Fabrication and characterization of mesoporous dielectric materials for ULSI interconnect applications

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Fabrication and Characterization of Mesoporous Dielectric Materials for ULSI Interconnect Applications

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
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*Fabrication and Characterization of Mesoporous
Dielectric Materials for ULSI Interconnect Applications*

STATEMENT OF ORIGINALITY

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

June - 2004

Date

Suzhu

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ABSTRACT

With the miniaturization of semiconductor devices, new dielectric materials with dielectric constant (k) lower than silicon dioxide ($k = 4.0$) are required to reduce propagation delay, cross talk noise and power dissipation of the interconnect system in ultra-large-scale integrated circuits (ULSI). This thesis presents the results of fabrication and characterization of mesoporous organosilicate films used as interconnect dielectrics. Two basic methods to establish porous network in the films, namely the sol-gel and sacrificial template approaches, have been used in this work.

Constitutive sol-gel films have been fabricated using tetraethyl orthosilicate (TEOS) and methyltriethoxysilane (MTES) as precursors. The use of organic/inorganic precursors has enabled thin films to be deposited without cracking. Acid/base two-step catalysis was used to control the microstructure of these films and the MTES catalyzed by the base can be regarded as a porogen in the broadest sense. Various surface modifications were carried out to ensure the reduced dielectric constant of the films remains stable.

Subtractive templated silsesquioxane low- k films have been synthesized by covalently binding a dendrimer template poly(amidoamine) (PAMAM) to a host polymer hydrogen methyl silsesquioxane (HMSQ) via a coupling agent. The curing mechanism of HMSQ and decomposition behavior of the template have been studied in air and in nitrogen. It is found that the HMSQ curing is an exothermic process accompanying a transformation from cage to network structure, and PAMAM decomposes more effectively in air than in nitrogen.

The dependence of material properties of the sol-gel films on MTES and templated films on the PAMAM template have been comprehensively investigated by a range of characterization techniques. A minimum dielectric constant of 2.0 has been realized for both films with pore sizes less than 10 nm. In contrast to the sol-gel films, the dielectric constant and leakage current of the templated films have been almost unchanged after two months ambient aging. Study on the leakage conduction at room temperature shows that both films follow a Schottky emission mechanism.

The interaction of copper (Cu) with the sol-gel derived low- k films has been studied. Cu adheres well to the films even after 450°C annealing. There is no significant increase

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in the dielectric constant and leakage current for the as-deposited and annealed Cu/low- k film/ n^+ Si capacitors compared to that of Au/Ti/low- k film/ n^+ Si capacitors, indicating that there has been no significant Cu diffusion through the organosilicate films with different porosities.

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CHAPTER 1 INTRODUCTION

As on-chip device densities increase and active device dimensions shrink, propagation delay, cross talk noise and power dissipation all become significant due to the increased parasitic resistance (R) and capacitance (C). The introduction of low resistivity metal and low dielectric constant (k) materials to replace the conventional aluminum (Al) and silicon dioxide (SiO_2) will partially mitigate these problems. In this chapter, the relevant factors and solutions to the dense interconnect problems are discussed. The objectives and scope of the work as well as the major contributions of the thesis will be presented in detail.

1.1 Background and Motivations

The semiconductor industry is continuing its quest to create ever more powerful microprocessor and memory chips by ultra-large-scale integration (ULSI) through the continual reduction of the minimum size of device features. The term ULSI refers to integrated circuits containing more than 10 million transistors. The latest microprocessors will have 410 million transistors and 7 km of interconnect per square centimeter of chip this year ^[1]. This rapid increase in the device density on chip results in a corresponding increase in the number of wiring levels and reduction in the wiring pitch. As device dimension shrinks below 0.25 μm , the dense interconnects will cause a significant increase in propagation RC delay, cross talk noise and power dissipation. These will seriously degrade the performance of deep sub-micron integrated circuits (ICs) ^[2]. Some measures have to be taken to address these problems.

1.1.1 Problems caused by dense interconnect in ULSI

RC delay

RC delay represents a measure of timing delay for signal propagation. It is a basic performance factor of an interconnect scheme. R denotes the resistance of an interconnect metal line and C denotes the effective capacitance between the line and its surrounding.

A schematic diagram of a typical multilevel interconnect system is shown in Figure 1.1^[3]. For simplicity, metal thickness and dielectric thickness above and below the interconnect are assumed equal.

Figure 1.1 Schematic diagram of an interconnect system cross-section with parasitic capacitance^[3]

A simple first-order model^[3] was developed to estimate the interconnection delay using the following equation:

$$RC = 2\rho k \epsilon_0 (4L^2 / P^2 + L^2 / T^2) \quad (1.1)$$

where ρ , k , ϵ_0 , L , P , T are the metal resistivity, dielectric constant, permittivity of free space, metal length, metal pitch and metal thickness, respectively.

It can be seen that the interconnect delay will become more significant with device scaling, as P and T continue to decrease and L always increases. It will become the major delay when the feature size shrinks below $0.5 \mu\text{m}$ as shown in Figure 1.2^[4]. Actually, it is the line-to-line capacitance that plays an increasingly important role with device miniaturization. It contributes almost 90% of the total capacitance at sub- $0.25 \mu\text{m}$ feature size. Therefore, the reduction of the line-to-line capacitance is one of the most critical issues for sub- $0.25 \mu\text{m}$ integrated circuit devices.

Figure 1.2 Interconnect capacitance versus feature size ^[4]

Cross talk noise

Cross talk refers to the generation of an electrical disturbance on an idle metal line due to a rapid voltage transition in an adjacent driven line. As integrated circuits operate at faster and faster speeds (> 1 GHz), the electrical pulses propagate through the interconnect structure and the resultant electromagnetic coupling can impose undesired voltages on the neighboring unpowered lines. Thomas *et al.* ^[5] have modeled this situation with results shown in Figure 1.3.

Figure 1.3 Cross talk between two interconnects

In Figure 1.3, cross talk is observed between two interconnects having a cross-section of $1\ \mu\text{m}^2$ separated by $1\ \mu\text{m}$ with a ground plane spacing of $2\ \mu\text{m}$. The driven line sees V_1 and the cross talk is V_2 . During the rise and fall of the waveform on the driven line, a substantial unwanted voltage as large as 50% of V_1 will be generated on the undriven line. If the spacing between the wires decreases to $0.5\ \mu\text{m}$, this cross talk would rise to about 70% V_1 . Cross talk therefore poses a problem for advanced IC as the device feature size scale down into a nanometer region.

Power dissipation

Power dissipation in a circuit of metal-oxide-semiconductor field effect transistor (MOSFET) is dominated by the switching power, which can be expressed as [6]:

$$P = 1/2 f_d C V^2 f \quad (1.2)$$

where C is the total on capacitance, V is the supply voltage, f is the operational frequency, and f_d represents the fraction of the gates that switch during a clock period.

Although an accurate estimate of power must include all types of circuits on a chip, a higher f leads to higher power dissipation. Therefore, to reduce power dissipation while maintaining high frequency, C must be reduced for the high performance circuits.

1.1.2 Solutions to the interconnect problems

Equations (1.1), (1.2) and Figure 1.3 provide some general insights as to how the interconnect problems of RC delay, cross talk noise, and power dissipation can be minimized. As they are in large part due to the increase of interconnect resistance and capacitance, so any approach to reduce the resistance and capacitance is a prospective solution to these problems.

Interconnect architecture

Before any new process technology is introduced into industry, it is common practice to extend current technologies and fully realize their potential by development of new designs. There are three types of interconnects based on the dimension: local interconnect, global interconnect and intermediate/semiglobal interconnect. Local

interconnect is used within a cell or a block using the finest pitch metal allowed by the design rules; global interconnect is used for inter-block communication using the upper metal layers; intermediate/semiglobal interconnect is in between of local and global interconnect. The optimization of the interconnect design is based on the principle that meets all the constraints while minimizing the metal pitch.

Multilevel interconnection (MLI) scheme as schematically shown in Figure 1.4 ^[6] is one of the circuit designs to address the dense interconnect problems. In MLI, circuit is designed to accommodate for smaller wire lengths and larger wire cross sections (preferably wider wires but not thicker wires, to minimize fringing line-to-line capacitance).

Figure 1.4 Schematic cross-section view of a three-level metallization scheme ^[6]

MLI technology offers:

- Reduced interconnection lengths and increased cross-sectional area of interconnects, enhanced performance due to reduced RC ;
- Densification due to use of third-dimensional space, i.e. higher packing densities;
- Design flexibility (and easier routing); and
- Use of third dimensions to implement newly found or developed materials and processes in devices.

Other new developed circuit designs include X architecture and repeater insertion. X architecture using 45-degree instead of 90-degree angles to connect transistors. Repeater insertion which breaking the long line into n smaller lines is becoming an increasingly common design methodology for driving long resistive interconnect. Since the propagation delay has a square dependence on the length of an interconnect line, subdividing the line into shorter sections can reduce the total propagation delay quadratically.

Material solution

The problems caused by the dense interconnect can be alleviated by the use of lower resistivity metal wires and lower dielectric constant interlayer dielectrics instead of the conventional Al/SiO₂ interconnect system.

Apart from superconductors, very few metals possess lower resistivity than aluminum. Copper is the most suitable alternative metal. The effective resistivity of Al is about 3.5 $\mu\Omega\text{-cm}$ and the effective resistivity of Cu is about 2.0 $\mu\Omega\text{-cm}$. So about 40% lower RC delay can be expected if aluminum wires were replaced by copper wires with the same cross section. Most manufacturers are already using Cu as metal wires by the dual-damascene process, which also provides advantages of cost and reliability over existing aluminum metallization process^[7].

In addition, new insulating materials with lower dielectric constant (i.e., lower capacitance) than that of traditional SiO₂ ($k = 4.0$) are needed to improve circuit performance. In contrast to the situation with metals, the choices for the best interlayer dielectrics (ILDs) are much more open. With Cu/low- k dielectrics instead of Al/SiO₂, further improvements in wiring performance become possible. With an ultra-low dielectric constant of $k = 2.0$, the RC delay could be reduced in principle by a factor of 3.5 relative to Al/SiO₂.

The roadmap for the low- k materials development forecasted in 2002 by Semiconductor Industry Association (SIA)^[8] is shown in Table 1.1.

Table 1.1 International technology roadmap of 2002 for interlevel metal insulator^[8]

Year of Production	2001	2002	2003	2004	2005	2006	2007
Interlevel Metal Insulator (minimum expected) - Effective Dielectric Constant (k)	3.0-3.6	3.0-3.6	3.0-3.6	2.6-3.1	2.6-3.1	2.6-3.1	2.3-2.7
Interlevel Metal Insulator (minimum expected) - Bulk Dielectric Constant (k)	<2.7	<2.7	<2.7	<2.4	<2.4	<2.4	<2.1

It can be seen that ultra-low- k materials ($k \leq 2.2$) will be needed in the very near future. Concretely, dielectrics with $k < 2.4$ and $k < 2.0$ will be needed for the feature size below 90 nm and 50 nm, respectively.

Damascene Technologies

In order to successfully integrate copper and low- k dielectric into integrated circuits, some technical issues associated with the transition from Al/SiO₂ to Cu/low- k such as lack of anisotropic etching of Cu, Cu diffusion, poor mechanical strength of low- k and poor adhesion of Cu to most of the dielectric layers have to be solved. The switchover to damascene architectures is one of the solutions to these problems^[9]. In the early 1990s, IBM demonstrated a damascene structure using physical vapor deposition (PVD) Ta (N) as a barrier layer against Cu diffusion, PVD Cu as a seed layer, electro-chemical plating (ECP) Cu for via & trench filling and chemical mechanical planarization (CMP)^[10].

The damascene approach used with Cu and low- k ILDs is illustrated in Figures 1.5^[11] and 1.6^[12]. Figure 1.5 shows the process flow for a single damascene interconnect structure. Figure 1.6 shows a generalized cross-sectional view of a dual damascene stack and the associated process requirements that will be further discussed in Chapter 2.

For both schemes, the entire wiring pattern is formed by first etching the ILD. This pattern is then filled with metal, and finally the metal is planarized and the extra metal on top of the ILD is removed.

Figure 1.5 Schematic process of damascene interconnect fabrication ^[11]

Figure 1.6 Copper/low-*k* dual damascene structure ^[12]

The introduction of Cu/low- k damascene structure in new developed circuitry and interconnect architecture will greatly mitigate the problems caused by the dense interconnection, leading to the further scaling down of devices with improved performances.

1.2 Objectives and Scope of this Research

From the introduction above, it is evident that new materials with lower dielectric constant than silicon dioxide are needed to reduce propagation delay, cross talk noise and power dissipation of interconnect structures in the ultra-large-scale integrated circuits. The main goal of this work is to synthesis of organic-inorganic porous films with low dielectric constant via spin-on approach. The reasons for this choice of main objective are (a) only porous films can achieve ultra-low- k region; (b) organic-inorganic hybrid materials have the potential to achieve comprehensive thermal and mechanical properties; and (c) the structure and properties of the porous films are more precisely controlled by spin-on technique. Two techniques to establish the porous network namely sol-gel and template synthesis will be considered. The detailed aims and scope of this work are outlined below:

1. Development of synthesis processes for ultra-low- k films with controlled pore structure

(i) Sol-gel route – silica (SiO_2), the traditional insulator, can be incorporated with air by sol-gel method. The advantages of sol-gel derived porous silica are the high mechanical strength of films even at high porosity and integration compatibility. The starting materials, their relative concentrations and chemical reactions in the sol solution as well as the processing parameters will be systematically investigated so as to obtain crack-free films with good structural, dielectric and mechanical properties. The mechanism of the pore formation during the sol-gel process will be studied. The general principles on how to control the porosity, pore size and the properties of the films will be elucidated.

(ii) Template route – an organic-inorganic hybrid polymer, such as poly(silsesquioxane) (PSSQ), with lower dielectric constant than silicon dioxide will be used as a matrix or wall material of porous films; a thermal labile polymer will be used as

a template or porogen (pore generator) for the generation of pores. The compatibility and interactions between the two phases will be studied to understand the effect of the template structure on the phase separation. The curing mechanism of the resin matrix and the thermal decomposition of the porogen will be investigated. The structure-property correlation will be derived. The synthesis of templated films with controllable structural, dielectric, thermal and mechanical properties will be achieved.

2. Characterization of the low- k porous films

The chemical bonds and thermal stability of the films will be determined by Fourier transform infra-red spectroscopy (FTIR) as well as thermal gravimetric analysis (TGA) and differential thermal analysis (DTA).

The pore structure of the films will be analyzed. Generally, the pore structure is characterized by the volume fraction of the pores – porosity, pore size and pore interconnectivity. Different techniques such as nitrogen adsorption, ellipsometry, specular X-ray reflectivity (SXR), atomic force microscopy (AFM), transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) will be employed to evaluate the pore fraction, pore size and pore interconnectivity. The results obtained from different facilities will be compared. The evaluation of the pore interconnectivity is more challenging. Some indirect methods will have to be developed.

The dielectric, electrical and mechanical properties such as dielectric constant, dielectric loss, leakage current, elastic modulus and hardness of the films will be determined. The relationship between microstructure and properties of the films will be systematically investigated.

3. Copper interaction with the porous low- k films

The transition from Al/SiO₂ scheme to Cu/low- k scheme has brought about many integration challenges. The important reliability concerns include the increased interlevel leakage current and time dependent dielectric breakdown due to the diffusion of copper to low- k materials. Therefore, it is necessary to study the interaction between the copper and porous low- k films.

1.3 Major Contributions of the Thesis

- Organosilicate films with ultra-low dielectric constant about 2.0 and pore size less than 10 nm have been successfully synthesized by sol-gel and template approaches.
- Controllable pore structures have been achieved for both sol-gel and template films on the basis of the investigation of the mechanism of pore formation.
- For the sol-gel films, various techniques have been used to minimize the surface hydroxyl groups and to increase the hydrophobicity of the films, so the dielectric constant of the films can be maintained at low value.
- For templated films, the common phenomenon of macroscopic phase separation between polymer blends, resulting in domains that are too large to produce nanoscopic porosity, has been avoided by the use of coupling agent with bi-functional groups. The curing mechanism of the silsesquioxane matrix and thermal decomposition behavior of the template polymer has been investigated.
- Various characterization techniques have been utilized to evaluate the physical, structural (porosity, pore size and pore interconnectivity), thermal, dielectric and mechanical properties of the porous low- k films. The relationship between the structure and properties for both the sol-gel and templated films has been established.
- The interaction of copper with the sol-gel derived porous films has been studied. The interface between copper and sol-gel films has been characterized at different annealing temperatures. The influence of as-deposited and annealed copper on the intrinsic dielectric properties and leakage current behavior of the films has been investigated.
- The conduction mechanisms for the sol-gel and templated films as well as the sol-gel films with copper as electrodes have been determined at room temperature in terms of the Schottky and Frenkel – Poole mechanisms.

1.4 Organization of the Thesis

This thesis contains ten chapters. Chapter 1 explains the background that motivates the study of low- k materials. The objectives and outline of the thesis and the major contributions of the work are also provided in this chapter. Chapter 2 gives a review on the major requirements for low- k material, the types of low- k candidates and the techniques to prepare porous low- k dielectric films from spin-on solutions. Two

techniques – sol-gel and template are discussed in detail. Chapter 3 presents the fabrication and characterization techniques for low- k films used in this work. Chapter 4 and Chapter 5 describe the synthesis and characterization of the sol-gel derived low dielectric constant silica films. Chapter 4 focuses on the surface modification of the films to ensure the dielectric constant of the films remain low. Chapter 5 discusses the influences of the ratio of the organic/inorganic precursors on physical, structural, dielectric and mechanical properties of the films. The preparation and characterization of the templated low- k films are discussed in Chapter 6 and Chapter 7. The thermal and dielectric properties of silsesquioxane films cured in nitrogen and in air are compared in Chapter 6. The synthesis and characterization of templated mesoporous silsesquioxane films are described in detail in Chapter 7. Chapter 8 briefly compares the preparation process and properties of the sol-gel and templated films. Chapter 9 presents the preliminary study of copper interaction with sol-gel derived films. Chapter 10 gives general conclusions of the thesis as well as proposed future work for related research.

CHAPTER 2 LITERATURE REVIEW

There are many property requirements for low-*k* material in addition to a low dielectric constant. The main requirements and the major low-*k* candidates including sol-gel derived and templated films are reviewed in the first part of this chapter.

Spin-on technique is a well-known deposition method for dielectric films. It is particularly suitable where depositions with good planarization and gap fill properties are required. There are two main techniques to prepare porous films from spin-on solutions. One is the sol-gel approach to directly construct a porous network. The other is the template method that constructs the porous network indirectly. In the second part of this chapter, these two techniques are introduced from both theoretical and practical points of view.

2.1 Requirements on Low-*k* Materials

Since the dielectrics serves as both the insulating layer between metallizations and as protective coating for the materials and devices underneath, there are many property requirements on the dielectrics in addition to a low dielectric constant. Table 2.1 ^[13] lists the major electrical, chemical, mechanical and thermal requirements for low-*k* materials.

Table 2.1 Material property requirements for low dielectric constant ILD materials ^[13]

Electrical	Chemical	Mechanical	Thermal
High electric-field strength	Chemical resistance	Thickness uniformity	High thermal stability
Low dissipation	Low moisture absorption	Good adhesion	Low thermal shrinkage
Low leakage current	Low solubility in H ₂ O	High hardness	High thermal conductivity
Low charge trapping	Low gas permeability	High tensile modules	Low coefficient of thermal expansion
High reliability	Etch selectivity	Crack resistance	Low thermal weight loss
<i>k</i> anisotropy	High purity	Low shrinkage	
	No metal corrosion	Low stress	
	Long storage time		
	Environmentally safe		

The desired electrical properties of the future low- k materials, in addition to a low dielectric constant, are low dissipation, high breakdown strength, high bulk resistivity and low leakage current. They should also be chemically and mechanically compatible with other materials that constitute the integrated circuits such as diffusion barrier/adhesion liners, as well as with the processes and packaging used in the manufacturing.

The introduction of voids decreases the dielectric constant by lowering the density of the material. But it is inevitable trade-off with the mechanical and thermal properties such as the mechanical strength and thermal stability^[14]. As a result of this difficulty, the introduction of low- k materials has been delayed for two generation nodes^[8, 15].

2.2 Candidate Low- k Materials

In order to reduce the k value relative to that of SiO_2 , it is necessary to incorporate atoms and bonds that either have a lower polarization or lower density^[16]. Several classes of dielectric materials are currently under consideration. They can be roughly classified as inorganic, organic or organic-inorganic hybrid materials on the basis of the type of materials; they can also be divided as chemical vapor deposition (CVD) materials or spin-on materials on the basis of deposition methodology. The following sections give a brief discussion of some typical low- k materials in each group.

2.2.1 CVD materials

Fluorinated silicon oxide (SiOF)

Doping SiO_2 with fluorine (F) atoms is one of the most straightforward ways to reduce the dielectric constant of the oxide films. Fluorine has the effect of lowering the distortion polarization contribution, which minimizes the response of molecules within the film to an applied electric field. The fluorinated silicon oxide films, i.e. fluorosilicate glass (FSG) films, are inorganic and easy to introduce into ULSI production without changing other processes drastically in manufacturing devices. Theoretically, a large amount of F can be added to reduce the k value of SiOF to 3.0, but there is a fundamental limit to the amount of F incorporation in SiO_2 before the dielectric property of the films becomes unstable^[17]. The main limitation of SiOF films is their moisture absorption.

Due to the hydrophilic behavior of fluorine, F can act as an adsorption sites for water in the deposited films. The presence of water in the films may not only increase the overall dielectric constant of ILD but also result in corrosion of the metal structure by the formation of HF^[18].

Fluorinated amorphous carbon (FLAC or a-C:F)

Fluorinated amorphous carbon films are carbon-based organic films that can have k values < 2.5 ^[19]. Their properties greatly depend on the fluorine and hydrogen content and on the extent of cross-linking achieved. The strong C-F bonds in the a-C:F film decrease its dielectric constant, and the C-C crosslinked structures maintain the film's thermal stability. Lower k can be obtained if there is a higher concentration of F incorporated into the films. However, such films usually have lower thermal stability and higher associated outgassing, especially from fluorine-containing fragment^[20]. As mentioned above, release of fluorine is especially undesirable because of its corrosive interaction with the metals used in the interconnection. A trade-off, therefore, must be made between low dielectric constant and thermal stability of the films.

Carbon doped silicon dioxide (SiOCH)

This type of materials incorporates carbon atoms in the form of alkyl into the SiO₂ network^[21]. The decrease of the dielectric constant of these films may be caused by three reasons: (1) doping a film with alkyl groups terminates some of the silicon bonds within the oxide lattice and lowers the electronic polarizability of the film; (2) the relatively large molecular volume of the alkyl groups decreases the film density; and (3) lower thermal stability of Si-alkyl groups allows for the generation of additional porosity by removal during the deposition or postdeposition annealing of the film^[22]. One of the most promising films in this class is Black Diamond with k values around 2.8 introduced by Applied Materials^[23]. The dielectric constant of the films can be further lowered by the introduction of higher carbon content. However that will degrade other properties, such as mechanical and thermal properties.

The incorporation of porosity can also reduce the dielectric constant of the films. Generally, SiOCH films have a constitutive porosity of about 5% – 15% with a pore size of about 1 nm^[24]. However, various techniques have been employed recently to produce

CVD oxycarbide (SiOCH) films with subtractive porosity as high as 40%. The techniques to generate pores include multiphase deposition with post-annealing^[25], chemical etching^[26, 27] and sacrificial organic layer deposition^[28].

