condition were observed, which indicated lamellar structures of pores oriented parallel to the surface. The first order peak corresponded to the periodic structure of around $107\text{\AA}$ ($2\pi/q$, where $q=0.05865\text{\AA}^{-1}$). However, one could not observe Bragg peaks with 20% porogen loading, which meant that the lamellar structure did not exist in the MSSQ/PEO5K_G5 (80/20) thin film. The main reason was due to the insufficient copolymer to form a perforated porous layer. Hence, the weight percentage porogen loading did play an important role on the lamellar structure.

6.3 Coefficient of Thermal Expansion

The CTE of MSSQ/PS-b-PEO (80/20) was determined to be $31\times 10^{-6}/^{\circ}\text{C}$. The determined CTE was satisfied by the thermal properties ($\text{CTE}<50\times 10^{-6}/^{\circ}\text{C}$) of low-k ILD materials. The R^2 value of the linear regression fits in Figure 21 was only ~ 0.27 , which meant that the linear regression did not fit the data well (when R^2 value is close to one, it means there is an excellent fit). Even though the CTE might lack accuracy, the thickness changes as a function of temperature could still be observed in Figure 20 due to the shift of the Kiessig fringes.

6.4 Improvement

Only one XR measurement was conducted on each nanoporous thin film. Therefore, the statistical results cannot be provided in this thesis. For future study, it is

suggested that at least three measurements on a single specimen should be conducted in order to provide statistical analysis on material properties such as a standard deviation.

In CTE measurement, it would be beneficial if the nanoporous thin film could be heated up to a higher temperature ($>400^{\circ}\text{C}$). Hence, one can examine whether the nanoporous thin film can withstand high temperature treatment without decomposition during the back-end IC manufacturing processes. Since the resolution of XR is 1.0 nm, it would be better to measure the nanoporous thin film with a higher CTE. The thickness change as a function of temperature would be larger (more than 1.0 nm). As such, X-ray reflectivity can determine the thickness at each temperature with more accurate results.

CHAPTER SEVEN CONCLUSIONS

In this thesis, X-ray reflectivity (XR) was applied to determine material properties, including density, thickness, and CTE of nanoporous organosilicates thin films. X-ray reflectivity also revealed the structural information, i.e., the lamellar structure of nanoporous thin films from the observation of Bragg peaks.

Among nanoporous thin films prepared from linear-dendritic copolymers, Bragg peaks were only observed for those generated from the 5th generation dendrons, irrespective of the PEO block length (molecular weight 4800 and 9800 g/mol). The expected lamellar structure was confirmed with the TEM image which showed a well-developed multilayered structure within the thin film comprised of alternating MSSQ and porous layers oriented parallel to the surface. For the MSSQ/PEO5K_G5 (60/40) nanoporous thin film, the porous layer (4 nm) between MSSQ layers (6 nm) calculated from XR was verified from the TEM image. Strong first order and weak second order Bragg peaks were also observed for the MSSQ/PEO10K_G5 (60/40) nanoporous thin film. The first order Bragg peak corresponded to an alternating bi-layer (MSSQ and porous layers) with a thickness of around 13 nm. The thickness determined from the second order Bragg peaks was around 9 nm, which was assumed to be the thickness of an MSSQ layer. Without the information of the third order Bragg peak, the thickness of a porous layer was predicted to be about 4 nm.

The amount of porogen does play an important role in the lamellar structure. Bragg peaks were only observed for the MSSQ/PEO5K_G5 nanoporous thin film with 40% porogen loading, and they were not observed for that with 20% porogen loading.

The structures of two nanoporous thin films were shown from the TEM images. For MSSQ/PEO5K_G5 (80/20), the nanometer-sized pores were randomly distributed within the MSSQ matrix, while the pores for MSSQ/PEO5K_G5 (60/40) created in lamellar porous layers were oriented parallel to the surface.

The more weight percentage porogen loading of a nanoporous thin film, the smaller critical angle/critical scattering vector would result. The thin film was less dense due to the higher volume fraction of pores generated from the higher weight percentage porogen loading. These hypotheses were consistent with the experimental results. For instance, among MSSQ/PEO5K_G4 nanoporous thin films with 10%, 40% and 60% porogen loadings, the density of the MSSQ/PEO5K_G4 (40/60) nanoporous thin film was the least dense ($\rho_m=0.54938 \text{ g/cm}^3$), whereas the MSSQ/PEO5K_G4 (90/10) nanoporous thin film had the highest density ($\rho_m=1.18532 \text{ g/cm}^3$). Furthermore, the density of MSSQ/PEO5K_G5 (60/40) ($\rho_m=0.91957 \text{ g/cm}^3$) was lower than that of MSSQ/PEO5K_G5 (80/20) ($\rho_m=1.03548 \text{ g/cm}^3$).