2.2.2 Spin-on materials

Organic polymeric materials

Only organic materials have k values near 2.0 with the exception of porous materials. For the spin on deposition of organic polymers, the polymer weight and solution concentration are tuned to enable spin on deposition. After deposition, the polymer is thermally cured to an insoluble film. The chemical bonds, C-C and C-H, with lower polarizability lower the dielectric constant of polymers. Substitution of hydrogen with F or -CF₃ groups will further decrease the electronic polarizability or dielectric constant due to strong electron withdrawing inductive effects of the F atoms. A variety of polymers with k values in the range of 1.9 – 2.9 have been reported^[29, 30]. Polytetrafluoroethylene (PTFE), poly(aryl ethers) (PAE), polyimides (PIs), Bis(benzocyclobutenes) (BCB), SiLKTM are the representative spin-on polymers^[31 - 32]. Thermomechanical property is one of the most critical concerns for this class of dielectrics. In order to obtain thermally stable low- k materials, organic thermosets that have higher T_g should be used. For instance, BCB^[33] and SiLKTM^[34] with dielectric constants of 2.65 produced by Dow Chemicals have T_g as high as 450°C.

Organic-inorganic hybrid films

The basic idea behind the development of organic-inorganic materials is the combination of inorganic and organic moieties on a molecular scale to achieve a synergistic combination of the properties typical of each of the constituents. Modification of the kind and proportions of the organic and inorganic constituents allows, in principle, a deliberate tailoring of properties between purely inorganic and purely organic materials.

The hybrid materials can be divided into two general classes^[35]. Class I is that in which the organic component is just entrapped or embedded in an inorganic host or vice versa. The organic and inorganic components are attracted by weak interactions only, such as hydrogen bonding, electrostatic attraction or van der Waals forces. Class II

corresponds to organic-inorganic hybrid materials where the constituents are connected with each other by strong covalent or ionic bonds. Although the preparation of these materials usually requires some effort to establish the chemical link, for example, the development of special precursors, the bonding between the two components overcomes problems of macro- or microphase separation or leaching and allows material development strategies similar to those for block copolymers in organic polymer chemistry. Schmidt^[36] coined the term Ormosils (organically modified silicates) for the one type of class II silicate materials.

There has been much interest in organic-inorganic hybrid low- k materials due to the fact that dielectric, mechanical and thermal stability of the films are difficult to obtain using purely organic or inorganic materials^[37, 38]. For sol-gel derived Ormosil films, the incorporation of organic groups into the silica network not only improves their properties but also facilitates the fabrication process. Crack-free films with thickness of up to a few microns can be obtained under ambient temperature and pressure^[39]. Another representative organic-inorganic hybrid low- k material is silsesquioxanes with dielectric constant of 2.5 – 3.0^[29]. In the silsesquioxanes, each Si atom is bonded to one terminal group such as hydrogen (HSQ) or methyl (MSQ). They have a ladder or cage structure with nominal stoichiometry $\text{RSiO}_{1.5}$ (the prefix sesqui- means 1.5). The reduction in k from that of SiO_2 is thought to be mainly due to the reduction in density.

Porous materials

An increasingly important consideration for future technology nodes is the dielectric extendibility to materials with ultra-low dielectric constant. Air has a dielectric constant of 1, but the complex structure of metal interconnection schemes excludes the use of air alone as the interlayer dielectric. A new approach proposes dielectrics that are rigid, can support the interconnection network, and yet they have lower dielectric constant.

The only homogeneous materials with dielectric constants in the range of 2.0 are highly fluorinated alkane derivatives and fluoroethers such as Teflon^[40] and Teflon-AF^[41, 42]. For unfluorinated systems the only foreseeable route to materials with $k \leq 2.0$ involves the introduction of porosity^[43 – 45]. This route is currently a more viable option for spin-on rather than CVD candidates. Most of the porous materials are not as well developed as the fully dense dielectrics. Nevertheless, a wide variety of porous materials

have been studied to date ^[46]. There are a number of reliability concerns that are particularly prominent for porous ILDs. One of these is mechanical strength because films with voids will undoubtedly be weaker than similar dense materials. Another set of potential problems involves the size and distribution of the pores in these materials. It is critical to the reliability that these parameters are carefully controlled ^[14].

Porous films are generally made in one of two ways: either through direct construction of a porous network, or indirectly by depositing a composite film, a component of which is later removed. The first type of materials is often produced by a sol-gel process in solution ^[47, 48]. The resultant gel can be an aerogel dried supercritically ^[49] or a xerogel dried by evaporation ^[50]. Preventing collapse of the porous network due to the capillary forces during drying is the key factor for these films. A commercial spin-on glass (SOG), Nanoglass, has been produced by Honeywell-Allied Signal. It has dielectric constant as low as 1.3 – 2.2 with porosity from 50% to 80% ^[51].

There are several possibilities of using the indirect method. For example, one can use a surfactant ^[52] or dendritic structure as a template ^[53] to build a composite structure, remove the template to leave voids. Alternatively, one can synthesize a covalently bonded hybrid and remove one of the constituents. In any case the undesired component of the film can be removed by thermal decomposition. The production of porous crystalline zeolites templated by surfactants has been described ^[54 – 56]. They have dielectric constants ranging from 1.5 – 2.1 with ordered interconnected pores ^[57, 58]. Macromolecules templated silsesquioxanes films with porosity of 20% to 30%, dielectric constant of 2.0 – 2.2 have also been reported ^[59 – 62].

Two advantages of the template approach over sol-gel method are (1) the templated film has a higher degree of cross-linking when the pores are created. The porous structure is, therefore, less affected by further densification; (2) closed mesoporosity can be obtained within certain boundary conditions related to the nature and total load of the templates.

2.2.3 Advantages of spin-on materials over CVD materials

The low-*k* materials are mainly produced by CVD or spin-on techniques at present. CVD process uses a glow discharge or thermal energy to create active species such as radicals and ions from the precursor monomer, and the films are deposited through

various gas-phase and surface reactions of these active species. They are generally well controlled and have an integration advantage in the manufacturing process of ULSI. Spin-on process is a wet chemical route; it uses a solution of precursors to produce the films. Compared to the conventional CVD thin-film technology, spin-on technique requires considerably less costly equipments. However the most important advantages of spin-on processing over the CVD deposition are as follows:

(1) The large variety of available synthetic precursors offers possibility to prepare a broad spectrum of high purity materials with relative ease. The soluble spin-on precursors also ensure the mixing of different constituents on a molecular level resulting in very homogenous product ^[63]. In addition, many of the materials such as hybrid materials cannot be made by any other routes;

(2) Spin-on option appears to be more extendible over multiple device generations. It can produce porous materials leading to ultra-low-*k* dielectrics that are currently difficult to obtain from CVD deposition ^[10, 64]. This feature is very important. Although it is very difficult to predict which material or materials ultimately will be selected for commercial application due to the extremely rigorous requirements with regard to material properties. It appears that porous materials will play a significant role in future ultra-low-*k* applications. Moreover, the spin-on technique has the ability to control precisely the microstructure (i.e., the pore volume, pore size and surface area) of the deposited films and allows a good uniformity of deposition.

2.3 Sol-Gel Technique

The term “sol-gel processing” is widely used to describe the preparation of materials using a wet-chemical route at room temperature. In the following sections, the composition of the solution, chemical reactions involved in the sol-gel process and the affecting factors on the microstructure of the final product will be discussed.

2.3.1 Composition and chemical reactions

A sol is a colloidal suspension of solid particles in a liquid. The dispersed phase is so small (1 nm to 1000 nm) that gravitational forces are negligible and interactions are

dominated by short-range forces, such as van der Waals attraction and surface charges. The sol can undergo a series of chemical reactions to form macromolecules. When the macromolecule reaches macroscopic dimensions and extends throughout the solution, a gel is formed. This point is usually called gel point at which the viscosity of the solution suddenly increases. A gel consists of a continuous solid skeleton enclosing a continuous liquid phase. After removal of the solvent, the sol-gel material is obtained.

The basic starting materials of a sol consist of precursor(s), solvent(s), water and catalyst(s). Two types of chemical reactions, namely hydrolysis and condensation, are involved in the sol-gel process.

The most common type of the precursors is the metal alkoxides having an organic ligand attached to a metal or metalloid atom, $M(OR)_Z$, where $M = Si, Ti, Zr, Al, Sn, Ce...$, R is an alkyl group, C_xH_{2x+1} , and Z is the valence or the oxidation state of the metal. Metal alkoxides react readily with water, an important criterion for hydrolysis to take place. The hydrolyzed metal alkoxides will then condense to form branched oligomers and polymers with a metal oxo based skeleton and reactive residual hydroxy and alkoxy groups. At the functional group level, three reactions are generally used to describe the sol-gel process. The reactions presented by alkoxysilanes precursors are shown below ^[65]:

Under most conditions, condensation commences before hydrolysis is complete. Silica material with siloxane (Si-O-Si) bonds is formed after these series of reactions.

Tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$) is the most thoroughly studied precursor. Other precursors include organotrialkoxysilane ($\text{R}'\text{Si}(\text{OR})_3$) and diorganoldialkoxysilane ($\text{R}'_2\text{Si}(\text{OR})_2$), where R' represents a nonhydrolyzable organic substituent, which can be same or different from R.

The stoichiometry of water : Si ratio (r) is four if TEOS is used as a precursor. The r has great effect on the structure of the final product, which will be discussed in the next section.

Water and the alkoxysilanes are immiscible, so a mutual solvent has to be used as a homogenizing agent to facilitate the hydrolysis reaction. Alcohols are the most commonly used solvent. They are miscible with water and most of the alkoxides. Furthermore, light alcohols, such as ethanol, are preferred because of their low boiling points and low viscosity. Low viscosity can facilitate hydrolysis and condensation by increasing diffusion and the reorientation rate of reaction species. Low boiling point facilitates solvent evaporation in subsequent processes. Nevertheless, when design a sol composition, the use of alcoholic solvent should be kept to a minimum because a higher quantity of alcoholic solvents may promote reverse reactions: reesterification and alcoholysis (Equations (2.2) and (2.3)).

Figure 2.1 ^[65] illustrates a phase diagram for the ternary-phase of TEOS, H_2O , synasol (95% ethanol, 5% water). For pure ethanol the miscibility line is shifted slightly to the right. The relative proportion between the components has to be adjusted to get soluble sol.

In order to get a reasonable reacting rate, catalysts are usually used. Both acids and base are capable of accelerating the sol-gel reactions. They play an important role in sol-gel processes. Many studies ^[66, 67] have shown that the rate and extent of the reactions as well as the final structure of the sol-gel material are most significantly influenced by the strength and concentration of the acid or base catalyst. Temperature and solvent are of secondary importance.

Figure 2.1 TEOS, H₂O, synasol ternary-phase diagram at 25°C ^[65]

2.3.2 Mechanism of chemical reactions

It is generally agreed that both hydrolysis and condensation of alkoxysilanes, catalyzed by an acid or a base, follow biomolecular nucleophilic substitution (S_N2-Si) mechanism. The acid-catalyzed mechanisms are preceded by rapid protonation of the -OR or -OH substituents bonded to Si, whereas under basic conditions hydroxyl or silanolate anions attack Si directly.

Acid-catalyzed hydrolysis

Under acidic conditions, it is likely that an alkoxide group is protonated in a rapid first step. Electron density is withdrawn from the silicon atom in the alkoxysilicone, making it more electrophilic and thus more susceptible to attack by water. Pohl and Osterholz ^[68] favor a transition state with significant S_N2-type character (Equation (2.4)). The water molecule attacks from the rear and acquires a partial positive charge. The positive charge of the protonated alkoxide is correspondingly reduced, making alcohol a better leaving group. The transition state decays by displacement of alcohol accompanied by inversion of the silicon tetrahedron:

Base-catalyzed hydrolysis

Under basic conditions, it is likely that water dissociates to produce nucleophilic hydroxyl anions in a rapid first step. The hydroxyl anion then attacks the silicon atom in the alkoxy silicone. Iler^[69] and Keefer^[70] propose an S_N2-Si mechanism in which OH⁻ displaces OR⁻ with inversion of the silicon tetrahedron:

Both acid-catalyzed and base-catalyzed hydrolysis are affected by steric and inductive factors.

Acid-catalyzed condensation

The acid-catalyzed condensation mechanism involves a protonated silanol species. Protonation of the silanol makes the silicon in the silanol species more electrophilic and thus more susceptible to nucleophilic attack. The most basic silanol are the most likely to be protonated. Therefore, condensation reactions may occur preferentially between neutral species and protonated silanols. Pohl and Osterholtz^[68] proposed the mechanism of acid-catalyzed condensation as shown below:

Base-catalyzed condensation

The most widely accepted mechanism for the condensation reaction involves the attack of a nucleophilic deprotonated silanol on a neutral silanol species as proposed by Iler^[69] Pohl and Osterholtz^[68] as well as Voronkov^[71].

According to Pohl and Osterholtz^[68], the hydroxyl anion reacts reversibly with silanetriol in a rapid first step leading to an equilibrium concentration of silanoate anion, $\text{RSi(OH)}_2\text{O}^-$. Silanoate anion reacts with neutral triol in a slower rate-determining step resulting in dialkyl-tetrahydroxydisiloxane and regeneration of hydroxyl anion. The condensation rate is maximized near neutral pH where significant concentration of both protonated and deprotonated silanols exist.

2.3.3 Effect of catalyst and water : Si ratio on the chemical reactions and material structure

Polymerization to form siloxane bonds occurs by either an alcohol-producing condensation reaction or a water-producing condensation reaction. A complete spectrum of structures ranging from molecular networks to colloidal particles may result depending on the reaction conditions. The pH value of the solution, determined by the type and strength of an acid or a base catalyst, and water : Si ratio play important roles.

Figure 2.2^[65] summarizes the pH-dependency of the hydrolysis, condensation and depolymerization (dissolution) rates of silicate growth in sol-gel process. In the chart, the larger 1/gel time indicates the higher condensation rate.

Figure 2.2 Schematic representation of the pH-dependence of hydrolysis (H), condensation (C) and dissolution (D) for an arbitrary value of water/Si ratio (1.5)^[65]

At low-pH conditions (below about pH 2), the hydrolysis rate is larger compared to the condensation rate. For $r > 4$, the hydrolysis will complete at an early stage of the reaction. After monomers are depleted, condensation between completely hydrolyzed species occurs, leading to the formation of weakly branched structures. The rate of dissolution is low; the condensation is essentially irreversible. For $r < 4$, condensation reaction commences before hydrolysis is complete. Alcohol-producing condensation rate is slower than the water-producing condensation rate; unhydrolyzed -OR groups effectively reduce the functionality, promoting the formation of more weakly branched structures.

At high-pH conditions (above pH 7), for $r > 4$, the hydrolysis of all polymeric species is expected to complete. Dissolution reactions provide a continual source of monomers; smooth colloidal particles can be obtained. If $r \ll 4$, unhydrolyzed sites are incorporated in the growing clusters. The probability of condensation at these sites is less than that at hydrolyzed sites. The resulting structure may range from dense structure to branched structure or uniformly porous objects depending on the number and distribution of the unhydrolyzed sites.

Intermediate values of pH (3 – 8) represent conditions in which a spectrum of transitional structures might be expected. Both the dissolution and condensation rates

increase smoothly with pH, whereas the hydrolysis rate goes through a minimum at approximately neutral pH. The increase in H_2O ratio, r , increases the dissolution and hydrolysis rates at any particular pH value. The structure of the gel can range from mass fractals to surface fractals to porous uniform clusters, depending on the pH and r . A larger r promotes the formation of more compact structures. Below pH 4, very weakly branched structures predominate; from pH 4 to pH 7, more branched structures formed with increasing pH; from pH 7 to pH 8, branched structures can be obtained and at sufficiently high r , smooth colloidal particles should be formed.

In summary, acid-catalyzed hydrolysis with low H_2O : Si ratio produces weakly branched, “polymeric” sols, whereas base-catalyzed hydrolysis with large H_2O : Si ratio produces highly condensed “particulate” sols (Figures 2.3). Intermediate conditions produce structures intermediate to these extremes.

Figure 2.3 Schematic diagram of the structure of weakly branched polymeric gel obtained from acid catalysis (left) and condensed colloidal gel from base catalysis (right)

2.3.4 Synthesis of sol-gel materials

The formation of xerogels from precursors such as TEOS through the sol-gel process is described by the following steps.

Step 1: Mixing – TEOS is mixed with water in the presence of a solvent. With the assistance of the catalyst, hydrolysis and polycondensation reactions occur according to Equations (2.1) to (2.3).

Step 2: Gelation – the sol is a low-viscosity liquid. After sufficient time has elapsed, the colloidal particles and condensed silica species link together to become a three-dimensional network.

Step 3: Aging – the aging of a gel is also called syneresis and involves maintaining the cast object for a period of time from hours to days. During aging, polycondensation continues and reprecipitation of the gel network occurs. The strength of the gel thereby increases with aging.

Step 4: Drying – drying removes the liquid from the interconnected pore network and make the network collapse further resulting in a decrease in its volume. The gel obtained after the drying stage is called either a xerogel if it is dried by evaporation or an aerogel if it is dried by supercritical extraction of the solvent.

The driving force for shrinkage during drying includes stresses produced by chemical reactions, osmotic, disjoining and capillary forces. Usually the most important of these is the capillary forces arising from the difference between the solid-vapor and solid-liquid interfacial energies. The gel contracts as the liquid evaporated from its pores because of the large stresses generated by the menisci in the tiny pores. During the initial stages of drying, the volume change of the gel is equal to the volume of evaporated liquid. The gel network is still flexible and can rearrange to accommodate the decreasing volume. All pores are filled with solvent and solid-air interfaces are not present. As drying proceeds, the gel network becomes more restricted and the removal of liquid leads to the formation of solid-air interfaces and the development of capillary stresses.

The interfaces between liquid, solid and vapor can be characterized by a contact angle, θ , as defined in Figure 2.4 ^[65].

Figure 2.4 Schematic illustration of a contact angle of a liquid on a solid surface ^[65]

The balance of tensions at the point of intersection leads to a relationship between the surface tensions that is known as Young's equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (2.8)$$

Liquid rises in a capillary tube to replace a solid-vapor interface with a solid-liquid interface. The capillary pressure is found to be ^[65]:

$$P_c = -\frac{2(\gamma_{SV} - \gamma_{SL})}{a} = -\frac{2\gamma_{LV} \cos \theta}{a} \quad (2.9)$$

where P_c is the capillary pressure, a is the radius of the tube, γ_{SV} , γ_{SL} and γ_{LV} is the specific energy of a solid-vapor, solid-liquid and liquid-vapor interface, respectively.

If the pressure is uniformly applied on the network, it will shrink uniformly and have no tendency to crack. However, quite often, large pressure gradients can develop through the thickness of the gel, such that the network is compressed more at the exterior surface than in the interior of the body, and this differential strain causes cracking. Porosity develops when, due to additional cross-linking or neck formation, the gel network becomes sufficiently strengthened to resist the compressive forces of surface tension.

Step 5: Dehydroxylation and densification – this step involves thermal or/and chemical treatment of the samples to remove the surface hydroxyls from the pore network. Thermal dehydroxylation relies on condensation reactions occurring on the gel surface at high temperature, the final product is a chemically stable ultra porous solid. In general, -OH groups are gradually lost with increasing temperature. However the -OH coverage according to Taylor ^[72] is still about 1 OH/nm² even after heating in air at 800°C, where the extent of viscous sintering may be substantial. The sequence of surface dehydroxylation is the initial removal of physically adsorbed water at low temperatures followed by the progressive removal of weakly hydrogen bonded hydroxyls, strongly hydrogen bonded hydroxyls and finally isolated hydroxyls.

2.3.5 Formation of thin films through sol-gel process

Certainly one of the most technologically important aspects of sol-gel processing is that, prior to gelation, the fluid sol or solution is ideal for preparing thin films by such common processes as dipping, spinning, or spraying. Among them spin coating is a simple method to deposit film on one side of the substrate. Another advantage of spin coating is that a film of liquid tends to become uniform in thickness during spin coating and remains so once uniformity is reached. This tendency arises due to the balance between the two main forces: the centrifugal force, which drives flow radially outward, and the viscous force (friction), which acts radially inward. The spin coating process can be divided into four stages: deposition, spin-up and spin-off and evaporation (Figure 2.5)^[73]. Evaporation may accompany the other stages.

Figure 2.5 Stages of the spin-coating process^[73]

An excess of liquid is dispersed on the surface during the deposition stage. In the spin-up stage, the liquid flows radially outward driven by centrifugal force. In the spin-off stage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, flow resistance and the viscosity rise because the concentration of the nonvolatile components increases, so the rate of removal of excess liquid by spin-off slows down. In the fourth stage, evaporation takes over as the primary mechanism of thinning.

There are differences between film and bulk gel formation. Features of film formation that are different from bulk gels are^[65]: (1) the overlap of the deposition and evaporation

stages; (2) aggregation, gelation and drying occur in seconds to minutes during spinning; and (3) fluid flow, due to spin-off, combined with attachment of the precursor species to the substrate impose a shear stress within the film during deposition.

The final film microstructure depends on the size and extent of branching (or aggregation) of the solution species prior to film deposition as well as the relative rates of condensation and evaporation during film deposition. Control of these factors enables the technologist to tailor the film porosity.

Firstly, the pH of the solution affects the film structure greatly. Acid-catalyzed condition results in rather weakly branched, extended polymers; interpenetration should allow the precursors to become densely packed during film formation promoting dense packing and low pore volume films. Base-catalyzed condition results in highly branched polymers. Noninterpenetrating or weakly interpenetrating polymers result in rather thick and more porous films. The porosity is attributed to both the compaction of individual clusters due to capillary pressure and interstitial porosity created by cluster aggregation.

Secondly, the overlap of the deposition and drying stages in spinning establishes a competition between evaporation (which compact the film) and continued condensation reactions (which stiffen the film, increasing its resistance to compaction). Thus the porosity of the film depends on the relative rates of condensation and evaporation.

Finally, shear fields are established in spinning that can influence the structure of the depositing film. A strong gradient normal to the substrate is established in which the shear stress increases with both radius and angular velocity (spin frequency). The shear stress may affect the relative rates of evaporation and condensation: increased shear rate causes an increase in the evaporation rate (analogous to a decrease in the condensation rate), resulting in denser films. A second shear-induced effect is alignment of precursor species parallel to the direction of the applied shear. The effect would cancel at the center of the film due to radial symmetry, whereas near the edges alignment effects would be maximized.

2.4 Template Technique

2.4.1 Introduction

The organic template approach was first documented by Dickey^[74] in 1949 to prepare a selective adsorbent using a sol-gel process. The porous films prepared by the template process rely on the incorporation of a template within a host matrix. In a broadest sense, a template may be defined as a central structure about which a network forms in such a way that extraction of the template creates a cavity with morphological and/or stereochemical features roughly corresponding to that of the template^[75]. As the template is used to guide the formation of the pores, it is also called as a pore generator (porogen) or a sacrificial material. Upon heating, the template undergoes decomposition and the volatile by-products diffuse out of the matrix. Under optimized processing conditions, a porous network forms and the pore size is directly correlated with the original porogen morphology. A schematic of the organic template approach to prepare a porous material is shown in Figure 2.6^[76].

Figure 2.6 Schematic of the organic template approach to prepare porous amorphous material^[76]

The advantage of the organic template approach is that the organic template volume fraction controls the porosity of the network. The template size and shape determine the pore size and shape.

A suitable template has to fulfill at least three conditions: (i) its geometry has to mirror the expected shape and diameter of the desired cavities; (ii) the template has to be stable against deformations during the solidification of the surrounding matrix; and (iii) it must be possible to remove the template from the matrix without destroying or altering

the morphology. The template generally can be eliminated by calcination, chemical oxidation, chemical rearrangements or hydrolysis. However the thermally removable template is the most commonly used. The fidelity of the imprint created by template removal depends on several factors: (i) the nature of the interaction between the template and the embedding matrix; (ii) the ability of the matrix to conform to the template; and (iii) the relative sizes of the template and the primary units used to construct the matrix.

Organic templated porous silicas are a subset of a larger class of hybrid organic-inorganic materials. One of the critical issues in the template process to produce porous ILD films is that the porogen and the host polymer should have a close association to achieve nanoscopically phase-separated microstructure in the films ^[77]. Phase separation in organic-inorganic systems shows striking similarities to phase separation in purely organic systems, i.e., it depends on the balance between unfavorable physical interactions such as hydrophobicity and favorable specific interactions such as covalent or H-bonding between the polymer and the solvent ^[78–80].

2.4.2 Techniques to prevent phase separation

There are two classes of materials prepared from soluble precursors that are distinguished by the nature of the template and matrix interactions – via noncovalent bonding and covalent bonding. They are representative of two fundamentally different approaches to template-mediated synthesis and processing of porous materials. The former produce mesoporous materials with little structure rearrangements, whereas the latter can produce both microporous and mesoporous materials with extensive structural rearrangements during processing, reducing the registration between the template size and the pore size created.

(1) Noncovalent bonding between the template and matrix

Noncovalently bonded organic templates include molecules, polymers and supramolecular arrays. When dissolved in solution these species can template small inorganic groups via electrostatic, van der Waals and hydrogen-bonding interactions to form nanostructured materials with tailorable pore shapes and sizes. Andersson and co-workers ^[81] developed a simplified procedure based on noncovalent interactions of the template and matrix. In their experiments, the template was assumed to interact by a

combination of electrostatic interactions and hydrogen bonds with monomer (methacrylic acid) prior to polymerization and with the carbonyl groups of the poly-(methyl methacrylate) matrix after polymerization. Another primary example of the noncovalently bonded methods is self-assembly approach developed by Kresge *et al.* [82, 83] involving the usage of surfactant. Surfactants are bifunctional molecules that contain a lyophilic head group and a lyophobic tail (i.e., they are amphiphiles) [84, 85]. The surfactant template can guide the organic and/or inorganic precursor according to strong noncovalent interactions to form a precise molding of the network around the surfactant assembly. In the case of charged surfactants, electrostatic interactions are thought to have a decisive role in the initial organization of the inorganic-surfactant array [86]. For neutral surfactants, hydrogen-bonding interactions are likely to be decisive [87]. The removal of the surfactant by thermolysis yields a mesoporous structure. The larger size and weaker interactions of the surfactant templates will increase the selectivity of the templates to form specific mesophases with little structural rearrangements. However, some researchers [88] pointed out that the self-assembly process required a rather long equilibration time in the presence of aqueous solvents, rendering this method incompatible with conventional rapid spin-coating manufacturing methods.

A special case of preparing porous films by noncovalent bonding between template and matrix is the solvent – as – porogen approach developed by Dow Corning [89]. In this technique, two types of solvents are used. A lower boiling point solvent is used as a disperse phase for the matrix resin; another higher boiling point solvent acting as a porogen is added to the resin formulation and it remains in the film after the spin coating process. After initial thermal ramping, the lower boiling point solvent is released and vitrification of the matrix is induced. The higher boiling point solvent, which is a poor solvent for the vitrified matrix, undergoes phase separation, thus forming nanometer scaled domains. Further heating leads to volatilization of the solvent and generation of templated porosity.

(2) Covalent bonding between the template and matrix

To form an intimate association of the template with the matrix, which limits the independent organization of the organic and inorganic moieties, the templates are introduced as ligands covalently bonded to matrix molecules. The pioneer work was done

by Wulff and co-workers^[90] who devised synthesis schemes in which functional groups were bound reversibly to a template as polymerizable vinyl derivatives. The derivatized template molecule was then co-polymerized with added monomer and cross-linking agents to form a highly cross-linked matrix. Template extraction created cavities that possess a shape and stereochemical arrangement of functional groups corresponding to that of the template.

There are basically three different approaches in the covalently template technique.

Sol-gel template method

The common sol-gel processing described in last section offers a simple method for the formation of porous silicates. A potential disadvantage of this sol-gel approach is that small pore sizes and narrow pore size distributions are achieved at the expense of pore volume^[91], however, which can be overcome by the template approach^[92].

Organic templated porous silicates are often formed by reacting mixtures of tetrafunctional alkoxides and/or organoalkoxysilanes and a template under acidic or basic conditions^[93]. The covalently bonded organic ligand is usually nonhydrolyzable and imparts partial organic character to an otherwise inorganic siloxane network. In other words, the covalently bound template alters the chemical reactivity of the inorganic precursor and confers hydrophobicity to an otherwise hydrophilic network. The organic ligands can be introduced as (a) pendant groups^[92, 94, 95], (b) bridging groups^[96 – 98], (c) polymerizable groups^[99, 100] that can undergo organic polymerization either sequentially or simultaneously with the inorganic polymerization, forming mutually interpenetrating organic-inorganic networks, and (d) supramolecules that can covalently bind to the Si-O network^[101].

At each successive stage of the sol-gel process, kinetic control must be employed to avoid phase separation and to “freeze-in” a homogeneous structure. It should be noted that the nature of porosity created at the moment the organic templates removal also depends critically in a complex way upon the preceding synthesis and processing because the composite morphology continues to evolve beyond the gel point by processes such as syneresis, capillary shrinkage, relaxation and sintering.

Copolymer approach

This approach involves covalent attachment of a thermally decomposable organic polymer to thermally stable organic matrix (polymers with high glass transition point (T_g) or thermoset polymer) to form a block copolymer. One example is to use polyimide as thermal stable polymer and poly(propylene oxide) (PPO) as thermal labile polymer. The block polymer is allowed to undergo self-assembly after spin coating and is annealed to the curing temperature of the polyimide causing nanoscopically phase-separation. By controlling the weight percentage of the second block, a spherical morphology can be obtained in which domains of the thermally labile block are surrounded by a matrix of the thermally stable polyimide. In a subsequent processing step, the nanoscopically phase-separated thin film is heated to effect decomposition of the PPO to volatile products. These products diffuse out of the polyimide matrix to yield the desired porous nanostructure. The critical features of this strategy are that the thermally labile block must be thermally stable until its degradation temperature, and the decomposition temperature must be below the glass-transition temperature of the polyimide matrix.

The block copolymer approach is challenging for low- k materials from a manufacturing point of view, because the preparation of block copolymer from silicates, which have higher mechanical properties compared to the carbon based polymers and is fully compatible with the current manufacturing requirements of the semiconductor industry, is not practical^[77].

Template covalently connected to oligomers

Here monomeric systems such as TEOS used in sol-gel technique are avoided, and precondensed oligomers such as silsesquioxanes (SSQs) are employed as the inorganic spin-on-glass component. In the following process, the oligomers are grown to be macromolecules through chain-propagation or curing. The template is removed at higher temperature creating voids.

While linear polymers and small-molecule amphiphiles have been successfully blended with TEOS to form nanoscopic structures^[102], the use of oligomeric silicates is significantly more complicated as they have a gross phase-separation with wide range of templating linear polymers^[77]. So the templates should have multi-end functional groups so that they can bind by the strong chemical covalent bonds to the SSQs to achieve the

nanoscopic phase separation. Another effective way of avoiding the macroscopic phase separation is to use a coupling agent, which has two functional groups at the ends of the molecule, to covalently link the template and matrix together.

2.4.3 Using dendrimer molecules as templates

The traditional polymerization usually involves AB-type monomers undergoing chain reaction or polycondensation to get multiple covalent bonds. Generally, polydispersed structures that are statistically controlled are obtained. All three classical polymer architectures, namely linear, cross-linked (bridged) and branched topologies are routinely prepared by these methods.

Dendrimers (from Greek *dendra* for tree) or dendritic polymers are a novel class of macromolecules first discovered in the early 1980's by Donald Tomalia and co-workers [103]. They are distinguished from linear and randomly branched polymers by the inclusion of precisely one branch point per repeat unit [104]. Their synthesis is simply sequentially staged (generations) quantized polymerization events. They are nanoscale objects that are composed of quantized numbers of atoms, monomers and terminal functional groups relative to the respective shell levels (generations) surrounding their cores. Other names for the dendrimer molecules are cascade, starburst, cauliflower, hyperbranched or fractal polymers.

Schematic illustrations of conventional linear polymer and the unusual structure of dendrimers are graphically represented in Figure 2.7.

Figure 2.7 Graphical representation of a conventional polymer molecule (left) and a three-dimensional dendritic macromolecule (right)

Dendrimers have received a considerable amount of attention in the literature ^[105] because of their novel physical properties arising from their unusual structure, with recent reports detailing supramolecular assembly ^[106], site isolation ^[107], light-harvesting ^[108], molecular encapsulation ^[109] and architectural shape changes ^[110]. Besides, dendrimers are also prime candidates as nanoscale templates for introducing closed-cell porosity. The main advantages of using dendrimer as a template or porogen compared to the linear polymer are tabulated in Table 2.2.

Table 2.2 Comparison of properties of linear polymer and dendrimers

Property	Linear	Dendrimer
Shape	Random coil	Spherical
Viscosity	High	Low
Solubility	Low	High
Crystallinity	High	Amorphous
Reactivity	Low	High
Compatibility	Low	High
Compressibility	High	Low
Structure Control	Low	Very high

- The dendrimers have a high degree of fractal-like branching leading to a low degree of entanglements and interactions between molecules, resulting in increased solubility and less hindered diffusion in viscous media.
- The critical feature in generating nanoporous dielectric film is the compatibilization of the thermally unstable organic template or porogen with the inorganic dielectric matrix to produce nanoscopic phase morphology. The presence of a large number of accessible chain end functional groups in the dendrimer may maximize the interaction between the organic template and the network forming inorganic polymer. The relative ease with which the chain end functional groups of dendritic macromolecules can be modified also permits the interaction to be varied, therefore controlling the phase separation.

- The dendrimers, produced by stepwise synthesis, are monodisperse. This means that these polymers have a precise molecular weight and size. By using dendrimers as templates, the resulting pore size can be controlled precisely and possess a monodisperse distribution.

Polyamidoamine (PAMAM) is one example of the dendrimers. They are synthesized by the repetitive addition of a branching unit to an amine core (typically ammonia or ethylene diamine.) The repeat unit is added to the growing polymer in two steps: Michael addition of methacrylate to the amine, followed by regeneration of amine termini with ethylene diamine ^[111]. Each complete grafting cycle is termed a generation and each generation of growth doubles the number of termini and approximately doubles the molecular weight. This is because branching occurs at the terminal amine and two methacrylate monomers will be added to each amine. The Starburst dendrimers from generation 0 (G0) to generation 10 (G10) are commercially available, which span a range of molecular weight from 517 to 935000 Daltons, and contain from 4 to 4096 terminal amines. The molecular models for PAMAM dendrimers from G0 to G4 and G6 are shown in Figure 2.8 ^[111].

Figure 2.8 Ball-and-stick molecular models of PAMAM dendrimers ^[111]

The chemical structure of a Starburst G2 PAMAM dendrimer is shown below. It has a molecular weight of 3256 and 16 surface primary amino groups.

2.4.4 Silsesquioxane host polymers

One of the critical issues for the low dielectric constant interconnect materials is the thermal stability. One of the promising candidates with good thermal property is thermosetting polymers based on silsesquioxanes. Silsesquioxanes have the empirical formula $(\text{RSiO}_{1.5})_n$, where R is hydrogen or an organic group. They are widely utilized in electronics industry^[112 - 114] since the first commercialization of silicon polymers as electrical insulating materials for use at high temperatures. The major reason that silicon resins were accepted by the market in the early days is their oxidative thermal stability^[115, 116]. Compared with organic resins with C-C backbones, silicon resins have already oxidized backbones, (Si-O-Si), and are inherently resistant to oxidation.

Silicon resins can be cross-linked (cured) to give insoluble and nonmeltable cured materials. The curing methods include silanol – silanol condensation, addition reactions (hydrosilylation) and radical reactions (initiated by thermal decomposition of peroxide)^[117]. Commercially, however, silanol – silanol condensation reaction is used almost predominantly. The condensation reactions, utilizing the residual silanol groups of the resin molecules and forming Si-O-Si bonds with the elimination of water, are affected by heat and catalyst. Usually a high temperature for cross-linking is necessary to obtain complete cure because of the lower reactivity of silanol groups caused by steric hindrance and limited molecular motion. The cured silsesquioxanes or polysilsesquioxanes have outstanding properties such as low dielectric constant, high breakdown voltage, good mechanical strength, high thermal stability and etch selectivity, etc^[118, 119]. These good qualities make them a suitable interconnect dielectrics to replace traditional SiO_2 .

Since the backbone of the polysilsesquioxanes is thermal stable Si-O-Si, the oxidative stability of silicon resins is mostly governed by the stability of organic groups attached to silicon atoms. When hydrogen is linked to the silicon (HSQ), the Si-H bond may dissociate and subsequent molecular rearrangement happens involving the exchange of Si-O and Si-H bonds between neighboring silsesquioxane oligomers^[120]. During the exchange process $\text{SiO}_{4/2}$ linkages (silicon bonded to four shared oxygen atoms) are formed. This is accompanied with the loss of the Si-H bonds and the appearance of the Si-H₂ linkages. Subsequently, scission of Si-H bonds results in evolution of hydrogen and Si-Si bonding while the continued exchange of Si-O and Si-H bonds at the same silicon

site ultimately leads to the formation of silane. The reactions can be reviewed below ^[121, 122].

The reactions are promoted by thermal decomposition and oxidation. Furnace temperature and oxygen concentration are two key processing variables that influence these reactions. It has been seen that phenyl and methyl groups are remarkably more stable than hydrogen ^[123]. Therefore, phenyl and methyl silicon resins do not lose much weight and increase their cross-link density upon oxidation at high temperature.

2.4.5 Template process of producing low-*k* porous films

There are many types of template process for producing porous films. Here we discuss the template process in which matrix is a polymer or oligomers that convert to polymer matrix upon heating, and template is thermally degradable polymer excluded surfactants.

The earlier work on the formation of porous low-*k* films using thermosetting polymer and a template was reported by Hedrick *et al.* ^[118]. This technique uses two materials, a main dielectric matrix and a template. During thermal treatment, the template is thermally decomposed and the decomposition products volatilize and permeate through the main matrix, creating nanosize voids within the matrix film at sites occupied by the template prior to the decomposition process. By controlling the dispersion or the distribution of one material within the other, the resultant microstructure can be tailored.

The complete procedure may comprise of (a) admixing, in a suitable solvent, a thermally labile template having a reactive site that enables covalent attachment to another molecular moiety, and a thermally stable, low dielectric constant host polymer having a high glass transition temperature T_g , (b) spin on the solution on the silicon substrates, (c) heating the as-deposited films to a temperature T_c , effective to start the chain-propagation reactions if monomers or oligomers are used, so a polymeric matrix is formed in which the template is present as a discrete phase within a continuous phase

formed by the host polymer; and (d) heating the polymer matrix to a temperature T_d , to degrade the porogen without affecting the host polymer, thereby producing a dielectric material with a porous structure, wherein T_d is greater than T_c but less than T_g .

The above procedures can be illustrated by Figure 2.9^[124], where primary structure unit is organized around a molecular template and solidified to form a matrix.

Figure 2.9 Reactive blending approach for the creation of ultra-low- k nanoporous materials for advanced microelectronic applications^[124]

To successfully synthesize the porous films via the template method, the following criteria must be satisfied^[92, 125]: (i) the template polymer should be thermally removable and must be uniformly incorporated in the inorganic matrix without aggregation or phase separation. This prevents the creation of pores larger than the size of the individual templates. (ii) The synthesis and processing conditions should result in a dense embedding matrix (i.e., a network that wraps tightly around the template) so that the pores are created only by template removal. (iii) The template removal should be achieved without matrix collapse so that the pores created preserve the original size and shape of the template. Hence for precondensed oligomers, its curing temperature must be lower than the decomposition temperature of the thermal labile polymer, so that the template block can remain fixated within the matrix prior to the decomposition.

CHAPTER 3 FABRICATION AND CHARACTERIZATION TECHNIQUES FOR LOW DIELECTRIC CONSTANT MATERIALS

In this work, porous organosilicate films are synthesized via sol-gel and template methods. The general synthesis procedures for these porous dielectrics and the analytical techniques used for their characterization are described in this chapter. The experimental compositions of the spin-on solutions and the procedures of chemical synthesis by the sol-gel and the template routes were developed systematically after many trial experiments. Although it is not practical to describe all the preliminary experiments, the main considerations and reasoning used to arrive at the final process will be outlined in the following two sections.

3.1 Synthesis of Sol-Gel Films

Porous silica films prepared by the sol-gel method involve hydrolysis and condensation reactions of alkoxysilanes in liquid solution as shown in Equations (2.1) – (2.3). A multiple-step sol-gel approach is developed to derive organically modified silicate materials in this work. The technical approach is conceptually straightforward: form a composite structure with highly porous structure embedded in a dense matrix. The deposition process does not require careful atmospheric control. The main considerations in determining the sol composition are emphasized below.

(1) Acid-base two step catalysis

As discussed in Chapter 2, the growth of silica sols may result in structures ranging from linear or randomly branched chains to discrete porous cluster to fully dense colloidal particles, depending on solution conditions. Generally, acid catalysis forms dense film and base catalysis produces high porosity film with larger pores. Therefore, in order to obtain porous films with controlled porosity, acid and base two-step catalysis strategy is adopted. The oligomers formed from acid and base catalysis will link together via condensation reactions.

(2) Selection of precursors

Tetraethyl orthosilicate (TEOS), a commonly used precursor of silica, was chosen as the inorganic precursor. In order to obtain crack-free films under ambient temperature and pressure, organic precursor has to be used with the inorganic precursor. Considering that organic groups would be pyrolyzed at higher temperature to leave pores behind, the organic precursor was catalyzed by a base while TEOS precursor was catalyzed by an acid. According to Voronkov *et al.* ^[71], in the case of base catalysis, the hydrolysis and condensation rate of organic precursors decrease with the increase in the length or branching of the chain of the alkyl groups due to the steric (spatial) and inductive effect. So alkyl substituents with fewer carbon atoms will have less hindrance. Methyl substituted TEOS namely methyltriethoxysilane (MTES), which has minimum retardation effect on the reaction rate, was selected to be the organic precursor in this work. The chemical structure of TEOS and MTES are given below:

Figure 3.1 Chemical structures of TEOS and MTES

Therefore, by use of TEOS catalyzed with an acid and MTES catalyzed with a base, a composite structure with highly porous structure embedded into a dense matrix will be formed as shown in Figure 3.2.

Figure 3.2 Schematic illustration of organically modified mesoporous silica films

(3) Determination of sol composition

The sol composition consists of precursors, solvent, water and catalysts. Their concentrations are not independent; changing concentration of one constituent will affect other constituents' relative concentration. For example, increasing the fraction of water generally promote hydrolysis. However, the precursor concentration is actually reduced when the water fraction is increased, but the solvent : silicate (precursor) ratio maintains constant. The decrease in the precursor concentration will in turn reduce the hydrolysis and condensation rates. Therefore, the composition of the sol should be considered comprehensively. The principle to determine the sol composition is to obtain dense film for acid catalyzed sol and porous structure for base catalyzed sol under reasonable reaction rate.

The water : Si ratio, which affects the film structure, was determined to be about 3 for the sol catalyzed by a base and about 5 for the sol catalyzed by an acid, respectively, to obtain porous structure and dense films. The concentration of catalysts determines the reaction rate. If the reaction rate is too fast, the solution may gel in a time as short as 5 minutes. If the reaction rate is too low, the solution is not spinnable even after one month. So the control of the catalysts fraction is important to allow the sol-gel reactions to be completed in a reasonable time. The role of alcohol solvent is to enable solubility of TEOS and MTES in water. Too much solvent will cause slow reaction rate and promote esterification reaction; too little solvent will give non-spinnable viscous solution.

(4) Surface modification

The purpose of the surface modification is to remove the residual surface silanol groups and to increase the hydrophobicity of the films, so that the films can prevent from the moisture uptake and maintain the dielectric constant low.

An overview of the fabrication scheme for the films is given in Figure 3.3.

Figure 3.3 Schematic illustration of synthesis of sol-gel derived organosilicate films

All the chemicals for the synthesis were purchased from Sigma-Aldrich. The purity of TEOS and MTES is 98% and 99%, respectively. All the glassware was dried before use.

Two types of sols were prepared: sol A consisting of linear oligomers, which would form a dense matrix, was prepared by adding TEOS in ethanol with hydrochloric acid (HCl) as a catalyst. The composition of sol A was as follows: TEOS : ethanol : H₂O : HCl = 1 : 6 : 5 : 1.9×10^{-3} in molar ratio. Sol B consisting of highly branched structure was made by dispersing MTES in ethanol with ammonium hydroxide (NH₄OH) as a catalyst. The composition of sol B was as follows: MTES : ethanol : H₂O : NH₄OH = 1 : 5 : 3 : 6×10^{-4} in molar ratio. Both sols were allowed to hydrolyze for about 24 hr with stirring before mixing together with different molar ratios of sol A : sol B. The films were spun coated on silicon substrates by a commercial spin coater in an ambient environment. The rotation speed is 3000 rpm for 30 seconds. Following spin coating, the as-deposited films were baked at 100°C and soaked in 10% hexamethyldisilazane (HMDS)-toluene solution for 1 hr at room temperature to allow surface modification by replacement of the unconverted surface silanol groups with unreactive methyl groups. The surface modified films were thermally treated in air up to 450°C with a heating rate of 2°C/min. After calcination, the films were further dehydroxylated under nitrogen in a rapid thermal processor (RTP, JIPELEC) chamber at 400°C. The thickness was found to be about 450 nm – 550 nm for films with one coated layer and about 850 nm – 1100 nm with two coated layers. The AB sol was also poured into a petri dish to form a xerogel, which was

used for thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). The above-mentioned preparations were all carried out in a class 100 clean room.

3.2 Synthesis of Templated Films

Organic/inorganic hybrid dielectric formed by embedding a dendrimer into an organosilicate network was designed and synthesized. Commercially available hydrogen methyl silsesquioxane (HMSQ) was used as matrix material and poly(amidoamine) (PAMAM) dendrimer was used as template or porogen. The use of silsesquioxane as a matrix material takes the advantage of its relatively low dielectric constant (k is about 2.8^[119]), so allows for a significant reduction in k values at relatively low porogen loading. The PAMAM dendrimer was chosen as a template due to its well-defined, branched and compartmentalized structure in the nanosize range. Thus it exhibits some unique properties such as containing abundant functionality and multiple chain-ends, enabling them to establish a close association with the matrix.

The chemical structure of a starburst PAMAM dendrimer generation 2 (G2) is shown in Figure 3.4. The central core, spacer and end group of the dendrimer are also labeled.

Figure 3.4 Chemical structure of G2 PAMAM dendrimer

In order to ensure chemical association of the sacrificial dendrimer with the HMSQ matrix, a coupling agent 3-(triethoxysilyl)propyl isocyanate (TPIC) with a simplified formula $R_1 - L - R_2$ was used. Here R_1 is a functional group that enables covalent

binding to the reactive site of the sacrificial polymer, L is a hydrocarbonlene linker, and R_2 is a functional group that enables covalent bonding to the host polymer.

By controlling the weight percentage of the porogen, film morphology with domains of the thermally labile block surrounded by the thermally stable HMSQ matrix was obtained. It is noted that the strength of the vitrifying resin must increase before the template decomposes in order to obtain stable porosity. In the subsequent processing step, the nanoscopically phase-separated thin film was heated to cure the HMSQ matrix. The film was continually heated to a pyrolysis temperature of the dendritic porogen to decompose it to volatile products. These products diffused out of the HMSQ matrix to yield the desired porous nanostructure. The formation of the pores is schematic illustrated in Figure 3.5.

Figure 3.5 Morphology of the templated films

The detailed procedures of producing the hybrid dielectric organic/inorganic films are described below.