The CTE of MSSQ/PS-b-PEO (80/20) was determined by XR via measuring thin film thicknesses at different temperatures. The CTE was determined to be $31 \times 10^{-6}/^\circ\text{C}$ from 40°C to 260°C . The determined CTE has met the requirement of ILD materials, which should be less than $50 \times 10^{-6}/^\circ\text{C}$.

CHAPTER EIGHT FUTURE STUDY

Pore morphologies of nanoporous organosilicates thin films could be a good field for future study of X-ray porosimetry. A controlled chamber with the capability of controlling environmental variables can be designed and constructed. Various processing parameters such as temperature, pressure, solvent type and gas type can be studied in this chamber to help determine their influence on the measurements. Using XR with the controlled chamber, X-ray porosimetry, pore morphologies including porosity and pore size of nanoporous organosilicates thin films can be determined. By increasing the partial pressure of an organic solvent vapor in the chamber, the pores can attract the condensed solvent vapor. This will result in a larger critical angle (θ_c) and an increment in thin film density. A larger difference between critical angles measured in vacuum condition and saturated vapor pressure condition on the reflectivity curve indicates a larger porosity of a thin film.

This experiment can be conducted by mounting the nanoporous thin film in the X-ray reflectometer and evacuating for a period of time. X-ray reflectivity data of thin films can first be collected in order to determine the critical angle in a vacuum environment ($P/P_0=0$). The partial pressure inside the chamber has to be increased up to the saturation point ($P/P_0=1$) and XR curves at different organic solvent partial pressures can be generated. The average density changes of nanoporous organosilicates thin films as a function of solvent partial pressure can be studied. Moreover, by comparing the reflectivity curves in vacuum and at saturation pressures, the porosity of nanoporous organosilicates thin films can be determined.

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APPENDIX A INTERCONNECT RC DELAY

Figure 24 shows a general cross section of the interconnect system. Interconnect RC delay can be expressed by Equation 20 [2].

$$RC = 2\rho k\epsilon_0 \left(\frac{4L^2}{P^2} + \frac{L^2}{T^2} \right) \quad \text{Equation 20}$$

where ρ is the interconnect resistivity (2.2 $\mu\Omega\text{-cm}$ for copper), k is the dielectric constant of ILD, ϵ_0 is the permittivity in vacuum, L , P , and T are the interconnect line length, spacing and thickness, respectively.

Figure 24. Interconnect system with parasitic capacitances [2].

As technology progresses, feature size shrinks and P and T in Equation 20 get smaller and smaller, resulting in an increment RC delay. The line length L of global interconnects also increases because the chip area usually keeps increasing, which forces L to increase in order to connect all the devices. As a result, a lower dielectric constant of ILD is desired for future technology generation.

APPENDIX B LOW-K ILD DESIRED PROPERTIES

Table 8. Desired properties of low-k ILD materials [3].

Electrical	Chemical	Mechanical	Thermal
Isotropic $k < 3$ at 1 MHz	No material change	Thickness uniformity within $<10\%$ and $<5\%$ wafer to wafer for 8" wafer at 3σ	$T_g > 400^\circ\text{C}$
Low Dissipation	Etch rate and selectivity better than oxide	Good adhesion to metal and other dielectrics	$\text{CTE} < 50 \times 10^{-6}/^\circ\text{C}$
Low Leakage Current	$<1\%$ moisture uptake at 100% relative humidity	Residual stress $<(\pm)100$ MPa	Low thermal shrinkage
Low Charge Trapping	Low solubility in H_2O	High hardness	$<1\%$ weight loss
High Electric Field Strength	Low gas permeability	Low shrinkage	High thermal conductivity
High Reliability	High Purity	Crack resistance	
High Dielectric Breakdown Voltage >2 MV/cm	No metal corrosion	Tensile modulus >1 GPa	Stable at temperature $>450^\circ\text{C}$
	Long shelf life		
	Low cost of ownership	Elongation at break $>5\%$	
	Commercially available	Compatible with CMP	
	Environmentally safe		