HMSQ was obtained from Honeywell International Inc., and all other chemicals were purchased from Sigma-Aldrich. All glassware was dried before use. In the first step, a 20 wt% G2 PAMAM dendrimer solution in methanol and TPIC acting as the coupling agent were dispersed in N-methyl-2-pyrrolidone (NMP) solvent with TPIC slightly in excess. The reaction was carried out with magnetic stirring in an oil bath at 60°C for 24 hr to obtain PAMAM/TPIC derivative. In the second step, HMSQ – propyl acetate solution containing 30 wt% of HMSQ was further diluted in propyl acetate to about 10 wt%. The PAMAM/HMSQ hybrid solution was prepared by adding the PAMAM/TPIC derivative to the diluted HMSQ solution in the selected ratio. The mixture was allowed to react for another 24 hr at room temperature with stirring. The mixture was then spun onto the silicon substrates and heat-treated in a nitrogen purged quartz tube furnace or air furnace

up to 400°C and held at that temperature for 30 minutes. This was followed by further ramping to 490°C and held at that temperature for another 30 minutes before cooling down to the room temperature. The PAMAM/HMSQ solution was also poured into a petri dish used for TGA/DTA analysis. The above-mentioned preparations were all carried out in a class 100 clean room.

3.3 Film Characterizations

3.3.1 Microstructure

The top and cross section of films were observed by atomic force microscopy (AFM) (NanoScope Digital Instruments or SHIMADZU SPM-9500), field emission scanning electron microscopy (FESEM) (JEOL JSM6340F) and transmission electron microscopy (TEM) (JEOL JEM-2010F). The surface morphology and pore structure including the pore size and pore interconnectivity of the films can be obtained from the micrographs.

AFM operates by measuring attractive or repulsive forces between a tip and the sample. In its repulsive contact mode, a tip at the end of a cantilever lightly touches on the sample. As a piezoelectric scanner scans the tip over the sample, an optical detection apparatus (laser, split photodiode) measures the vertical deflection of the cantilever, which indicates the local sample height. In noncontact mode, the AFM derives topographic images from measurements of attractive forces.

FESEM produces clearer, less electrostatically distorted images with spatial resolution of 3 to 6 times better than conventional SEM. It can work under low voltage with superb resolution and image quality of 2.5 nm at 1 kV. A thin conductive layer is needed for insulating materials. Elemental composition of the films imaged in a FESEM can be examined qualitatively with energy dispersive X-ray spectroscopy (EDS). EDS, which collects X-rays generated from the atom in its path, identifies all elements with an atomic number greater than carbon.

TEM is used to image the finest details of internal structure of material lattice. Usually images obtained are two-dimensional sections of the material under study. The resolution for the JEOL JEM-2010 is 0.1 nm and the magnification range is from 50× to 1,500,000×. The acceleration voltage of the electrons in the TEM used is 200 kV that provides high resolution. Samples for TEM must be specially prepared to a thickness that

allows electrons to transmit through the sample. The sample preparation facilities include dimpler grinders and high precision ion millers.

3.3.2 Thermal stability

The thermal stability of the films was investigated by TGA and DTA using a Perkin-Elmer 7 system. TGA is used for precise measurement of specimen weight changes as a function of time and temperature in various gaseous environments. DTA measures the difference in temperature between a sample and a thermally inert reference as the system temperature is varied. The plot of this differential temperature versus the system temperature provides information on exothermic and/or endothermic reactions taking place in the sample.

3.3.3 Refractive index and film thickness

The refractive index and thickness of the porous films were measured using a reflectometer (Filmmetrics F20). For some samples, these properties were also verified by ellipsometry (VB 250, VASE Ellipsometer). Both equipments determine the thin film characteristics by measuring a change in a property of the light or polarized light reflected from the thin film over a range of wavelengths (i.e., by measuring the reflectance spectrum), and then analyzing the data by data fitting.

The Filmmetrics F20 measures thin film characteristics by either reflecting or transmitting light through the sample, and then analyzing this light over a range of wavelengths. Because of its wave-like properties, light reflected from the top and bottom interfaces of a thin film can be in-phase so that reflections add, or out-of-phase so that reflections subtract. Whether the reflections are in- or out-of-phases (or somewhere in between) depends on the wavelength of the light, as well as the thickness and properties of the film.

Optical thin film thickness measurements require the successful completion of two tasks: acquisition and then analysis of an accurate reflectance spectrum. To determine film thickness, FILMeasure, the software of Filmmetrics F20, calculates a reflectance spectrum that matches as closely as possible to the measured spectrum. FILMeasure begins with an initial guess for what the reflectance spectrum should look like theoretically, based on the user's input of a film structure for the sample. Then

FILMeasure varies the parameters it is solving for until the calculated reflectance spectrum matches the measured data.

The approach to determine the refractive index (n) and extinction coefficient (k) is same as that used to measure thickness, except a model is used to obtain a good fit. This is due to the fact that the refractive index at any given wavelength is not independent of the refractive index at adjacent wavelengths but follows a smooth dependency that can be accurately modeled by a theoretical equation. Filmeasure uses different models depending on the type of material being measured: Cauchy model, Drude model, Lorentz model, Bruggeman model and so on. Usually, Cauchy model is suitable to describe transparent insulating materials such as SiO₂. In the Cauchy model, the optical constants as a function of wavelength (with 2 terms) are described by:

$$n(\lambda) = n_0 + \frac{n_1}{\lambda^2} \quad (3.1)$$

$$k(\lambda) = k_0 \exp\left(\frac{k_1}{\lambda}\right) \quad (3.2)$$

where n_0 , n_1 , k_0 and k_1 are the Cauchy model parameters, λ is the wavelength.

For an ellipsometer, it determines the thickness and refractive index of films by measuring unique ellipsometric angles of Ψ and Δ from recorded angular positions of the polarizer and analyzer. These values are then applied to the following relationship defining the ratio of complex Fresnel reflection coefficients of p-polarized waves, r_p , to s-polarized waves, r_s . This ratio, ρ , is expressed in Equation (3.3). Cauchy model can also be used. Hence, both the optical constants and thickness of films are variable of r_p and r_s , and can be solved. The data acquisition and analysis software used was WVASE32.

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \quad (3.3)$$

The porosity of the films can be calculated from the refractive index (at 632.8 nm) based on the Lorentz-Lorenz relationship^[126]:

$$(n_f^2 - 1) / (n_f^2 + 2) = (1 - V_f) (n_s^2 - 1) / (n_s^2 + 2) \quad (3.4)$$

where n_f , n_s are the refractive indices of the porous film and the solid skeleton, respectively, V_f is the volume fraction of the pores. In our case, n_f , n_s are the refractive indices of the porous film and silica, respectively.

3.3.4 Composition and chemical bonding

Fourier transform infrared spectroscopy (FTIR) is used for qualitative and quantitative analysis of dielectrics in term of composition and bond structure. The technique is based on the absorbance of infrared radiation and is sensitive to bulk changes in the rotational, bending, and stretching vibrational modes of the molecules in the film. FTIR is an extremely useful technique to verify the composition of the film before and after processing steps. For porous dielectrics, due to their large internal porous surface, bulk changes are detected as a consequence of minute changes at the pore walls. The basic structure of compounds can be determined by the spectral locations of chemical bonds absorptions that occur at characteristic frequencies (or wavelength). FTIR measurements were carried out on a Perkin-Elmer Spectrum 2000 spectrometer. The wavenumber range of the measurements was from 4000 cm^{-1} – 400 cm^{-1} .

3.3.5 Contact angle

The concept of contact angle is rooted in the concept of surface energy as described in Figure 2.4 and Equation (2.8). The wetting of the surface can be defined based on the contact angle:

$0^\circ < \theta < 90^\circ$ for wetting or hydrophilic

$90^\circ < \theta < 180^\circ$ for non-wetting or hydrophobic

The contact angles of the films were measured by an optical contact-measuring device – OCA 20 (Dataphysics). A drop of deionized (DI) water was deposited on a surface of the films to measure the contact angle, software SCA 20 was used to determine the contact angle.

3.3.6 Pore structure

Some of the most important features of the low- k dielectrics are related to the pore structure. A basic description of pore structure includes porosity, pore size and pore interconnectivity. Porosity is defined as the fraction of the total volume of the film comprised by the pores:

$$P = \frac{V_p}{V} \quad (3.5)$$

where P is porosity, V_p is pore volume and V is total volume of the film.

Pore size refers the width of the pores. According to International Union of Pure and Applied Chemistry (IUPAC) ^[127], pores can be divided into three types based on the size of the pores: micropores with pore size < 2 nm; mesopores with pore size between 2 nm and 50 nm; and macropores with pore size > 50 nm.

Pore interconnectivity refers the linkage of pores. It is either open-pore if it is accessible by the probe or closed-pore if its size is smaller than the probe diameter and is inaccessible. Note, however, that different analytical methods will provide different thresholds of open and closed pores. Figure 3.6 ^[128] shows idealized pore structures.

Figure 3.6 Schematic illustration of the types of pores ^[128]

Precise characterization of the structure of porous thin films is crucial to the application of porous low- k materials as intermetal and interlayer dielectrics. Methods for

characterizing the pore structure are generally based on three different physical principles. The first class of methods is based on a stereological analysis, using various types of microscopes such as SEM, TEM and AFM, providing a direct observation of the cross section of the solid. The second class of methods is nonintrusive methods based on radiation scattering, wave propagation, positron lifetime spectroscopy and so on. They are generally sensitive to both open and closed pore structures. The third class of methods is intrusive methods based on gas adsorption, mercury porosimetry and calorimetric methods.

In this work, the porosity in the films was evaluated with two methods: optical reflectometer as described in section 3.3.3 and specular X-ray reflectivity (SXR). The pore connectivity of the films was determined by nitrogen adsorption porosimetry and SXR technique. The working assumption is that the nitrogen adsorption isotherm can only access open-pore whilst SXR can access both open-pores and closed-pores. The pore sizes of the films were mainly obtained directly from SEM, TEM and AFM observations. Small angle X-ray scattering (SAXS) was also used to obtain pore size for a small number of samples.

Nitrogen porosimetry

Nitrogen adsorption porosimetry is one of the most important and widely used methods for the characterization of a variety of porous solids. It is based on the measurement of mass or volume of adsorbate condensed in the pores. Therefore, only information relating to open pores can be obtained. Different approaches are used for the calculation of the sizes of mesopores and micropores. The calculation of pore size in mesoporous films relies on the analysis of a hysteresis loop that appears as a result of the difference in effective radius of curvature of a condensed liquid meniscus during adsorption and desorption ^[129]. An adsorption/desorption isotherm is usually recorded as volume of gas adsorbed versus relative pressure, P/P_0 (sample pressure/saturation vapor pressure). Using relative pressure to construct the isotherm eliminates changes in pressure from small variation in temperature. The dependence of the relative pressure P/P_0 on the meniscus curvature is described by the Kelvin equation:

$$\ln\left(\frac{P}{P_0}\right) = \frac{f\gamma V_L}{r_k RT} \quad (3.6)$$

where γ and V_L are surface tension and molar volume of the liquid adsorptive, respectively. f is a constant relating to the pore shape and it equals 2 for cylindrical pores. R is the universal gas constant ($= 8.3144 \text{ J}/(^{\circ}\text{K mole})$), and T is the absolute temperature. r_k is the Kelvin radius or the meniscus curvature.

From Equation (3.6), r_k can be derived from the measurement of P/P_0 . The pore radius, r_p , is related to the Kelvin radius as:

$$r_p = r_k + t \quad (3.7)$$

where t is the thickness of the layer adsorbed on the pore walls. This thickness is defined by the Brunauer, Emmet, Teller (BET) equation ^[129, 130]:

$$t = \frac{d_0 CK(P/P_0)}{[1 - K(P/P_0)][1 + K(C - 1)(P/P_0)]} \quad (3.8)$$

where d_0 is the thickness of one monolayer of adsorbate, C is the BET constant, and K is a coefficient satisfying the requirement that at $P = P_0$, $t \leq 5 - 6$ monolayers.

The BET equation is also useful for measurements of specific surface area. The volume of adsorbate necessary for filling the first monolayer is measured and the surface area is calculated from the surface area occupied by each adsorbate molecule.

The Kelvin equation is no longer valid for the calculation of micropores. Not only do the values of the surface tension and the molar volume deviate from those of the bulk liquid adsorptive, but also the concept of a meniscus becomes meaningless. A theory developed by Dubinin and Radushkevitch (DR) ^[131] is usually used to calculate micropore sizes. The process involved is micropore volume filling rather than layer-by-layer adsorption on the pore walls. The adsorption potential A and the characteristic adsorption energy E_0 are a function of the micropore size and the amount of adsorption W at the relative pressure P/P_0 is given by

$$W = W_0 \exp[-(A/E)^n], (n = 2) \quad (3.9a)$$

$$E = \beta E_0 \quad (3.9b)$$

$$A = RT \ln(P/P_0) \quad (3.9c)$$

where W_0 is the micropore volume and β is the affinity coefficient. A linear plot of $\ln(W)$ versus A^2 gives W_0 and βE_0 . The value of βE_0 provides the isosteric heat of adsorption. E_0 gives the average pore size $w_0 = K/E_0$ where $K \approx 12$ is a coefficient slightly changing with E_0 [129, 132]. So the micropore structure such as micropore volume can be obtained from the DR equation.

In this work, the structural properties of bulk xerogels were determined by nitrogen adsorption isotherm (ASAP 2000C, Micromeritics Instrument Group, Norcross, GA) at 77 K, the temperature of liquid nitrogen. At this temperature, inert nitrogen will physically adsorb on the surface of the sample. The analysis of pore sizes and specific area of xerogels were carried out with the ASAP 2000C analytic software.

Specular X-ray reflectivity

SXR is a technique for characterizing thin film properties including thickness, density and interface roughness. Although its capabilities overlap with a number of other thin film measurement techniques such as ellipsometry, ion beam analysis, cross-sectional TEM, it has the virtues of high resolution, straightforward analysis and no sample preparation.

In SXR, an incident beam of X-rays is directed towards the sample surface at an angle θ to the surface of the sample. The refractive index is determined by the following factors:

$$n = 1 - \delta - i\beta \quad (3.10)$$

where n is refractive index, δ is a parameter proportional to the electron density of the sample and β is a parameter related to the absorption of X-rays.

When X-rays cross an interface between two media of different refractive indices n_1 and n_2 , they are refracted according to Snell's law:

$$n_1 \sin \theta_i = n_2 \sin \theta_r \quad (3.11)$$

where θ_i and θ_r are the angles of incidence and refraction (measured with respect to the normal), respectively.

For most materials the refractive index is less than 1 at X-ray energies with wavelengths of a few tenths of a nanometer. Hence there is a critical angle, above which a well-collimated beam of X-ray is no longer totally reflected off the free surface but starts penetrating into the sample, as shown in Figure 3.7.

Monochromatic X-rays

$$\theta < \theta_c$$

Total external reflection

$$\theta > \theta_c$$

Reflection and transmission

Figure 3.7 Schematic illustration of the critical angle in SXR

The X-ray undergoes total external reflection below the critical angle, θ_c , which is given by^[133]:

$$\theta_c = \lambda \sqrt{\frac{\rho_c \gamma_c}{\pi}} = \sqrt{2\delta} \quad (3.12)$$

where λ is the X-ray wavelength, ρ_c is the electron density of the sample, and γ_c is the classical electron radius (2.8179×10^{-15} m).

Usually, SXR data is recorded as the intensity of reflectivity versus the incident angle. There are two ways to analyze SXR data. In the first method, a data fitting program is used to determine the film structure indirectly. The film thickness, density and interface roughness are obtained by fitting the experimental SXR curve to calculations of

different model structures and optimizing by least-squares minimization to obtain a set of best-fit parameters.

In the second approach, which does not involve modeling, the porosity of the film is obtained by comparing the average film density to an assumed density of the nonporous material:

$$P (\%) = 1 - (\rho / \rho_0) \times 100\% \quad (3.13)$$

where P is the porosity of the film, ρ is the mass density of the film, and ρ_0 is the mass density of the dense material.

From Equation (3.12), it can be seen that the average electron density of a film is determined directly from the critical angle. The expression of mass density of a film, ρ , is similarly obtained by applying Snell's law as ^[134]:

$$\rho = \frac{\pi^2 c^2 \epsilon_0}{3 \lambda^2 N_A e^2} M_c m \theta_c^2 \frac{\sum X_j M_j}{\sum X_j Z_j} \quad (3.14)$$

where c is the speed of light in vacuum, ϵ_0 is the permittivity of free space, λ is the X-ray wavelength, N_A is the Avogadro constant, e is the electron charge, m is the electron mass, M_c is the atomic mass of carbon, θ_c is the critical angle of the film, and X_j , M_j , Z_j are the atomic fraction, molar mass and atomic number of the element j , respectively. The atomic mass of carbon is used because the atomic mass unit is defined as 1/12 the weight of the carbon-12 isotope.

Basically the average mass density of the film can be calculated if the stoichiometry is known. In this work, SXR was performed using a vertical Siemens D5005 X-ray diffractometer with 401 mm measurement circle that provides an accuracy of 0.0001°. The reflectivity data was collected with Cu K_α radiation (wavelength of 1.54 Å) at 40 kV and 40 mA. "Refsim Ver1.1" (Bruker AXS Analytical X-ray System) was used to do the data fitting.

SAXS measurement

Small angle X-ray scattering measurements, which is a well-established techniques to study the structure of materials on the length scales of 2 nm to 200 nm ^[135], was used to evaluate the pore size of the films. SAXS intensity is caused by the inhomogeneity of distribution of electron density. In our case, the inhomogeneity of the distribution of electron density arises from the SiO₂ network and pores. Babinet theorem ^[136] states that, an ensemble of cavities in a homogeneous medium could be considered equally well in place of an ensemble of particles. From this, it is possible to consider the pores as the convenient ‘scatterer’:

Figure 3.8 Scatters in SAXS measurement

The experiment is performed in a transmission mode. SAXS pattern represents the scattering variation due to the point-to-point variations in electron density. The variation can be expressed by the actual measured intensity ($I(\vec{q})$) of the X-ray illuminated volume V by the following transformation ^{[[137, 138]]}:

$$I(\vec{q}) = I_0 \left[\int_V \rho(\vec{r}) \exp(i\vec{q} \cdot \vec{r}) d^3\vec{r} \right]^2 \quad (3.15)$$

where $\vec{q}$ is the scattering vector with modulus $q = |\vec{q}| = (4\pi/\lambda)\sin\theta$, 2θ is the scattering angle, λ is the wavelength of the radiation;

I_0 is a constant defined by the conditions of the SAXS instrument;

$\vec{r}$ is the vector that defines the position of a point relative to an arbitrary origin;

and $\rho(\vec{r})$ is the spatial distribution of electron density.

SAXS deals with the size range well above the interatomic distance, so that $\rho(\vec{r})$ can be approximated as a continuous variable of the position $\vec{r}$ in the spectrum.

Thus, the intensity distribution (SAXS pattern) as a function of $\vec{q}$ is uniquely determined by the structure in terms of its electron density distribution, which is the structure. If the scattering is spherically symmetric, $I(\vec{q})$ depends only on q , then

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin qr}{qr} dr \quad (3.16)$$

where $p(r)$ is so called pair-distance distribution function (PDDF) which gives the number of difference electron pairs with a mutual distance between r and $r + dr$ within the scatter pore.

Like the electron spatial distribution function, $\rho(\vec{r})$, $p(r)$ is also a function of the structure. In the case of spherical pores within a Gaussian pore size distribution centered at r with a standard deviation σ , $I(q)$ can be described as ^[139]:

$$I(q) = \int_0^\infty \frac{1}{\sqrt{2\pi\sigma^2}} \left(3 \frac{\sin(qr) - qr \cos(qr)}{(qr)^3} \right)^2 \exp\left(-\frac{(r_i - r)^2}{2\sigma^2}\right) dr \quad (3.17)$$

where r_i is the pore size variable.

Equation (3.17) gives the direct relationship between the measured scattering intensity q and the pore radius of r .

The experiments were carried out using a Bruker Nanostar instrument. All X-ray paths were kept in vacuum of about 10^{-4} Torr (0.0133 Pa), including the sample holder in order to prevent scattering and adsorption of X-rays by air. The radiation was Cu K_α ($\lambda =$

1.54 Å) and the distance from sample to the detector was 1060 mm. The operating voltage and current of the X-ray was 40 kV and 35 mA, respectively. The q range covered in SAXS was from 0.05 nm^{-1} to 0.15 nm^{-1} and the scanning time was 50,000 seconds per sample. The scattered intensities were corrected for transmission and deducted from parasitic and substrate scattering. After the scattering curve was collected, it was fitted to determine the pore size using the Equation (3.17) via FISH software (SAXS software by Heenan, RAL).

For SAXS measurement, the films were deposited on mica substrates with thickness of 100 μm . The thin substrate increases the transmission of X-ray through the films to obtain stronger signal-to-noise ratio.

XRD measurement

X-ray diffractometer (XRD) is usually used for characterization and identification of periodic atomic structure of crystals. When X-rays interact with a crystalline substance (Phase), one gets a diffraction pattern. Let us consider an X-ray beam incident on a pair of parallel atomic planes P1 and P2, separated by an interplanar spacing d .

Figure 3.9 Schematic diagram for Bragg's law of diffraction

The two parallel incident rays 1 and 2 make an angle (θ) with these planes. A reflected beam of maximum intensity will result if the waves represented by 1' and 2' are in phase. The difference in path length between 1 to 1' and 2 to 2' must then be an

integral number of wavelengths. We can express this relationship mathematically in Bragg's law at first approximation.

$$\lambda = 2d \sin \theta \quad (3.18)$$

where θ is the incident angle of X-ray beam, λ is the wavelength of the X-ray and d is the perpendicular distance between the reflection-planes.

The possible d -spacing are determined by the shape of the unit cell. Rewriting Bragg's law we get:

$$d = \frac{\lambda}{2 \sin \theta} \quad (3.19)$$

XRD can also be used to identify the ordered porous structure in the films, because they also have a periodic structure of differing electron densities. If the phases of the waves scattered from each layer coincide, the film will achieve maximum reflectivity. Generally, the XRD pattern for ordered mesoporous materials is composed of distinct diffraction lines appearing at low angles, which are used for the determination of the structure.

In this work, XRD was performed using a vertical Siemens D5005 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 40 mA.

3.3.7 Dielectric properties

Dielectric properties are key issues of low- k materials. For dielectric measurements, the films were prepared on heavily doped n type silicon wafers with a resistivity of 5 $\text{m}\Omega\cdot\text{cm}$. This is to ensure that the Si substrate is in accumulation state during measurements. An array of titanium/gold dots was evaporated onto the films in an e -beam evaporator (Denton Vacuum) through a shadow mask. A blanket layer of titanium/gold was also deposited on the backside of the wafer to act as a second contact. The test structure is schematically illustrated in Figure 3.10.

Figure 3.10 Schematic illustration of dielectric test structure

The dielectric constant was evaluated using a Keithley CV analyzer at frequency of 1 MHz. Since the measurements involved very small capacitances, a parallel circuit mode of capacitance measurement was chosen. Admittance is the fundamental electrical parameter measured by commercial capacitance meters. This is given by parallel capacitance C_p and conductance G of the sample through the measurement. The dissipation factor D is calculated from the following equation:

$$D = \frac{G}{\omega C_p} \quad (3.20)$$

where ω is the angular frequency, $\omega = 2\pi f = 2\pi \times 10^6 \text{ rad/s}$.

In the measurement, a high frequency capacitance-voltage (C - V) swept from -20 V to 20 V was carried out to determine the accumulation region of C - V curve for the quasi metal-insulator-metal (MIM) capacitors. In the accumulation region, all charges applied to the gate are balanced by majority carriers in the silicon substrate. These thin layers of charges formed on both sides of the dielectrics give rise to an equivalent parallel-plate capacitance. The dielectric constant, k , of the samples can be calculated using the parallel plate capacitance formula given by ^[140]:

$$k = \frac{Ct}{\epsilon_0 A} \quad (3.21)$$

where C is the accumulation capacitance of the sample, A is the area of the gate, t is the thickness of the sample, and ϵ_0 is the permittivity in vacuum ($8.854 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$).

The shape of the gate of the quasi MIM capacitor should preferably be circular thereby providing the smallest perimeter to area ratio. The area of the gate should be made large enough so as to achieve a measurable capacitance. Furthermore, a large gate will render the fringe capacitance at the periphery of the gate less significant.

The dielectric constant can also be evaluated theoretically by the Bruggeman effective medium approximation model ^[141]:

$$f_1 (k_1 - k_e) / (k_1 + 2k_e) + f_2 (k_2 - k_e) / (k_2 + 2k_e) = 0 \quad (3.22)$$

where $f_{1,2}$ are the volume fraction of the two components, respectively; $k_{1,2}$ are the dielectric constant of the components, respectively; k_e is the effective dielectric constant of the material. In our case, air and SiO₂ are the two components, $f_{1,2}$ are obtained from Lorentz-Lorenz relationship (Equation (3.4)).

3.3.8 Electrical properties

For electrical measurements, the films were also prepared on heavily doped *n* type silicon wafers. The *I-V* characteristics of the films were tested with a HP 4155A semiconductor parameter analyzer in ambient environment. The voltage was swept from -20 V to 40 V and the leakage current density (*J*) versus applied electric field (*E*) can be determined from the *I-V* measurement:

$$J = \frac{I}{A} \text{ (A/cm}^2\text{)} \quad (3.23)$$

where *I* is the leakage current and *A* is the electrode area.

$$E = \frac{V}{t} \text{ (V/cm)} \quad (3.24)$$

where *V* is the voltage and *t* is the film thickness.

3.3.9 Mechanical properties

The mechanical properties of the dielectric films play a crucial role in the integration process. Relevant mechanical quantities include elastic modulus and hardness ^[142 – 144]. The elastic modulus is defined as the ratio of the uniaxial stress along an axis of the material to the accompanying normal strain along that axis. Hardness is defined as the resistance of penetration of its surface. For thin films, it is impossible to detach the film from the substrate and to measure the mechanical properties with this “free standing” film. Alternative way to measure the mechanical properties of the film is to deform it on a very small scale. A convenient way to accomplish this is by indentation testing on a nanometer scale ^[145, 146]. The nanoindentation utilizes a diamond tip that is pressed into the material of interest and subsequently retracted. Nanoindentation is also applicable for thin dielectric films with subtractive porosity although there is still a considerable discussion about the true meaning of the data obtained as the influence of pore crushing is not well understood ^[147].

The experiments were performed using a TriboScope nanomechanical testing system attached to a scanning probe microscope (NanoScope digital instruments). A Berkovich diamond tip was used as both an indenter and imaging probe. The tip-area function (A) was calibrated with fused silica according to the procedure reported in the literature ^[147]. Based on the calibrated tip-area function, the relationship between the projected contact area (A) and the contact depth (h_c) was obtained and inputted into the Data Analysis section for use on all future indents. During indentation, the indentation depth versus time and the load versus time were recorded simultaneously and displayed as a standard Load/Depth curve. Hardness (H) and reduced elastic modulus (E_r) were determined from the unloading part of the force-depth (F - d) curve.

It is noticed that the reduced modulus E_r accounts for the fact that the measured displacement includes contribution from both the specimen and the indenter ^[148]:

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu^2}{E} \quad (3.25)$$

where E_i and ν_i are the elastic modulus and Poisson's ratio of the indenter material, and E and ν are the elastic modulus and Poisson's ratio of the indented material.

The elastic modulus and Poisson's ratio of the indenter are 1140 GPa and 0.07, respectively. The Poisson's ratio of 0.22 is assumed for organosilicate films ^[149]. So the elastic modulus of the films can be derived from Equation (3.25).

In the hardness and modulus experiments, about ten to fifteen indentations were performed on each sample and the indentations were made at least 25 μm apart to avoid interaction between the stress fields resulting from neighboring indentations.

CHAPTER 4 SURFACE MODIFICATION OF SOL-GEL DERIVED LOW DIELECTRIC CONSTANT SILICA FILMS

In the sol-gel chemical reactions, silanol groups are generated in the hydrolysis step, and they are converted into siloxane linkages in the following condensation reactions. The residual silanol groups in the final film are undesirable, as they will absorb moisture from atmosphere causing the high value of dielectric constant of the films. In order to minimize the concentration of hydroxyl groups, a series of measures, including incorporation of organic precursors, chemical surface modification, heat-treatment in different ambient and temperatures, have been taken. Their effects on the dehydroxylation and dielectric properties of the films are systematically studied in this chapter.

4.1 Effect of Organic Precursor

4.1.1 Effect of organic precursor on cracking behavior

Generally, there are two types of precursors in sol-gel synthesis ^[150 – 153] – inorganic precursors such as $\text{Si}(\text{OR})_4$ and organic precursors such as $(\text{R}_1)_x\text{Si}(\text{OR})_{4-x}$, where R or R_1 is an alkyl group with x having the integer number of 1 to 3, R or R_1 can be same or different.

When inorganic TEOS was used as the sole precursor, it was found that crack-free films could only be obtained with film thickness less than 0.5 μm . The thicker films cracked after heat-treatment in both nitrogen and air atmospheres. This phenomenon was also observed by other researchers ^[154 – 159]. Schroeder ^[160] and Dislich ^[161] even concluded that inorganic films thicker than about 1 μm were virtually impossible to obtain without crack even if the supercritical drying technique was used. The cracking is attributed to the high capillary forces set up in the very fine pores by the remaining solvent as discussed in Chapter 2.

To address this problem, an organic precursor, MTES, was considered to incorporate to TEOS forming an organically modified silicate. MTES was selected due to its low

steric effect and high chemical reaction rate. Comparing MTES to TEOS (Figure 3.1), one $\text{C}_2\text{H}_5\text{O}-$ group is replaced by the $-\text{CH}_3$ group. Because the methyl group is a nonhydrolyzable organic substituent, the potential number of functionalities able to form siloxane network is reduced from 4 to 3. When TEOS is used as sole precursor, the resultant network consists of only Si-O-Si linkage. When MTES and TEOS are used

as precursors, the resultant network consists of Si-O-Si and $\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si-O-Si} \end{array}$ linkages and these organic and inorganic components are chemically bonded to each other through strong covalent bonds by the cross polycondensation of TEOS and MTES precursors. Thus the organic methyl groups will exist in the final silica network. This is demonstrated by FTIR measurement. Figure 4.1 shows the FTIR spectra of films prior to any surface treatments with and without organic precursors. The molar ratio of the organic and inorganic precursor for the hybrid film is 1.

Figure 4.1 Absorbance FTIR spectra of films with and without organic precursor

The most intense absorption peak of the Si-O bond that constitutes the skeletal SiO_2 network is located at 1060 cm^{-1} due to the transverse optical (TO) vibration mode corresponding to the asymmetric stretching of the intertetrahedral oxygen atoms in the Si-

O-Si linkage. The broad peak between 3300 cm^{-1} – 3700 cm^{-1} corresponds to a stretching of -OH and physisorbed moisture on the surface in several modes.

Besides the common Si-O-Si and Si-OH bonds, three additional FTIR peaks are found for the film prepared from MTES/TEOS precursors: (1) a peak centered around 1100 cm^{-1} as a shoulder peak at the high frequency end of 1060 cm^{-1} peak; (2) a peak located at 1277 cm^{-1} ; and (3) a peak located at 2975 cm^{-1} . The peak centered on 1100 cm^{-1} is attributed to the longitudinal optical (LO) vibration mode of the Si-O-Si linkage. The presence of such a peak implies that the MTES/TEOS film is more porous in nature [162]. Another two additional peaks located at 1277 cm^{-1} and 2975 cm^{-1} are assigned to the vibration of the Si-C bond and the -CH₃ unit, respectively. So the organic groups are incorporated to the silica network in the form of silicon-carbon bonds units.

The presence of -CH₃ groups significantly affects the gelation behavior of the films. In the gelation of TEOS films, the sol-gel reactions form a three-dimensional gel network at low temperature, causing gelation without any loss of solvent. The wet silica gel with fluid in the interstices then needs to be dried to form a porous film. As the liquid evaporate, the solid network is drawn into the remaining liquid to prevent exposure of the energetic solid-vapor interface. The network is sucked under the surface of the liquid by the capillary tension. If the pressure in the liquid were uniform, the network would be hydrostatically compressed and there would be no risk of fracture. However, because of the low permeability of the gel network, the tension is greater in the liquid near the drying surface, and this produces differential strain leading to crack formation. In order to reduce the significant drying stresses, supercritical drying usually has to be used to get crack-free films [164, 165].

For MTES/TEOS films, the -CH₃ groups modify the network by reducing network connectivity [163]. The gelation point of the MTES/TEOS films will appear at higher temperature than that of the TEOS films. So the gelation can occur only after evaporation of most of the solvent or by-products at elevated temperature. This feature allows the formation of porous film with low drying stresses. As a result, crack-free and thicker silica films can be achieved by this means at ambient temperature and pressure.

Figure 4.2 shows the FESEM cross-section micrograph of a MTES/TEOS film. The image reveals a rather uniform structure without crack; the thickness of the film is about $1\text{ }\mu\text{m}$.

Figure 4.2 FESEM micrograph of a film with equal moles of MTES and TEOS

Figure 4.3 shows the thickness measurement for the film with MTES/TEOS molar ratio = 1.0 using a reflectometer (Filmmetrics F20). The calculated curve is obtained from FILMeasure software analysis as described in Chapter 3 (section 3.3.3). The resultant average thickness is about 1078 nm, in agreement with the FESEM observation.

Figure 4.3 Typical result of optical thickness measurement for the film with equal moles of TEOS and MTES

Therefore, with the incorporation of the organic precursor of MTES, it is possible to get crack-free sol-gel films with thickness of about 1 µm.

4.1.2 Effect of organic precursor on dielectric properties

Apart from the drying mechanism, the dielectric properties are also different for the TEOS and MTES/TEOS films because of the different structures. Figure 4.4 shows the dielectric constant and dissipation factor for the two types of silica films before any other dehydroxylation treatments.

Figure 4.4 Dependence of dielectric properties of the films on the type of precursors

The dielectric constant and dissipation factor after fabrication are 12.79 and 0.19 for the TEOS film, and 4.33 and 0.0462 for the MTES/TEOS film. The dielectric constant and dissipation factor of the TEOS film are three and five times larger than that of the MTES/TEOS film, respectively. There are two reasons responsible for these differences. The first is the increased porosity in the MTES/TEOS films resulting in lower dielectric constant. The higher porosity of the MTES/TEOS films has been shown in the FTIR spectra (Figure 4.1). Although light is incident normal to the sample in the FTIR measurement, the peak centered at 1100 cm^{-1} as a shoulder peak at the high frequency end of 1060 cm^{-1} peak is a result of the scattering of pores^[162]. It can be seen in Figure 4.1 that the MTES/TEOS film has such a peak while the TEOS film does not have. Thus the MTES/TEOS film has higher porosity, which in turn results in lower dielectric constant. The mechanism of pore generation in the MTES/TEOS films will be discussed in detail in Chapter 5.

The second reason of the lower dielectric constant and dissipation factor for the MTES/TEOS film is the presence of the hydrophobic $-\text{CH}_3$ groups in the silica network.

Silica films will unavoidably contain a certain degree of residual hydroxyl or silanol groups at pore surfaces due to the incomplete condensation reactions. These silanol groups readily absorb moisture from atmosphere. The absorbed moisture increases the dielectric constant and dissipation factor of the silica films and also cause via hole poisoning and other integration problems. The presence of organic -CH_3 groups in the final MTES/TEOS films can confer the hydrophobic property to the films so as to resist the moisture infusion from the atmosphere. The hydrophobicity of the films can be evaluated through the measurement of contact angle of the films. Larger contact angle indicates higher hydrophobicity. The contact angle of films with TEOS or MTES/TEOS as precursor(s) is shown in Figure 4.5.

Figure 4.5 Contact angle of the films with and without organic precursor

The incorporation of MTES increases the contact angle from 42.8° for the TEOS film to 61.3° for the MTES/TEOS film. Hence the presence of -CH_3 groups in the SiO_2 network can protect the films from absorbing moisture and is beneficial to the dielectric properties.

4.2 Effect of Surface Modification

Although the presence of Si-CH_3 organic groups in the MTES/TEOS film reduces the dielectric constant, the dielectric constant of the film is still as high as 4.33 after

fabrication and increases to about 5.4 within three days (Figure 4.4). The increment is about 25.6%. The porosity of the film derived from refractive index measurement and the Lorentz-Lorenz relationship is about 57%. The dielectric constant should be about 1.96 according to Bruggeman theoretical calculation (Equation (3.22)). Thus the higher dielectric constant of the film is probably due to the moisture absorbed by the silanols groups in the film. The low contact angle of 61.3° for the MTES/TEOS film indicating the hydrophilic nature of the film supports this inference. Although the film was thermally treated, the temperature was only 450°C – not high enough to remove the most strongly bonded hydroxyls on the film surface. However, the temperature cannot be raised too high in order to retain the pores in the film and to take into consideration the constraints of process integration.

In addition to thermal treatment, another effective method of dehydroxylation is chemical surface treatment ^[166 – 169]. In this work, HMDS or trimethylchlorosilane (TMCS) was considered as chemical modification agent. The overall chemical reactions of HMDS and TMCS with surface silanols are:

The main difference between TMCS and HMDS is that TMCS contains halogen atoms. The HCl generated during the reaction can potentially corrode metal lines in integrated circuit processes ^[170]. The use of HMDS avoids this problem as no halogen or acidic byproducts are produced during the reaction. In the experiments, the sol-gel low-*k* films were soaked into the 10 vol% HMDS-toluene solution; the chemical reaction was conducted with different time. Figure 4.6 shows the effect of HMDS on removal of the surface -OH groups.

The amount of methyl increase and hydroxyl groups decrease evidently after treatment in HMDS-toluene solution as shown by the increasing and decreasing peak areas around 1277 cm⁻¹ and 3300 cm⁻¹ – 3700 cm⁻¹, respectively. This is because some of the -OH groups in the film have been replaced by -CH₃ groups in the HMDS.

Figure 4.6 Absorbance FTIR spectra of MTES/TEOS films with different HMDS soaking time

The quantitative changes in C-H and Si-OH bonds due to the HMDS surface treatment are monitored by measuring their normalized peak areas. Since Si-O-Si bond in the films are not expected to play a main role in the surface treatment, the peak area of Si-O-Si bond is used for normalizing the C-H and Si-OH peaks. Figures 4.7 and 4.8 show the quantitative changes in methyl and silanol groups after HMDS treatment.

Figure 4.7 Effect of HMDS treatment on the methyl concentration

Figure 4.8 Effect of HMDS treatment on the dehydroxylation

After 1 hr of soaking in HMDS-toluene solution, the normalized C-H peak area increases by 9.91% and the normalized -OH peak area decreases by 20.56%. The film surface becomes more hydrophobic as the contact angle of the film increases from 61.3° to 85.3° (Figure 4.9).

Figure 4.9 MTES/TEOS film after 1 hour of HMDS treatment
has a contact angle of 85.3°

If the dehydroxylation reaction time is prolonged to 24 hr, the normalized FTIR specific area of methyl increases by 23.81% and the normalized hydroxyl peak area

decreases by 39.14% compared to the no surface-treated film. More -OH groups are substituted by -CH₃ groups with extended soaking time.

The effect of the HMDS surface treatment on the dielectric properties of the films is shown in Figure 4.10.

Figure 4.10 Dielectric constant and dissipation factor of the films as a function of HMDS soaking time

The dielectric constant and dissipation factor of the films decrease markedly after HMDS treatment due to the decrease of moisture absorbing species. However, the

dielectric properties of the film with 24 hr soaking in HMDS are actually inferior to the film soaked for 1 hr even though extended reaction time is more effective in dehydroxylation. One possible explanation for this observation is that the methyl groups begin filling up some of the pore space. As a consequence, the porosity of the film decreases, leading to a lower dielectric constant. This assumption agrees with porosity evaluation and is also consistent with the literature ^{[[171, 172]}.

The electrical property of MTES/TEOS films is also affected by the HMDS modification. The leakage current density of the films, derived from the I - V measurements as stated in Chapter 3 (Equations (3.23) and (3.24)), is shown in Figure 4.11.

Figure 4.11 Comparison of J - E property for the MTES/TEOS films with and without HMDS modification

Similar to the dielectric constant, the leakage current of the films also decreases after HMDS chemical modification. It has been suggested that electrons injected into the thermal oxide films can be captured by water-related traps ^{[[173]}. Such traps may initiate a chemical reaction, producing a negatively charged center and hydrogen. The porous nature of the sol-gel derived silica films may result in more of such traps. The reduction in the number of Si-OH centers and absorbed water by exposing the film to the HMDS can reduce water-related traps and in turn reduce the leakage current of the films.

Although the dielectric properties has been improved by the HMDS surface modification, the dielectric constant of the film is still as high as 3.1. Chemical modification is insufficient to remove the entire surface silanol groups. Additional dehydroxylation treatments are needed to keep the dielectric constant of the films low.

4.3 Effect of Heat-Treatment Atmosphere

In order to study the influence of heat-treatment atmosphere on the properties of the sol-gel organosilicate films, the films were thermally treated in one of the following gases and the results were compared:

- (1) oxygen, up to 450°C for 30 minutes in tube furnace;
- (2) nitrogen, up to 450°C for 30 minutes in tube furnace;
- (3) air, up to 450°C for 30 minutes in furnace;
- (4) air + N₂: annealing under nitrogen at 400°C for 30 minutes in RTP after heat-treatment in air up to 450°C for 30 minutes; and
- (5) air + forming gas (5% H₂ + 95% N₂): annealing in forming gas at 400°C for 30 minutes after heat-treatment in air up to 450°C for 30 minutes.

All the films were produced from MTES : TEOS = 1 : 1 and dehydroxylation treated in 10% HMDS solution for 1 hr before the above heat-treatment. All the films were processed under identical conditions.

4.3.1 Effect of heat-treatment atmosphere on dehydroxylation

The FTIR spectra of the films annealed in various atmospheres are given in Figure 4.12. The peak intensity of organic groups centered at 1277 cm⁻¹ and 2975 cm⁻¹ and the peak intensity of hydroxyl groups at 3300 cm⁻¹ – 3700 cm⁻¹ vary with different annealing atmospheres.

Figure 4.12 FTIR spectra of porous films heat-treated in different atmospheres

Firstly, it can be seen clearly that all the organic species still exist in the final structure except the film annealed in oxygen. For this film, all organic species have disappeared as indicated by the disappearance of the peaks at 1277 cm^{-1} and 2975 cm^{-1} , which are assigned to Si-C bond and C-H bond, respectively.

Secondly, the intensity of hydroxyl groups varies depending on the annealing gases. If the film thermally treated in air is taken as a reference, the -OH peaks of the oxygen and nitrogen treated films increase whereas the -OH peak areas of air + N_2 and air + forming gas treated films decrease. The quantitative comparison of the change in the area of Si-OH groups for the films heat-treated in different atmospheres is tabulated in Table 4.1. The Si-OH peak areas are normalized by their respective Si-O peak as in Figures 4.7 and 4.8.

Table 4.1 Change of -OH concentration for the films annealed in different atmospheres

Annealing Atmosphere	O ₂	N ₂	Air	Air + N ₂	Air + Forming Gas
Change in -OH Peak Area (%)	+136.31	+6.37	0	-34.60	-49.50

For the oxygen-annealed film, the concentration of -OH groups is much higher compared to the films annealed in other atmospheres. Based on the FTIR measurements,

all the $-\text{CH}_3$ ligands are pyrolyzed (Figure 4.12). The lack of protection from absorbing moisture by the hydrophobic groups is the main reason for the high concentration of silanols in the film.

For the nitrogen-annealed film, the fraction of $-\text{OH}$ groups is a little higher. This slight increment may result from the lower sol-gel condensation rate, which converts the silanol groups to siloxane linkages, in an inert gas environment.

For the air + nitrogen or air + forming gas two-step dehydroxylation treated films, the amount of $-\text{OH}$ groups are much less than the film annealed in air – reduces 34.60% and 49.50%, respectively. For the air + nitrogen film, the further annealing in nitrogen was carried out in a pre-evacuated chamber at 400°C . Thus the moisture can be removed during the process. When the further annealing is performed in the forming gas, the hydrogen will react with the Si-OH group to form Si-H , which also decreases the silanol concentration in the film.

In conclusion, the dehydroxylation rate for different gases is according to the following sequence: air + forming gas > air + N_2 > air > N_2 > O_2 . The film becomes more hydrophobic after air + nitrogen or air + forming gas two-step annealing due to the reduction of surface silanols, as confirmed by the contact angle measurement (Figure 4.13).

Figure 4.13 Contact angle of two-step annealed films

The contact angle changes from 85.3° for the air-annealed film (Figure 4.9) to 94.5° for the air + N₂ annealed film and 101.9° for air + forming gas heated film. Hence, the two-step annealing is very effective in dehydroxylation of the films.

4.3.2 Effect of heat-treatment atmosphere on dielectric properties

The dielectric constant (*k*) and dissipation factor (*D*) of the MTES/TEOS films thermally treated in different atmospheres are listed in Table 4.2.

Table 4.2 Dielectric properties of the films heat-treated in different atmospheres

Time (day) Annealing Gas		1	2	4
O ₂	<i>k</i>	5.0	N.M.	N.M.
	<i>D</i>	0.5	N.M.	N.M.
N ₂	<i>k</i>	4.0	N.M.	N.M.
	<i>D</i>	0.3	N.M.	N.M.
Air	<i>k</i>	3.068	3.40	3.597
	<i>D</i>	0.0413	0.0316	0.0323
Air + N ₂	<i>k</i>	1.89	2.115	2.237
	<i>D</i>	0.0348	0.0197	0.0280
Air + Forming Gas	<i>k</i>	2.007	2.035	2.126
	<i>D</i>	0.0239	0.0244	0.0339

N.M. = not measured

It is noted that the oxygen treated film, which contains the most amount of silanols as discussed in last section, has the highest dielectric constant.

The air + nitrogen and air + forming gas treated films, which contain the least amount of silanols, has the lowest dielectric constant. Films with ultra-low dielectric constant of about 2.0 can be obtained after air plus nitrogen or air plus forming gas treatment.

For the nitrogen treated film, the dielectric constant is greater than the air treated film. This is due to the fact that the nitrogen treated film contains higher -OH concentration

and lower porosity derived from the refractive index measurements. The higher porosity in the air annealed film is brought about by the higher chemical reaction rate in the sol-gel process as well as the pyrolysis of the organic species. The latter can be seen from the TGA/DTA data (Figure 4.14).

Figure 4.14 TGA/DTA data conducted in different atmospheres

The TGA and DTA graphs are very different for the xerogels conducted in nitrogen and in air. In the nitrogen atmosphere, there is a one-step abrupt weight-loss in TGA. The weight-loss range is from room temperature to about 130°C. There is an endothermic peak around 100°C in the DTA, correspondingly, indicating that the abrupt weight-loss is

due to the evaporation of the solvent and water molecules trapped in the material. From 130°C upward, no peaks appear in DTA, the weight-loss rate is very slow and basically constant suggesting that water and ethanol being continuously expelled from the materials due to the condensation reactions in the sol-gel process.

In comparison, for the xerogel heat-treated in air, there are two abrupt weight-loss stages in TGA, corresponding to an endothermic peak and an exothermic peak in DTA. The first weight-loss, occurring in the same temperature range as that in nitrogen, is also due to the evaporation of the solvent and water. The second abrupt weight-loss happens at around 400°C and there is a related exothermic peak in DTA, indicating that some species such as $-\text{CH}_3$ have been thermolyzed. The burn-off of the covalent methyl ligands will leave voids in the matrix ^[174–176]. Higher porosity leads to lower dielectric constant.

The FTIR (Figure 4.12) and TGA/DTA (Figure 4.14) results show that the decomposition rate of the organic groups in different gases has the following sequence: $\text{N}_2 < \text{air} < \text{O}_2$. When the film is thermally treated in air, some organic components are removed from the film resulting in an increased pore volume; some organic groups, however, still exist in the final film conferring hydrophobicity to the film. Further annealing of the film in nitrogen will not destroy the hydrophobic organic groups but remove the remaining hydroxyl, thus maintaining the low dielectric constant of the film. A RTP was used instead of tube furnace to provide nitrogen ambient for the air + nitrogen film because the RTP can be pre-evacuated before the chamber being filled with nitrogen. As a result, the residual air or oxygen content in the chamber can be kept at a lower level. Thus the hydroxyl groups can be removed during the process with little loss of organic groups.

The leakage current density of the organosilicate films annealed in different gases is displayed in Figure 4.15.

From Figure 4.11 and Figure 4.15, the MTES/TEOS film shows a leakage current density of $2.2 \times 10^{-4} \text{ A/cm}^2$ at an electric field of 1 MV/cm prior to any modifications. The leakage current density drops to $6.5 \times 10^{-6} \text{ A/cm}^2$ after the HMDS soaking and air anneal. It further decreases to $1.9 \times 10^{-6} \text{ A/cm}^2 - 2.4 \times 10^{-6} \text{ A/cm}^2$ after nitrogen or forming gas second step annealing. This decrease in the leakage current of the films is due to the reduced water-related traps.

Figure 4.15 Leakage current density of the films heat-treated in different atmospheres

4.4 Effect of Heat-Treatment Temperature

Figure 4.16 shows the FTIR spectra of MTES/TEOS films heated at different temperatures. For all the samples, the molar ratio of MTES and TEOS is 1.0. Surface modification was carried out in 10% HMDS solution for 1 hr, and heat-treatment was conducted firstly in air then in nitrogen in RTP.

Figure 4.16 FTIR spectra of the films thermally treated at different temperatures

As-deposited organosilicate film contains a large amount of silanol groups as indicated by the large peak area around $3300\text{ cm}^{-1} - 3700\text{ cm}^{-1}$. As the annealing temperature increases from 300°C to 450°C , the concentration of the $-\text{OH}$ groups decreases as expected.

Table 4.3 tabulates the optical and dielectric properties of the films heated at 300°C , 400°C and 450°C , respectively.

Table 4.3 Effect of thermal treatment temperature on the film properties

Temperature ($^{\circ}\text{C}$)	300	400	450
Refractive Index	1.309	1.224	1.202
Porosity (%)	24.30	47.01	51.95
Dielectric Constant	3.121	2.299	2.204

The porosity of the film thermally treated at 300°C is found to be much lower than that of other two samples; whereas the porosity of both 400°C and 450°C samples are closer. The quantitative change in porosity and dielectric constant for the films treated at 400°C and 450°C with respect to the film heated at 300°C is shown in Figure 4.17.

Figure 4.17 Changes of dielectric constant and porosity of the films annealed at 400°C and 450°C with respect to the 300°C film

The porosity increases by about 93.46% and 134.4%, and the dielectric constant decreases by about 26.28% and 32.37% for the 400°C and 450°C films compared to the 300°C film. At higher temperature, the rates of sol-gel hydrolysis and condensation reactions are faster and more complete. So the film contains less silanol groups and more pores. Besides, the $-CH_3$ groups cannot pyrolyze until the temperature reaches around 400°C in the air as indicated by the TGA and DTA analysis (Figure 4.14). The effective removal of organic components from the film also results in an increased pore volume. Both the lower content of silanol groups and higher porosity are responsible for the reduced dielectric constants for the 400°C and 450°C annealed films.

The effect of heat-treatment temperature on the leakage current characteristics of the films is displayed in Figure 4.18.

Figure 4.18 J - E property of films treated at different temperatures

The decrease in leakage current at a higher annealing temperature is also due to the reduced hydroxyl or silanol groups in the films.

The pore size of the films was determined by small angle X-ray scattering (SAXS) measurements. For SAXS samples, the films were deposited on mica with a thickness of 100 μm to increase the transmission of X-ray through the samples. Figure 4.19 shows the experimental and data fitting of SAXS plots of three heat-treated films. The SAXS pattern represents the scattering variation due to the point-to-point variations in electron density. The data fitting was performed according to Equation (3.17).

Figure 4.19 Experimental and data fitting of SAXS results for the films annealed at different temperatures

From the scattering curve, it can be observed that the intensity constantly reduced from $q = 0.005 \text{ nm}^{-1}$ to $q = 0.03 \text{ nm}^{-1}$. Data below $q = 0.005 \text{ nm}^{-1}$ is not collected due to the beam stop. From $q = 0.03 \text{ nm}^{-1}$ above, the intensity is almost constant at about 2. The pore size of the films obtained from the data fitting is tabulated in Table 4.4.

Table 4.4 Data fitting to SAXS results for the films under different heat treatment temperatures

Temperature (°C)	Radius (nm)	Pore Size (nm)
300	16.24	32.48
400	16.77	33.54
450	16.97	33.94

The pore size of the films does not change much with the annealing temperature in the range of 300°C – 450°C. The annealing temperature of 450°C does not cause the interconnection of the films. The pore size of final film is about 33.34 nm, which is in the range of mesopores.

4.5 Summary

The low dielectric constant films have been successfully synthesized with sol-gel approach. Many techniques are used to remove the residual silanol groups and increase the hydrophobicity of the films so that the films can resist moisture attack from atmosphere and improve the dielectric properties of the films.

The use of the organic precursor MTES with the inorganic precursor TEOS introduces organic ligands into the SiO₂ network. It has several effects on the properties of the films:

- (1) Reduces the connectivity of the network and changes the mechanism of drying, so films up to 1 μm can be obtained without crack;
- (2) Some of the incorporated organic components are pyrolyzed at high temperature result in an increased porosity; and

- (3) Some of the organic groups are present in the final films making the film surface more hydrophobic.

In the experimental temperature range of 25°C to 450°C, the dielectric constant of the films reduces with increasing temperature. Moreover, the pore size does not increase with temperature, implying the thermal treatment temperatures do not cause pore interconnection. The amount of silanol groups also decreases with increasing annealing temperature. However, they cannot be completely eliminated by thermal treatment.

The surface hydroxyl groups are further reduced by HMDS chemical modification in which -OH groups are replaced by nonhydrolyzable methyl groups. Further annealing the films in nitrogen or forming gas after annealing in air ensures that the films contain minimal amount of silanols.

The experimental results show that the incorporation of the MTES increases the contact angle from 42.8° of the TEOS film to 61.3° of the MTES/TEOS film. The surface of the films becomes more hydrophobic after HMDS soaking and in air + nitrogen two-step annealing as the contact angle increases to 85.3° and 94.5°, respectively.

The dielectric constant reduces from 4.33 for no HMDS treated MTES/TEOS film to 3.07 for HMDS treated MTES/TEOS film and further reduced to the ultra-low- k region of 1.89 for HMDS and nitrogen dehydroxylated MTES/TEOS film. Therefore, the HMDS modification and air + nitrogen two-step annealing are very effective in dehydroxylation of the organosilicate films. Ultra-low dielectric constant about 2.0 can be obtained while the leakage current density of the films is in the level of 10^{-6} A/cm².

CHAPTER 5 EFFECT OF MTES/TEOS RATIO ON THE PROPERTIES OF SOL-GEL ORGANOSILICATE FILMS

For low- k applications, it is important to examine the porosity and pore structure of the dielectric films. A basic description of pore structure includes pore size, porosity and pore interconnectivity. The first parameter is important in that it must be smaller than the minimum device feature size to avoid short circuits. Although porosity can lower the dielectric constant, normally it has negative impact on other materials properties such as mechanical and thermal properties. Consequently, porosity should be no higher than needed to achieve the desired dielectric goals. Pore interconnectivity is important in cases where the films are exposed to moist environments. It is generally agreed that porosity in the form of closed cells can prevent adsorption and diffusion of moisture and contaminants, so cause fewer integration problems. The characteristics of the microstructure of the porous films are, therefore, of paramount importance in realizing ILD dielectric properties. However, little systematical work has been done so far on this area especially for the organically modified sol-gel films. Thus this becomes the objective of this chapter.

The mechanical properties of porous dielectrics are also critical to the integration capability of these films. The low- k candidate materials must be compatible with modern semiconductor processes such as etching, stripping, chemical mechanical planarization (CMP), cleaning, deep ultraviolet (UV) lithography and device packaging processes^[177, 178]. In this chapter, the mechanical as well as the important dielectric and electrical properties of the films will be studied systematically as a function of MTES concentration. These results together with the structural properties of the films will give a comprehensive description of the sol-gel films used as ILD dielectrics.

It is emphasized that all the samples used in this chapter underwent HMDS surface modification and the air and nitrogen two-step annealing as described in Chapter 4.

5.1 Hydrophobicity of the Films

The FTIR spectra of films with different molar ratios of MTES and TEOS are shown in Figure 5.1.

Figure 5.1 FTIR spectra of mesoporous films with different ratios of MTES and TEOS

Two organic peaks centered at 1277 cm^{-1} and 2975 cm^{-1} , which are assigned to the vibration of the Si-C bond and the $-\text{CH}_3$ unit, respectively, increase in intensity with MTES concentration. As more organic groups are incorporated into the films at higher MTES concentration, the films become more hydrophobic. This is supported by the contact angle measurements.

Figures 5.2 and 5.3 show the contact angle of the films as a function of the MTES loading.

MTES/TEOS = 0, $\theta = 73.7^\circ$ MTES/TEOS = 0.5, $\theta = 90.3^\circ$ MTES/TEOS = 4.0, $\theta = 101.7^\circ$

Figure 5.2 Optical images of a water droplet on the MTES/TEOS films

Figure 5.3 Contact angle of the films as a function of MTES fraction

The films change from being hydrophilic to hydrophobic as the MTES concentration increases. The contact angles of films increase from 73.7° for the TEOS film to about 90.3° for the film with $\text{MTES/TEOS} = 0.5$ and to 101.7° for the film with $\text{MTES/TEOS} = 4.0$.

In addition, it can be seen from Figure 5.1 that the absorption intensity of the shoulder peak, located at 1100 cm^{-1} , also increases with increasing MTES concentration. This suggests that the porosity of the films increases with MTES fraction^[162].

5.2 Dependence of Structural Properties of the Films on the Molar Ratio of MTES and TEOS

5.2.1 Porosity and pore interconnectivity

It is qualitatively known that the pore volume in the films increases with increasing MTES/TEOS ratio from FTIR. In order to quantitatively examine the porosity and pore interconnectivity of the porous films, nitrogen adsorption porosimetry and SXR techniques were employed. The motivation behind this choice of techniques is that the nitrogen adsorption method can access only open pores whereas SXR can characterize both open and closed pores. So by comparing the results of nitrogen adsorption and SXR, the pore structure can be found. Although the nitrogen adsorption was performed using

bulk organosilicate xerogels, it had been shown that they could represent the film property as long as the bulk xerogels have gone through the same drying process as the films [179, 180].

Figure 5.4 shows the nitrogen adsorption-desorption isotherms of bulk organosilicate samples with different MTES/TEOS molar ratios.

(e) MTES/TEOS = 4.0

Figure 5.4 N₂ adsorption isotherms of the films with different ratios of MTES/TEOS

In the case of the sample with a molar ratio of MTES/TEOS = 0.5, the film exhibits a highly microporous property as indicated by the type I N₂ isotherm with no hysteresis loop. For the sample with a molar ratio of MTES/TEOS = 0.67, the desorption branch does not follow the adsorption branch of the isotherm and a very narrow triangular hysteresis loop is observed. The adsorption isotherms for samples with MTES/TEOS = 1.0 and 2.0 exhibit pronounced triangular hysteresis loops. The triangular hysteresis loop in the adsorption isotherm is known as the type IV N₂ isotherm and indicates the existence of mesopores. The isotherm for the sample with MTES/TEOS = 4.0 has a hysteresis loop of shape intermediate between a triangular one and one with parallel adsorption and desorption branches. In this case, the desorption branch is also much steeper than the adsorption branch.

The gradual development of hysteresis loops and the change in their shapes can be explained as a result of the increase in mesopore size for the materials with different molar ratios of MTES/TEOS. That is the mesopore sizes of the films are in the following order: MTES/TEOS = 0.5 < MTES/TEOS = 0.67 < MTES/TEOS = 1.0 < MTES/TEOS = 2.0 < MTES/TEOS = 4.0.

The results of a detailed analysis of the isotherms for different samples are summarized in Table 5.1. In this Table, the BET surface area, micropore volume and mesopore size are obtained directly from the experimental report. The mesopore volume

is obtained by subtract the micropore volume from the total volume (obtained from experimental report). The porosity (P) of the bulk organosilicate is calculated from the following Equations:

$$P = \frac{V_{total}}{V_{bulk}} \times 100\% \tag{5.1}$$

$$V_{bulk} = \frac{1}{d_{bulk}} = \frac{1}{Pd_{air} + (1 - P)d_{dense}} \text{ (cm}^3\text{/g)} \tag{5.2}$$

where V_{total} is the total pore volume (micropore volume + mesopore volume) obtained from N_2 adsorption, V_{bulk} is the bulk material volume, d_{bulk} is the density of the bulk material, d_{air} is the density of air, and d_{dense} is the density of the skeleton organosilicate material.

The air density is 0.00125 g/cm^3 , the density of silica skeleton is taken as 2.25 g/cm^3 . For simplicity, we assume $P \times d_{air} = 0$. So the porosity can be calculated as:

$$P = \frac{V_{total}}{1/d_{dense} + V_{total}} \% \tag{5.3}$$

Table 5.1 Structural properties of the organosilicate materials obtained from N_2 adsorption

Molar Ratio of MTES/TEOS	BET Surface Area (m ² /g)	Micropore Volume (cm ³ /g)	Mesopore Size (nm)	Mesopore Volume (cm ³ /g)	Porosity* (%)
0.5	430.19	0.113	2.58	0.0504	26.88
0.67	429.36	0.123	3.05	0.085	31.88
1.0	382.76	0.061	4.62	0.112	28.02
2.0	204.20	0.054	6.21	0.056	19.84
4.0	156.44	0.0484	8.38	0.0238	13.98

* The density of the dense material is taken as 2.25 g/cm^3

Clearly, the bulk gels, regardless of the MTES and TEOS ratios, have two types of pores: micropores and mesopores. It also appears that the micropore volume, mesopore

volume and porosity of the samples decrease while mesopore size increases with increasing concentration of MTES.

The porosity of the films was also measured by SXR. The main difference of SXR and N₂ adsorption technique is that the former can access both open and closed pores, while the latter can access only open pores. In SXR characterization, the porosity of the film is obtained by comparing the film mass density with the density of dense silica. The film density can be derived from Equation (3.14), which is proportional to the film stoichiometry and the film critical angle from the SXR data.

$$\rho = \frac{\pi^2 c^2 \epsilon_0}{3 \lambda^2 N_A e^2} M_c m \theta_c^2 \frac{\sum X_j M_j}{\sum X_j Z_j} \quad (3.14)$$

For the elements present in the final film (C, H, O, Si), the M_j is equal to $2 Z_j$ except H that M_j is equal to Z_j . It can be seen from the FTIR spectra (Figure 5.1) that there is little hydrogen in the final films. So we can simply assume that $\frac{\sum X_j M_j}{\sum X_j Z_j} = 2$. Consequently, the mass density of the films is just related to the critical angle as described below:

$$\rho = \frac{2 \pi^2 c^2 \epsilon_0}{3 \lambda^2 N_A e^2} M_c m \theta_c^2 \quad (5.4)$$

Figure 5.5 shows the SXR results of samples with different MTES/TEOS molar ratios. Based on the SXR theory, two critical angles should be observed from the X-ray reflectivity curve corresponding to the Si substrate and the film. However, for some films only the Si critical angle is observed. The existence of the film only perturbs the shape of this critical angle^[134]. In such a circumstance, the reflectivity curve must be simulated to extract the film critical angle^[134]. It can be seen from Figure 5.5 that only one peak is apparent for all the sol-gel films. In order to resolve the SXR data into two critical angles, a Gaussian model of fitting multiple peaks was used. The Gaussian model is based on the summation of two parameterized Gaussian functions. The critical angle of Si was

reported to be 0.201° [134] and hence was fixed during data fitting. The other peak position was determined by estimating the initial Gaussian half width and using least-squares fit to obtain the minimum standard deviation.

Figure 5.5 SXR curve of porous organosilicate films with different MTES/TEOS ratios

Figure 5.6 shows the extraction of the critical angle of the film with MTES/TEOS = 1 and Table 5.2 tabulates the properties of the films with different fractions of MTES derived from Gaussian model.

Figure 5.6 Extraction of critical angle of the film using Gaussian model of fitting multiple peaks

Table 5.2 Film properties derived from SXR curves

MTES/TEOS (molar ratio)	Critical Angle (degree)	Density (g/cm ³)	Porosity* (%)
0.5	0.149	1.057	53.03
0.67	0.144	0.99	56.13
1.0	0.133	0.84	61.44
2.0	0.1225	0.71	68.25
4.0	0.113	0.61	73.00

* The density of the pore wall material was taken as 2.25 g/cm³

Another simulation method was used to confirm the above analysis. The data fitting program, “Refsim Ver1.1” (Bruker AXS Analytical X-ray System), was used and the result is shown in Figure 5.7. The data fitting is realized by adjusting several free parameters, such as surface roughness, film mass density and thickness. The values of surface roughness and thickness were evaluated based on the AFM and ellipsometry measurements, respectively.

Figure 5.7 Experimental and data fitting of SXR curve using Refsim Ver 1.1 software

The Refsim simulation results show that the porosity of the film with 1:1 molar ratio of TEOS and MTES is 56.96%, which is quite close to the value of 61.44% obtained from the Gaussian peak split method (Figure 5.6).

It is known that the N₂ adsorption method can access only open pores whereas SXR can characterize both open and closed pores. Thus by comparing the nitrogen adsorption data and SXR data, the pore structure parameters of the films can be determined and the results are tabulated in Table 5.3.

Table 5.3 Pore interconnectivity of the films with different MTES/TEOS ratios

Molar Ratio of MTES/TEOS	Open Porosity* (%)	Total Porosity** (%)	Closed Porosity*** (%)
0.5	26.88	53.03	26.15
0.67	31.88	56.13	24.25
1.0	28.02	61.44	33.42
2.0	19.84	68.25	48.41
4.0	13.98	73.00	59.02

* data obtained from N₂ adsorption

** data obtained from SXR

***closed porosity = porosity obtained from SXR - porosity obtained
from N₂ adsorption

In summary, the BET surface area and micropore volume, obtained from N₂ adsorption reflecting the open pore structure, decrease with the increasing molar ratio of MTES and TEOS, whereas the pore size, total porosity and percentage of closed pore of the films increase with increasing MTES/TEOS ratio.

We suggest that the main reason of the above phenomenon is the different mechanisms of hydrolysis and condensation of silica precursors in different pH conditions, as discussed in Chapters 2 and 3. When a precursor is catalyzed by an acid, a

dense film will be formed due to the high hydrolysis and low condensation rate. When the precursor is catalyzed by a base, the growing polymers, during condensation reaction, will have more chance to fold back and link to itself to form closed loops (rings) due to the low hydrolysis rate and branched structure. The pore sizes resulting from a base catalysis are also greater than that obtained from an acid catalysis. Therefore, MTES catalyzed by a base will produce discrete porous structure as shown in Figure 3.2. As the molar fraction of MTES increase, the amount of pores also increases correspondingly. As a result, the total porosity, closed porosity and pore size all increase with MTES fraction. A similar behavior was also observed by Fahrenholtz *et al.* [181] for base-catalyzed organic modified xerogels.

Another factor resulting in the increase in the closed pore structure is the $-\text{CH}_3$ groups, which are incorporated into the silica network during the sol-gel process through co-polymerization. Although some of the $-\text{CH}_3$ units remain in the final films (Figure 5.1), some of them pyrolyze during heat-treatment. Figure 5.8 shows the TGA/DTA analysis of the composite xerogels with different ratios of MTES/TEOS.

Figure 5.8 TGA/DTA data of the organosilicate gels with the variation of MTES/TEOS ratios

In TGA, all the curves demonstrate two weight-loss stages. An initial weight-loss from room temperature to about 130°C is mainly attributed to the evaporation of solvent and water molecules trapped in the materials. From 130°C to about 400°C, the rate of weight-loss is basically constant suggesting that water and ethanol are continuously expelled from the materials due to the condensation reaction. There are corresponding endothermic peaks in DTA curves.

The second sharp weight-loss at around 400°C is attributed primarily to the oxidative pyrolysis of methyl groups. It can also be seen from the DTA diagram that there are correspondingly sharp exothermic peaks at around 400°C. The pyrolysis of the covalent methyl ligands in the films leaves voids in the matrix. The amount of weight-loss of films around 400°C increases with the fraction of MTES. The exothermic peaks are also higher at higher MTES loading. Table 5.4 lists the percentage of weight-loss from 400°C – 450°C for different ratios of TEOS and MTES.

Table 5.4 TGA weight-loss of the organosilicate samples from 400°C – 450°C

MTES/TEOS (molar ratio)	4.0	2.0	0.67	0.5
Weight-Loss (%)	7.77	4.79	3.30	2.26

The weight-loss for the film with $\text{MTES/TEOS} = 4.0$ is about 3.5 times that of the film with $\text{MTES/TEOS} = 0.5$ in this temperature range. More methyl groups are removed at higher MTES concentration, resulting in higher closed form porosity in the films.

In addition, it can be seen from TGA, the weight loss of the materials from 450°C to 700°C is less than 2% when annealed in air, indicating the thermal stability of the xerogels.

5.2.2 Pore size

The pore size of the films was evaluated by TEM observations. Figure 5.9 shows plan-view TEM images of the films with different molar ratio of MTES and TEOS. The lighter (less electron density) regions in the images correspond to the voids.

(a) $\text{MTES/TEOS} = 0.5$

(b) $\text{MTES/TEOS} = 1.0$

(c) MTES/TEOS = 2.0

Figure 5.9 TEM microstructure of the films with different concentrations of MTES

These TEM images reveal a rather uniform microstructure without phase separation. The pores are clearly visible as small well-defined bright areas in TEM. It is found that the pore sizes for the films with MTES : TEOS = 0.5, 1.0 and 2.0 are around 2 nm – 3 nm, 4.5 nm – 6 nm and 6 nm – 8.5 nm, respectively. The pore sizes are in the range of mesopores. The results agree well with the nitrogen adsorption measurements. Obviously, the pore sizes become larger at higher MTES concentration. This is because the base catalyzed precursor will give rise to larger pores than does the acid catalyzed precursor. Besides, the small pores may also merge at higher porosity. The smaller pores seen by TEM are difficult to resolve by SAXS because of the larger scattering angles.

5.2.3 Pore arrangement

XRD was used to examine whether the pores are ordered. If there is a periodic structure, the film will achieve maximum reflectivity. Figure 5.10 shows the XRD pattern of films with different ratios of MTES and TEOS precursors. No obvious peaks appear for all the samples, implying that the pores are arranged randomly in the films. These results agree with the TEM observations.

Figure 5.10 XRD patterns of the films with different MTES fractions

5.3 Effect of MTES/TEOS Ratio on the Optical and Dielectric Properties of the Films

The refractive index of the films and the corresponding porosity derived from the Lorentz-Lorenz relationship as a function of the MTES/TEOS ratio are shown in Figure 5.11.

Figure 5.11 Dependence of refractive index and porosity of the films on MTES concentration

When the MTES/TEOS molar ratio changes from 0.5 to 4, the refractive index of the film reduces from 1.22 to 1.05 and the porosity of the film increases from 47.9% to 87.5%. The films containing more methyl groups tend to have lower refractive indices. This is because Si-CH₃ groups have larger molar volume and smaller polarizability than those of Si-O bonds, so the substitution of Si-CH₃ for Si-O decreases the refractive index of the films. The increase in porosity of the films with increasing concentration of MTES is consistent with the SXR measurement.

The experimental and theoretical dielectric constant of the films as a function of the MTES concentration is compared in Table 5.5.

Table 5.5 Comparison of the experimental and theoretical dielectric constant of the films

Molar Ratio of MTES and TEOS	Experimental k	Bruggeman Theoretical k
0.5	2.248	2.238
0.67	2.149	2.131
1.0	2.115	1.958
2.0	1.991	1.761
4.0	1.976	1.213

* The k value was measured on the third day of fabrication

The experimental dielectric constants of the films decrease with increasing MTES loading due to the increase in the porosity. The k values of the films reduce from $k = 2.25$ with MTES : TEOS = 0.50 to $k = 2.11$ with MTES : TEOS = 1.0 and to $k = 1.98$ with MTES : TEOS = 4.0. The films with dielectric constant around 2.0 can be obtained with MTES/TEOS ≥ 1.0 . The Bruggeman ^[141] theoretical prediction of dielectric constants of the films (Equation (3.22)) is quite close to the experimental ones except for the film with MTES : TEOS = 4.0. The experimental k value is much higher. This may be attributed to the increased amount of trace ions in this film as indicated by the higher leakage current density in the following Figure in next section.

5.4 Effect of MTES/TEOS Ratio on the Electrical Properties of the Films

The leakage current characteristic through the organosilicate films at up to 1 MV/cm is displayed in Figure 5.12.

Figure 5.12 *J-E* properties of the organosilicate films with different ratios of MTES/TEOS

The organosilicate films shows a leakage current density of 7.01×10^{-10} , 1.58×10^{-9} , 1.90×10^{-8} , 6.13×10^{-7} , 2.30×10^{-2} A/cm² at an electric field of 1 MV/cm for MTES : TEOS molar ratios of 4.0, 2.0, 1.0, 0.67, 0.5, respectively. This leakage current of the films increases with the increasing MTES fraction or the porosity. The result is not unexpected; since the porous films have a high internal surface area, electron or hole transport may be faster along the surface path. It should also be pointed out that the leakage current is more sensitive to the changes in the film preparation and storage conditions. Trace impurities trapped in the films during sample preparation or in the metals during e-beam deposition can result in a higher leakage current. In addition, although the porous films are hydrophobic, if the testing ambient is not purged with N₂ during testing, the measured currents can be 1 – 2 orders of magnitude higher ^[182]. This indicates that moisture adsorption occurs to a small extent.

In general, the intrinsic electrical parameters such as leakage current are determined by the conduction mechanisms in the dielectrics. The conduction mechanism of the sol-gel films can be investigated by examining the $J - E$ data in terms of the Frenkel-Poole and Schottky emission mechanisms. The Schottky emission generated by the thermionic effect is caused by the electron transport across the potential energy barrier via field-assisted lowering at a metal – insulator interface. The current density in the Schottky emission can be expressed as ^[183],

$$J = A^* T^2 \exp\left(\frac{\beta_{Sc} E^{1/2} - \phi_{Sc}}{k_B T}\right) \quad (5.5a)$$

$$\beta_{Sc} = \left(\frac{q^3}{4\pi\epsilon_0 k}\right)^{1/2} \quad (5.5b)$$

where A^* is the effective Richardson constant, β_{Sc} is Schottky field lowering coefficient, E is applied electric field, ϕ_{Sc} is contact potential barrier, T is absolute temperature, k_B is the Boltzmann constant, ϵ_0 is the permittivity in vacuum, q is the electron charge, and k is the dielectric constant of the insulating film.

Rearrangement of Equation (5.5a) results in a linear relationship between $\ln J$ and $E^{1/2}$:

$$\ln J = \frac{\beta_{Sc}}{k_B T} E^{1/2} + [\ln(A^* T^2) - \frac{\phi_{Sc}}{k_B T}] \quad (5.6)$$

The Frenkel-Poole (F – P) emission is due to field-enhanced thermal excitation of trapped electrons in the insulator into the conduction band. The current density is given by ^[183]

$$J = J_0 \exp\left(\frac{\beta_{FP} E^{1/2} - \phi_{FP}}{k_B T}\right) \quad (5.7a)$$

$$\beta_{FP} = \left(\frac{q^3}{\pi\epsilon_0 k}\right)^{1/2} \quad (5.7b)$$

where $J_0 = \sigma_0 E$ the low-field current density, σ_0 the low-field conductivity, β_{FP} the F – P field lowering coefficient, ϕ_{FP} the height of trap potential well. For trap states with Coulombic potentials, the expression is virtually identical to that of the Schottky emission. The barrier height, however, is the depth of the trap potential well, and the quantity is larger than in the case of Schottky emission by a factor of 2^[183].

Rearrangement of Equation (5.7a) also yield a linear relationship between $\ln J$ and $E^{1/2}$ given by

$$\ln J = \frac{\beta_{FP}}{k_B T} E^{1/2} + [\ln(J_0) - \frac{\phi_{FP}}{k_B T}] \quad (5.8)$$

The $\ln J$ versus $E^{1/2}$ plot for the films with different MTES fractions is shown in Figure 5.13.

Figure 5.13 $\ln J$ versus $E^{1/2}$ plot of the films with different MTES fractions

The leakage current densities are linearly related to square root of the applied electric field. The current corresponds either to Schottky emission or to Frenkel-Poole mechanism based on Equations (5.6) and (5.8). The two processes can be distinguished by comparing the theoretical value of β_{theory} with the experimental one. The β_{theory} is

derived from Equation (5.5b) and (5.7b) taking the measured dielectric constant of the film as the k value. The experimental lowering coefficient β_{slope} is calculated from the slope of the curve $\ln J - E^{1/2}$ as the slope $= \frac{\beta_{slope}}{k_B T}$ (Equations (5.6) and (5.8)). The various values of $\beta_{theory,Sc}$, $\beta_{theory,FP}$ and β_{slope} measured at 25°C are shown in Table 5.6.

Table 5.6 Various values of the dielectric constant and the constant β at 25°C

MTES/TEOS (molar ratio)	Experimental Dielectric Constant	β_{slope} (Jm ^{1/2} /V ^{1/2})	$\beta_{theory,Sc}$ (Jm ^{1/2} /V ^{1/2})	$\beta_{theory,FP}$ (= 2 $\beta_{theory,Sc}$) (Jm ^{1/2} /V ^{1/2})
0.5	2.248	3.88×10^{-24}	4.05×10^{-24}	8.11×10^{-24}
0.67	2.149	3.04×10^{-24}	4.15×10^{-24}	8.29×10^{-24}
1.0	2.115	3.18×10^{-24}	4.18×10^{-24}	8.36×10^{-24}
2.0	1.991	4.76×10^{-24}	4.31×10^{-24}	8.62×10^{-24}
4.0	1.976	2.38×10^{-24}	4.32×10^{-24}	8.65×10^{-24}

It can be seen that β_{slope} is closer to $\beta_{theory,Sc}$ than $\beta_{theory,FP}$ for all the films. Therefore, it is reasonable to believe that the carriers measured at room temperature are transported through the Au/Ti/sol-gel film/n⁺ Si capacitors by the field-assisted Schottky mechanism in the mid electric field (0.09 MV/cm – 1.1 MV/cm). It is noted that the MTES/TEOS = 4.0 sample has a slope that is quite different from others. So apart from the Schottky mechanism, there may be some other mechanisms yet to be determined. However, a temperature dependent $I - V$ measurement was not achieved in this work due to limitation of the instrument's capabilities.

The deviation from the Schottky emission in the lower electric field is due to the ohmic conduction, which is dependent on charged carriers such as electrons and ions in the intrinsic organosilicate polymer. The deviation from the Schottky emission in the higher electric field may be due to the defects or traps in the sol-gel organosilicate films. The sol-gel films can be viewed as an amorphous SiO₂ (with some C and H), but with a higher defect density than solid SiO₂ due to its highly branched microstructure and

residual -OH groups. The defects such as broken bonds increase greatly at the higher MTES concentration.

With the literature as a reference, Schottky emission mechanism was reported by Cai ^[184] who investigated the sol-gel derived silica films at room temperature. Fang *et al.* ^[185] who studied Al/CVD low-*k* materials identified Schottky and Frenkel-Poole emissions at 30°C and 200°C, respectively. Additionally, Wu *et al.* ^[186] found that the carriers in CVD organosilicate low-*k* films measured at 200°C and 250°C followed Frenkel-Poole emission. Liu *et al.* ^[187] investigated sol-gel derived porous silica low-*k* films and found that the leakage current of the Al/films measured at room temperature obeyed Schottky mechanism in mid electric field (0.2 MV/cm – 1 MV/cm) and Frenkel-Poole mechanism at high electric field (1.2 MV/cm – 1.7 MV/cm).

5.5 Dependence of Mechanical Properties of the Films on MTES Concentration

The dielectric properties of low-*k* materials are tuned preferentially to obtain low dielectric constant. However, their mechanical properties should also be carefully maintained. In particular, the introduction of porosity compromises both the elastic modulus and hardness of these materials. In this work, the mechanical properties of the films were measured with a nanoindenter. The main concern in using nanoindentation for extraction of thin film mechanical properties is related to the spatial extent of the elastic deformation field. This extends well beyond the actual depth of indentation and, for a soft dielectric layer on a hard Si substrate, can result in an overestimation of the true modulus.

The reduced elastic modulus and hardness of the films with various MTES concentrations as a function of ratio of the contact depth (h_c) to the film thickness (t) are shown in Figures 5.14 and 5.15, respectively. Usually h_c/t is used instead of the contact depth to take the influence of the thickness into the consideration.

Figure 5.14 Reduced elastic modulus of the films as a function of h_c/t

Figure 5.15 Hardness of the films as a function of h_c/t

All of the films show qualitatively similar results independent of the MTES concentration. Starting at a relatively small value at very low loads, the elastic modulus and hardness increase with indentation depth due to the presence of the silicon substrate, which has significantly higher elastic modulus and hardness than the sol-gel films.

Fortunately, the measured elastic modulus and hardness clearly reach a plateau at $h_c/t < 0.1$. The plateau values of E_r and H , therefore, relate to the reduced elastic modulus E_r and H of the films. This phenomenon is in good agreement with the commonly used rule of thumb stating that reliable data can only be obtained from indentation depths below 10% of the layer thickness^[147].

While the hardness of the films can be obtained directly from the experimental curve, the elastic modulus of the films has to be calculated from Equation (3.25)^[148].

$$\frac{1}{E_r} = \left[\frac{(1 - \nu^2)}{E} \right]_{\text{specimen}} + \left[\frac{(1 - \nu^2)}{E} \right]_{\text{indenter}} \quad (3.25)$$

The Poisson's ratio and elastic modulus of the nanoindenter are 0.07 and 1140 GPa, respectively. The Poisson's ratio of 0.22 is assumed for the sol-gel films and has been proven not to change significantly with the film density^[149]. The average elastic modulus and hardness of the films plotted against the initial MTES/TEOS ratio are shown in Figure 5.16.

Figure 5.16 Average elastic modulus and hardness of the films

Both elastic modulus and hardness of the films decrease with increasing concentration of MTES. This is because a higher MTES/TEOS ratio results in higher porosity. The average elastic modulus reduces from 14.6 GPa for the TEOS film to 5.8 GPa for the MTES : TEOS = 1 : 1 film, and then to 2.6 GPa for the film with MTES : TEOS = 4 : 1. A similar trend is also observed for the hardness, where the values are reduced from 1.75 GPa for the TEOS film to 0.74 GPa and 0.35 GPa for the 1 : 1 and 4 : 1 MTES : TEOS films, respectively.

The introduction of both organic components and voids into silica films results in a significant change in both hardness and modulus, as the resultant films become more compliant and softer than the dense silica films^[188–191].

The relationship between the elastic modulus and hardness of the films is plotted in Figure 5.17. An almost linear curve is found, being consistent with the literature^[192], reflecting the constant influence of porosity on the mechanical properties of the films.

Figure 5.17 Hardness against elastic modulus of the films

The indent deformation was monitored by AFM images. For $h_c/t < 0.1$, the indentations are totally elastic. No plastic deformation or cracking occurs and therefore the indent traces are not visible. However, plastic deformation develops at higher loads as shown in Figure 5.18.

Figure 5.18 AFM images formed by nanoindenter

5.6 Effect of Aging Time and Aging Condition on the Properties of the Films

If the films are exposure to atmosphere, they may absorb moisture and their dielectric constants will increase due to the strong polarizability of the H_2O molecules. The moisture uptake susceptibility is determined by both the hydrophobicity of the film surface and the pore structure. The porous organosilicate films obtained from MTES/TEOS precursors were monitored for moisture uptake by measuring the dielectric properties of the films with time. Two types of aging conditions were considered: (i) sample kept in an ambient environment – about 25°C and 75% humidity and (ii) sample kept in a desiccator.

The measured capacitance and conductance of the sample kept in the ambient environment are shown in Figures 5.19 and 5.20, respectively. Both the capacitance and conductance of the film increase with time after the moisture adsorption.

Figure 5.19 Measured capacitance of the film with equal moles of TEOS and MTES changing with voltage (ambient aging)

Figure 5.20 Measured conductance of the film with equal moles of TEOS and MTES changing with voltage (ambient aging)

The capacitance of the film is almost linear because of the heavily doped n^+ wafer substrate used. A signal noise exhibited in the form of random telegraph signals (RTS) is observed in the conductance versus voltage curves. And the magnitude of the RTS seems increases with aging time. This phenomenon may result from the occupation and depopulation of embedded individual trapping defects or carriers in the film. RTS is also frequently observed in the sub-micron sized metal-oxide-semiconductor field-effect transistors ^[193] due to the random capture and reemission of a charged carrier at the trap center.

The time dependence of the dielectric constant and dissipation factor of the film, derived from Figures 5.19 and 5.20, is presented in Figure 5.21.

Figure 5.21 Time dependence of the dielectric properties of the film with 1 : 1 molar ratio of TEOS and MTES

It is found that there is an initial increase in the dielectric constant during the first 5 days, from 1.9 to 2.2, then the increase slows. The dielectric constant is still about 2.56 after nearly two months of aging. The results suggest that there is no significant moisture condensation inside the pores even though there is approximately 61.4% porosity. Absence of moisture uptake further implies the possibility that the films have a majority

of closed pores. This is consistent with the TEM observation and SXR as well as N_2 adsorption characterization results.

The leakage current characteristic of the organosilicate films kept in an ambient environment also changes over time. Figure 5.22 shows the leakage current density of the films with different molar ratios of TEOS and MTES measured one month after fabrication.

Figure 5.22 Leakage current density of the films with different MTES fractions measured one month after fabrication

The leakage current increases with aging time as a result of absorbing moisture. As compared to Figure 5.12, the increment at 1 MV/cm for the films with MTES/TEOS ratios of 0.5, 0.67, 1.0, 2.0 and 4.0 are 2.5 $\times$, 2.36 $\times$, 2.17 $\times$, 1.93 $\times$ and 1.87 $\times$, respectively. The increment decreases with increasing MTES loading because of the increase in surface hydrophobicity (Figure 5.3) and fraction of closed pores in the films (Table 5.3). The increments of the leakage current are not very significant indicating that the majority of the pores are in closed form.

When the sample was kept in a dry box, the humidity is greatly decreased to about 30%. The dielectric properties and leakage current of the films are found to change little within the experimental period. The dielectric constant of the film with equal mole of

MTES and TEOS is still about 2.04 and leakage current density is about 2×10^{-6} A/cm² at 1 MV/cm after about of one month aging. The measured properties are shown in Figures 5.23 and 5.24.

Figure 5.23 Time dependence of dielectric properties of the film with MTES/TEOS = 1.0 (aging in a desiccator)

Figure 5.24 Time dependence of leakage current density at 1 MV/cm of the film with MTES/TEOS = 1.0 (aging in a desiccator)

5.7 Summary

Uniform mesoporous silica films with a composite structure of highly porous structure embedded into a dense matrix have been successfully fabricated using MTES and TEOS as precursors. The acid/base two-step catalysis that has different mechanisms of hydrolysis and condensation controls the microstructure of the silica films. The porosity, pore size and properties of the composite films can be adjusted effectively and easily by the concentration of MTES, which is catalyzed by a base.

The structure of the pores is systematically investigated by nitrogen adsorption, SXR, ellipsometry, TEM and XRD. Some indirect techniques such as aging experiment and TGA/DTA are used to confirm the pore structure, especially the pore interconnectivity. The results show that the pores are randomly arranged in the films. The mesopores in the films consist of open and closed pores. The total porosity, percentage of closed pores and pore size of the films increase with increasing concentration of MTES. For the film with MTES/TEOS of 1.0, the pore size is about 5 nm and the porosity is about 61.4% with 33.4% of closed pores.

The thermal stability of the films is found quite well from the TGA evaluations even for the film containing 73% porosity.

The pore structure is corroborated by the dielectric measurements of the films. The dielectric constant of the films is found to decrease whilst the leakage current density of the films increase with increasing MTES concentration. An ultra-low dielectric constant about 2.0 can be achieved with MTES/TEOS molar ratio ≥ 1.0 .

The leakage transport mechanism has been analyzed in detail by extracting the information from the electrical characteristics of the films. The carriers transport at room temperature follows Schottky emission model in the electric field of 0.09 MV/cm to 1.1 MV/cm.

The dielectric constant and leakage current of the films change over time. In the room ambient, the dielectric constant of the film with equal MTES and TEOS is found to increase from 1.9 to 2.2 in the first five days after fabrication and then the change slows. The dielectric constant is about 2.56 after two months aging.

Although the dielectric properties of the films have been improved by the incorporation of porosity, the mechanical stability of the films is compromised. It is found from nanoindentation that the mesoporous films exhibit much lower hardness and

elastic modulus than the silica film. The average elastic modulus and hardness reduce from 14.6 GPa and 1.75 GPa for the TEOS film to 2.6 GPa and 0.35 GPa for the film with MTES : TEOS = 4 : 1.

A fabrication process of ultra-low- k films with controllable properties via sol-gel synthesis has been presented in this chapter. The main limitation of the process is the difficulty to obtain films consisting of only closed-pores. The many dehydroxylation steps in the synthesis also make the process complicated and time consuming. Thus, it is necessary to consider alternative spin-on processes to fabricate ultra-low- k dielectric films.

CHAPTER 6 COMPARISON OF THERMAL AND DIELECTRIC PROPERTIES OF SILSESQUIOXANE FILMS CURED IN NITROGEN AND IN AIR

Ultra-low- k films can be obtained from silsesquioxanes (SSQs), which have an empirical formula of $(\text{RSiO}_{1.5})_n$, where R is hydrogen or an organic group ^[194]. The silsesquioxanes have a mixed cage and network structure before curing and part of the cage structure will be transformed into the network structure by curing as shown in Figure 6.1 ^[195].

$\text{R} = \text{H}, \text{HSQ}; \text{R} = \text{CH}_3; \text{MSQ}, \text{R} = \text{H} \text{ or } \text{CH}_3, \text{HMSQ}$

Figure 6.1 Chemical structure of silsesquioxanes ^[195]

The properties of a SSQ film are strongly dependent on the curing process used ^[196, 197]. In most previous reports ^[198 – 200], the silsesquioxanes were cured at low temperature in nitrogen ambient to avoid dissociation of hydrogen or methyl groups in the SSQs. However, some sacrificial polymers can be pyrolyzed more effectively in air than in nitrogen ^[201 – 203]. Therefore, for SSQ films containing organic polymers, it is more convenient to heat the films in an air ambient. However, air containing oxygen is a more reactive gas than nitrogen. So the thermal stability and dielectric properties of the silsesquioxane films annealed in air will become a great concern. In this chapter,

hydrogen methyl silsesquioxane (HMSQ) films are fabricated by the spin on technique. The films will be thermally treated in nitrogen or in air. The curing mechanism such as network/cage structure conversion and the loss of organic groups at different temperature stages will be investigated quantitatively and the results will be compared. The thermal and dielectric properties of the two types of HMSQ films will also be studied systematically.

6.1 Comparison of the Chemical Structure and Thermal Stability of the Films

The HMSQ films were deposited on Si substrates from diluted HMSQ solutions as described in Chapter 3. The decomposition profile of HMSQ materials thermally treated in both nitrogen and air from TGA/DTA studies is shown in Figure 6.2.

A two-stage weight-loss behavior is found in the TGA characteristic for HMSQ regardless of annealing atmospheres. The initial weight-loss from room temperature to about 250°C is mainly attributed to the evaporation of solvent. The subsequent weight-loss at higher temperature is attributed primarily to the evolution of water from the polycondensation reaction of silanols (at the terminal sites of each oligomer) and oxidative pyrolysis of hydrogen and methyl groups.

For the HMSQ heat-treated in nitrogen, the onset of second stage of weight-loss is at about 400°C indicating that there is no obvious cross-linking below 400°C. The weight-loss rate is almost constant in the temperature range from 400°C to 800°C and the amount of weight-loss is found to be about 6.2% in this temperature range.

In comparison, for the HMSQ heat-treated in air, the second stage of weight-loss begins at about 350°C and is mainly in the range of 350°C to 500°C. The amount of weight-loss is about 10.3% from 350°C to 800°C.

In the DTA diagram, there is a corresponding sharp exothermic peak around 470°C for air-cured HMSQ, representing the oxidation and decomposition of Si-H and C-H bonds. However, for nitrogen-cured HMSQ, a relatively small exothermic peak at around 485°C appears showing smaller amount of materials decomposition.

Figure 6.2 TGA/DTA properties of the HMSQ conducted in nitrogen and air

The change in the chemical structure and composition of HMSQ as a function of curing temperature in the range of 300°C – 490°C were also monitored by FTIR. Figure 6.3 shows the FTIR absorption spectra of the HMSQ films annealed in nitrogen and in air, respectively, after different temperatures of curing.

Chapter 6 Comparison of Thermal and Dielectric Properties of
Silsesquioxane Films Cured in Nitrogen and in Air

(a) cured in N_2

(b) cured in air

Figure 6.3 FTIR spectra of the HMSQ films cured at different temperatures and atmospheres

Similar absorption peaks are found for the two types of films. The two strong peaks, one at 1040 cm^{-1} and the other at 1120 cm^{-1} , are assigned to the asymmetric and

symmetric stretching vibration of the Si-O bond ^[204], representing the network and cage structures of the HMSQ films, respectively ^[122]. The peaks centered at 1277 cm⁻¹ and 2975 cm⁻¹ are the vibrations of the Si-C bond and CH₃ unit, respectively. A Si-H peak near 2250 cm⁻¹ has also been identified ^[205]. Three distinct changes in intensity of the characteristic peaks are observed as the curing temperature increases for both nitrogen- and air-cured films: (i) the Si-H peaks decrease; (ii) C-H peaks decrease; and (iii) the Si-O symmetry peaks decrease while the Si-O asymmetry peaks increase.

The quantitative changes of the Si-H (2250 cm⁻¹) and the C-H (2975 cm⁻¹) bonds in HMSQ films at different temperatures are analyzed by measuring their respective normalized peak areas. The purpose of using the normalized peak area is to eliminate the effect of film thickness on the intensity of the characteristic peaks. The sum of the peak areas of the Si-O-Si linkage including cage structure (1120 cm⁻¹) and the network structure (1040 cm⁻¹) is taken as the normalization factor. Table 6.1 shows the dependence of Si-H and C-H bond on temperature for the films cured in nitrogen and in air, respectively.

Table 6.1 Loss of the Si-H and C-H bonds for the HMSQ films cured in nitrogen and in air

Temperature (°C)		25	300	350	400	450	490
Cured in N ₂	Si-H Loss (%)	0	17.29	21.03	27.22	40.35	67.32
	C-H Loss (%)	0	2.06	13.22	21.15	21.30	27.24
Cured in Air	Si-H Loss (%)	0	10.88	19.49	33.46	56.02	100
	C-H Loss (%)	0	3.19	5.61	21.20	26.36	51.83

The Si-H bonds completely disappear and only half of the original amount of the CH₃ units remains for the air-cured films after heat-treated at 490°C for 30 minutes; whereas the loss rates for both Si-H and C-H are much slower for the nitrogen-cured films.

Although the films annealed at different temperatures show similar bands at 1040 cm⁻¹ and 1120 cm⁻¹, the ratio of the two bands varies among the studied films. This

suggests that the transformation percentage from cage to network structure differs among the nitrogen- or air-cured films. At lower curing temperature, the intensity of the Si-O symmetric peak (1120 cm^{-1}) is higher than that of the Si-O asymmetric peak (1040 cm^{-1}). However, as the curing temperature increases, the intensity of the Si-O asymmetric peak becomes higher and the intensity of the Si-O symmetric peak becomes lower, suggesting that the cage Si-O structure has gradually transformed into the network Si-O structure at elevated temperatures. For the films cured in nitrogen, the temperature at which the network peak becomes almost equal in intensity to the cage structure peak is about 400°C , whereas for air-cured films, this parity appears at 350°C .

A quantitative analysis for the transformation of cage structure into network structure is conducted based on the variation of the peak areas of the 1120 cm^{-1} and the 1040 cm^{-1} peaks at different temperatures. It should be noted that the increase in the intensity of Si-O network is contributed by two factors. The first one is the transformation from the cage structure of Si-O-Si to network structure at higher temperatures. The second one comes from the pyrolysis of Si-H and Si-CH₃ bonds at higher temperatures. Some of the thermolyzed Si-H and Si-CH₃ bonds may form Si-O-Si linkages due to the oxidation and bond reformation as described in Chapter 2 (Equations (2.10) – (2.12)). The oxygen concentration in the furnace is a key factor to affect the oxidation of Si-H and Si-CH₃ bonds. For the films cured in nitrogen, we assume that 30% of the broken bonds are oxidized by the oxygen impurity. For the films cured in air, 100% of the broken bonds will form Si-O linkages. As the loss percentage of Si-H and Si-CH₃ for the films cured in air or in nitrogen is known (Table 6.1), the increment in the peak area of the network contributed from cage structure and from the bond rearrangement or oxidation of Si-H and Si-CH₃ bonds can be distinguished.

By subtracting the fractional peak area (A_{RT}) of the Si-O-Si network band at room temperature ($\text{RT} = 25^{\circ}\text{C}$) from that for elevated curing temperature (A_{T}), the conversion (x) from cage structure to network structure at each curing temperature can be obtained as described in Equation (6.1). All the areas used in the equation are normalized by their respective Si-O-Si area.

$$x(T) = (A_T - A_{RT}) / A_{RT} \tag{6.1a}$$

where $A_{RT} = \frac{(A_{1040cm^{-1}})_{RT}}{(A_{1040cm^{-1}} + A_{1120cm^{-1}})_{RT}}$ (6.1b)

$$A_T = \frac{(A_{1040cm^{-1}} - A_L)_T}{(A_{1040cm^{-1}} + A_{1120cm^{-1}})_T} \tag{6.1c}$$

A_L is the part contributed from bond rearrangement or oxidation of Si-H and Si-CH₃. It is obtained by comparing the normalized peak area of Si-H and Si-CH₃ at temperature T with that at room temperature.

The structural conversion from cage structure to network structure for the HMSQ films after curing at different temperature is tabulated in Table 6.2.

Table 6.2 Structural conversion for the HMSQ films annealed in nitrogen and in air

Temperature (°C)	25	300	350	400	450	490
Conversion (%) (cured in N ₂)	0	6.35	8.97	13.22	32.53	66.11
Conversion (%) (cured in air)	0	2.63	11.61	28.44	51.32	70.84

The conversion from cage structure to network structure is higher for the films heat-treated in air than that in nitrogen above 300°C. After 400°C and 490°C curing, the conversion is 13.22% and 66.11% for nitrogen-cured films and 28.44% and 70.84% for air-cured films, respectively.

By combining the experimental results from FTIR and TGA/DTA, the curing process of HMSQ both in nitrogen and in air is shown to be an exothermic process accompanied by the loss of small molecules, which is more obvious for air-cured films. The symmetry of the Si-O-Si structure for the oligomeric state is partially broken and become

randomized during network formation. These results are consistent with reported works [122, 202, 206].

6.2 Comparison of the Physical and Dielectric Properties of the Films

The refractive index of the films cured in air and in nitrogen as a function of temperature is shown in Figure 6.4.

Figure 6.4 Optical property of the HMSQ films as a function of temperature

The refractive index of nitrogen-cured films decreases gradually with curing temperature from 25°C to 450°C. It then increases slightly when the curing temperature is raised from 450°C to 490°C. The dependence of the refractive index for air-cured films on the curing temperature exhibits similar trends except that the refractive index begins to rise at about 400°C.

The decrease in the refractive index of the films with temperature is probably due to the change in chemical composition and structure of the films. For an insulating material, the refractive index is proportional to the molar polarization of the chemical bonds and inversely proportional to the molar volume of the constituents. For the HMSQ films cured in air and in nitrogen, (i) the refractive index of the films reduces with increasing temperature because the hydroxyl groups with larger polarizability are gradually replaced

by the siloxane linkages during the solvent evaporation and film curing; (ii) the refractive index of the films decreases with temperature as the pyrolysis of methyl groups leaves pores behind; and (iii) the refractive index of the films increases at higher temperature, as the Si-H and Si-CH₃ bonds that have lower molar polarization are pyrolyzed and the cage structure with larger molar volume is partially replaced by the network structure with smaller molar volume. The dependence of the refractive index of the films on temperature shown in Figure 6.4 is the development of these factors. Comparing the refractive index of nitrogen-cured and air-cured films, the air-cured films has lower refractive index from the temperature range of 25°C to 400°C. This is because the curing process in the air is faster than that in nitrogen at same temperature, so more Si-O-Si linkage is formed at the expense of -OH groups, and more organic groups are thermolysed leaving more porosity in the films. Nevertheless, the refractive index of air-cured films becomes higher than the nitrogen-cured films after 400°C due to more networks formed. Additionally, the thermolysis of organic groups also has adverse effect on the refractive index as methyl groups have lower molar polarization. The refractive index is about 1.335 and 1.35, respectively, for nitrogen-cured and air-cured HMSQ films after 490°C annealing.

The mass density of the HMSQ films can be determined by SXR analysis. Figure 6.5 shows the SXR data for the films cured at 490°C in nitrogen and in air, respectively.

Figure 6.5 SXR data of the HMSQ films cured in nitrogen and in air at 490°C

Clearly, two critical angles arising from the dielectric material and the silicon substrate are observed in both reflectivity curves. The first critical angle due to the dielectric thin film is at about 0.178° for the nitrogen-cured film and 0.183° for the air-cured film. The film density can also be derived from Equation (5.4) as the hydrogen element is not abundant in the final films (Figure 6.3). The resultant film density is about 1.51 g/cm^3 and 1.59 g/cm^3 for nitrogen-cured and air-cured HMSQ films, respectively. The nitrogen-cured film has less density due to the existence of more Si-H, Si-C bonds and more cage form of Si-O that have larger volume than the network ones.

The dielectric properties of the films also depend on curing temperature as shown in Figures 6.6 and 6.7.

Figure 6.6 Comparison of dielectric constant of the HMSQ films cured in nitrogen and in air

Figure 6.7 Comparison of dissipation factor of the HMSQ films cured in nitrogen and in air

The nitrogen-cured and air-cured films display the same dependence in their dielectric properties on temperature as that of refractive index due to the similar mechanism. The dielectric constant of the films decreases with temperature until 450°C for nitrogen-cured films and 400°C for air-cured films. This is because the fully cured silsesquioxanes usually have reduced dielectric constant compared with uncured resins [207, 208]. The slight increase in the dielectric constant at higher temperature is due to the loss of Si-H and Si-CH₃ groups as well as the breaking up of the cage structure. The dielectric constants are about 2.64 and 2.71 for nitrogen-cured and air-cured HMSQ films after 490°C heat-treatment, respectively. With reference to the literature, Kim *et al.* [204] found that the dielectric constant for methyl silsesquioxane films cured in nitrogen decreased with increasing temperature (experimental range from 25°C to 350°C). Kim *et al.* [209] observed that the dielectric constant of HMSQ was almost unchanged when the films were thermally heated at 450°C or 480°C for 50 minutes (they did not mention the annealing gas used).

The dissipation factor of the films decreases monotonically with the heating temperature regardless of the curing gases. This is due to the fact that the orientation of

the dipoles in HMSQ relaxes easily to a random state when the films soften at higher temperature. The dissipation factors of air-cured films before 350°C are lower because those films contain lower fraction of -OH groups due to the faster curing. The higher dissipation factor of air-cured films after 350°C may be attributed to the higher defect density resulting from the pyrolysis of organic groups.

6.3 Comparison of the Electrical Properties of the Films

For the leakage current characteristics, the nitrogen-cured and air-cured HMSQ films also show similar behavior with the curing temperature.

Figure 6.8 *J-E* curves of the HMSQ films cured in N₂

Chapter 6 Comparison of Thermal and Dielectric Properties of Silsesquioxane Films Cured in Nitrogen and in Air

Figure 6.9 *J-E* curves of the HMSQ films cured in air

For both nitrogen and air-cured films, the leakage current of the films decreases with curing temperature since the hydroxyl groups located at the ends of the molecules decrease with curing. The comparison of the leakage current density of the films at 1 MV/cm under different curing conditions is shown in Figure 6.10.

Figure 6.10 Comparison of leakage current density for the films cured in different gases

The films cured in air have lower leakage current density at 1 MV/cm than the nitrogen-cured films before 400°C due to the faster curing. With the increase of temperature, more organic groups are thermolyzed in air resulting in more porosity and defects. So the leakage current of films cured in air increase slightly after 400°C. The leakage current densities of nitrogen-cured and air-cured films are about 6.53×10^{-8} A/cm² and 7.63×10^{-8} A/cm², respectively, at an electric field of 1 MV/cm.

By combining the thermal, physical and dielectric analysis, it is found that there is no significant difference in physical and dielectric properties between nitrogen-cured and air-cured HMSQ films though there is greater loss of species for the films annealed in air. Therefore, the HMSQ films can be either cured in nitrogen or in air in the experimental temperature range of 25°C to 490°C.

6.4 Summary

There is a necessity to study the influence of curing atmosphere on the thermal and dielectric properties of HMSQ films owing to the fact that some sacrificial polymers decompose more effectively in air than in nitrogen. In this chapter, the curing mechanism for both nitrogen- and air-cured films has been investigated quantitatively from 25°C to 490°C. It is found that the curing for the two types of HMSQ films are exothermic processes accompanying the loss of Si-H and C-H bonds. There is a structure transformation from cage into network structure during the curing. Both the loss rate and network conversion increase with increasing temperature. Comparing the nitrogen-cured and air-cured films, the air-cured HMSQ films begin to cure at lower temperature and achieve a higher loss percentage of small molecules and a higher conversion degree.

Comparing the physical and electrical properties of the films cured in nitrogen and in air, it is found that the air-cured films have higher refractive index and higher mass density after 490°C anneal. The dielectric constant and leakage current density of air-cured films are also slightly higher than that of nitrogen-cured films. The dielectric constants for nitrogen-cured and air-cured HMSQ films after 490°C heat-treatment are about 2.64 and 2.71, respectively, which are much lower than that of SiO₂. The insertion of the cage structure with Si-H and Si-CH₃ groups makes HMSQ films having a lower density and polarizability than the SiO₂ films, leading to the lower dielectric constant.

CHAPTER 7 SYNTHESIS AND CHARACTERIZATION OF TEMPLATED POROUS SILSESQUIOXANE FILMS

The silsesquioxane films can be made porous by incorporating templates. The templates will be removed later and leave voids behind. In this chapter, templated porous dielectric films have been prepared by using HMSQ as a matrix and PAMAM dendrimer as a template or porogen. In order to obtain a nanoscopic phase separation of the matrix and the template, a coupling agent that can chemically bind the host polymer and the porogen together has been used.

The porous PAMAM/HMSQ materials will be characterized with various advanced techniques. Firstly, the decomposition behavior of the PAMAM porogen will be investigated in nitrogen and in air so as to find the more effective degradation atmosphere. Then the dependence of the structural, dielectric and mechanical properties of the films on the sacrificial polymer concentration will be investigated systematically.

7.1 Solubility of PAMAM Dendrimer and HMSQ Resin in the Solvents

Polymer molecules are rather different from low molecular weight molecules. They constitute long chains with a large number of segments, forming tightly folded coils that can be entangled to each other. Numerous cohesive and attractive forces both intra and intermolecular, such as dispersion, dipole-dipole interaction, induction, hydrogen bonding and van der Waals forces hold these coils together. For dissolution to occur, the solvent molecules must overcome these forces that hold the polymer molecules together in the solute and solvate the solute molecules. At the same time, the solvent molecules themselves must be separated from each other by the molecules of the solute. Actually, one can consider polymer solutions as liquid mixtures made of long macromolecular chains and small, light molecules of solvent. It is well known that the dissolution of polymers depends not only on their physical properties, but also on their chemical structure, such as polarity, molecular weight, branching, cross-linking degree and crystallinity. Based on these features, one may expect noticeable differences in the dissolution behavior shown by polymers. Due to their size, coiled shape and the attraction forces between them, polymer molecules are dissolved more slowly than low molecular

weight molecules. There are two stages involved in the polymer dissolution. In the first stage, the polymer undergoes swelling, and this is followed by the dissolution step itself. Although the general principle that states *like dissolves like* is also appropriate in the case of polymers, the underlying theories are often extremely complex and an understanding of the "why" of a particular system can be very difficult.

The selection of solvents or solvent blends for the HMSQ and PAMAM dendrimer were based on the experience, observation, trial and error. Considering that the polymer solution may form quite slowly, the solubility results were obtained two to three days after the polymer was added into a particular solvent. Table 7.1 tabulates the solubility of HMSQ and PAMAM dendrimer in the common solvents.

Table 7.1 Solubility of the polymers in common solvents

Solvent	HMSQ	PAMAM
1. Acetylacetone	√	×
2. Chloroform	√	×
3. Dimethylformamide	×	×
4. Ethanol	×	×
5. 2-Ethoxyethanol	×	×
6. Iso-butanol	×	×
7. Methanol	×	√
8. Methoxyethanol	×	×
9. N-methyl-2-pyrrolidone	×	√
10. Propyl acetate	√	×
11. Tetrahydrofuran	√	×
12. Toluene	√	×

√ – dissolvable; × – immiscible

It can be seen that only a few solvents can dissolve HMSQ and PAMAM molecules. Furthermore, no single solvent enables dissolve both HMSQ and PAMAM polymers. This may be due to the difference in polarity, molecular weight and branching of HMSQ

oligomer and PAMAM polymer. HMSQ is a relatively nonpolar resin while PAMAM dendrimer is a polar polymer. In order to make a solution of HMSQ and PAMAM, two miscible solvents have to be used. After repeated experimentations, a clear solution containing HMSQ and PAMAM was finally obtained by use of propyl acetate and N-methyl-2-pyrrolidone as co-solvent. The boiling points of propyl acetate and N-methyl-2-pyrrolidone are 102°C and 202°C, respectively. The high boiling points of these solvents prevent phase separation between the several components in the solution at low temperature.

7.2 Reactions of Coupling Agent to PAMAM Dendrimer and Silsesquioxane Resin

As mentioned before, silsesquioxane is a relatively nonpolar resin and PAMAM dendrimer is a polar thermoplastic polymer. Initially, it seems that a clear film containing HMSQ and PAMAM should be obtained since there are abundant N-H and -NH₂ groups in the PAMAM molecules, which are capable of forming hydrogen bonds with HO-Si at the terminal end of HMSQ. However, it was found from the experiments that opaque films were always obtained even if the spin-on solution contained very low loading of PAMAM. This phenomenon indicates that the phase separation occurs after the solvents evaporation during the spin-on. The existence of the hydrogen bonds is not strong enough to link the HMSQ and PAMAM together. In order to prevent the premature phase separation, which will lead to the coalescence of the PAMAM and result in larger pores in the final film, the establishment of chemical bonding between the two molecules is necessary. Hence, a coupling agent that can provide such chemical bonding is employed.

In this work, 3-(triethoxysilyl)propyl isocyanate (TPIC) was selected as a coupling agent in the synthesis of the PAMAM/HMSQ films. TPIC has two functional groups located at the two ends of the molecule: -N=C=O and (CH₃CH₂O)₃-Si-. -N=C=O enable covalent attachment to the PAMAM sacrificial dendrimer and (CH₃CH₂O)₃-Si- can cross-link with the HMSQ host polymer. The chemical reactions involved are schematically described in Figure 7.1.

Figure 7.1 Scheme of TPIC additional reactions to PAMAM and HMSQ

In the experiment, TPIC was first allowed to react with the PAMAM using NMP as the solvent as described in section 3.2 of Chapter 3. This reaction is nucleophilic substitution in nature: the -NH_2 in PAMAM dendrimer is a nucleophilic reactive site and the functional group isocyanate in TPIC enables nucleophilic covalent binding. The formation of the new bond of -HNCONH- was detected by FTIR. Figure 7.2 presents the FTIR spectra of the reactants and the additional PAMAM derivative.

Figure 7.2 FTIR spectra of reactants and addition product of PAMAM and TPIC

For the pure TPIC, the very strong absorption centered at about 2274 cm^{-1} is the stretching vibration of $\text{O}=\text{C}=\text{N}-$ in isocyanate ^[205]. For the PAMAM dendrimer, FTIR reveals amide I, II bands, where the amide I ($-\text{NH}_2$) band corresponding to the carbonyl stretching mode centers at about 1653 cm^{-1} , amide II ($-\text{NH}$) corresponding to N-H bending vibrations occurs at approximately 1550 cm^{-1} ^[205]. The broad band centered at about 3300 cm^{-1} is assigned to the stretching vibration absorption of N-H in $-\text{CONH}-$ ^[205]. For the PAMAM/TPIC derivative, the following changes compared to the reactants are found: (i) the characteristic peak of $\text{O}=\text{C}=\text{N}-$ centered at 2274 cm^{-1} in TPIC spectrum is markedly reduced; (ii) the amide I band centered at 1653 cm^{-1} in PAMAM curve disappears, and (iii) a new absorption peak centered at 1684 cm^{-1} forms indicating the formation of $-\text{HN}-\text{CO}-\text{NH}-$ bond.

Hence the functional group $-\text{N}=\text{C}=\text{O}$ in TPIC is covalently linked to the PAMAM porogen via the formation of $-\text{HN}-\text{CO}-\text{NH}-$ bond. Another functional group of triethoxysilyl in the TPIC is expected to chemically bind to the HMSQ host polymer. The triethoxysilyl is hydrolyzable in nature; it will convert into silanol ($-\text{Si}-\text{OH}$) moieties upon hydrolysis induced by moisture. Fortunately, the curing process of the HMSQ also involves terminal $\text{Si}-\text{OH}$ groups that condense to form a network structure. Thus the cross condensation of the silanols in the HMSQ and PAMAM/TPIC will occur. With this approach, PAMAM molecules can be linked at specific sites within the HMSQ matrix. A clear film of PAMAM and HMSQ is formed and it remains optically clear during the heating process, consistent with the formation of nanoscopic heterogeneities. So the phase separation or agglomeration of organic sacrificial material that will ultimately lead to the formation of larger pores is avoided.

7.3 Decomposition Behavior of PAMAM Dendrimer in Different Atmospheres

The HMSQ films were made porous by the addition of PAMAM porogen template. The experimental procedures have been described in detail in Chapter 3. The decomposition of the sacrificial polymer strongly depends on the heat-treatment atmosphere. The annealing gases commonly used are nitrogen and air. Figure 7.3 compares the FTIR spectrum of PAMAM/HMSQ films heated at 490°C in nitrogen or in air.

Figure 7.3 FTIR comparison of 15 wt% PAMAM hybrid films heated in nitrogen and in air

The following differences are noted for the films calcinated in air and in nitrogen: (i) the Si-H bond at 2250 cm^{-1} is only present in the spectrum of nitrogen-annealed film; (ii) the peaks for Si-C and C-H bonds, located at 1277 cm^{-1} and 2975 cm^{-1} , have lower intensity for air-annealed film than that for nitrogen-annealed film; and (3) the intensity of Si-O-Si network structure centered at 1040 cm^{-1} is stronger for air-annealed film than that for nitrogen-annealed film. Therefore, it can be concluded from the FTIR spectra that more organic species are lost and more cage structure is converted to network structure for air-annealed films. It is noted that the differences between the PAMAM/HMSQ films annealed in air and in nitrogen are quite the same as that for pure HMSQ films cured in nitrogen and in air, implying that the addition of the PAMAM porogen does not alter the curing process of the HMSQ.

The degradation rate of the PAMAM in different ambient was analyzed by DTA and TGA. Figure 7.4 gives the TGA/DTA results of PAMAM/HMSQ hybrid with 15 wt% of PAMAM fraction carried out in nitrogen and in air.

Figure 7.4 TGA/DTA data of the PAMAM/HMSQ hybrid conducted in different atmospheres

Two stages of weight-loss behavior are found from the TGA data regardless of the annealing atmospheres. The initial weight-loss for both films is from room temperature to about 230°C and is mainly attributed to the evaporation of the solvent and confirmed by the presence of an endothermic peak in DTA. For PAMAM/HMSQ hybrid thermally treated in nitrogen, the second stage weight-loss starts at about 400°C and the weight-loss

rate remains constant until 530°C. The basically constant loss rate suggests that water (due to the polycondensation reaction of silanols) and other thermally unstable molecules such as hydrogen and methyl are continuously expelled from the material. Only a very small exothermic peak, corresponding to the thermolysis of species, appears at about 550°C in the DTA analysis. On the contrary, for the PAMAM/HMSQ hybrid heated in air, the onset of second stage of weight-loss begins at about 350°C. The weight-loss rate is not constant in the weight-loss range of 350°C to 490°C: there is an abrupt acceleration in the weight-loss rate from 460°C to 490°C. The weight-loss is due to the curing of HMSQ and the decomposition of the PAMAM/TPIC derivative in the temperature range of 350°C – 460°C and 460°C – 490°C, respectively. This is supported by a corresponding obvious sharp exothermic peak around 500°C in DTA. Comparing quantitatively, there is about 3.6% weight-loss in the second stage of weight-loss for the hybrid annealed in nitrogen. For the air heat-treated hybrid, there is about 26.8% weight-loss from 350°C to 490°C of which 20.7% occurs in the temperature range of 460°C – 490°C.

The weight-loss profile is also correlated to FTIR spectra and dielectric measurement. Figure 7.5 shows the FTIR spectra of the PAMAM/HMSQ air-heated film with 15 wt% of PAMAM as a function of temperature.

Figure 7.5 FTIR spectra of air-heated PAMAM/HMSQ films with 15 wt% of PAMAM as a function of temperature

The FTIR peaks vary in intensity with the temperature. The peaks corresponding to Si-C, C-H and Si-H bonds located at 1277 cm^{-1} , 2975 cm^{-1} and 2250 cm^{-1} decrease monotonically with increasing temperature, indicating the loss of the organic groups at higher temperature. The Si-H peak almost totally vanishes for the film heated at 490°C , suggesting that Si-H bond is pyrolyzed at that temperature. The development of the cage/network structure transformation for the PAMAM/HMSQ films with temperature is similar to the HMSQ films (Figure 6.3), that is, the cage structure converts to network structure at higher temperatures.

The dielectric constant of the air-annealed PAMAM/HMSQ film containing 15 wt% PAMAM as a function of temperature is shown in Figure 7.6.

Figure 7.6 Dependence of dielectric constant of the PAMAM/HMSQ films on temperature in air

The k value has a remarkable reduction from 450°C to 490°C implying that the PAMAM template thermolyzes at a temperature between 450°C to 490°C to generate pores. A dielectric constant as low as 2.2 is achieved after annealing the film at 490°C .

By considering the experimental results from TGA/DTA, FTIR and dielectric measurements, it can be seen that the decomposition of the sacrificial polymer is more effective in air than in nitrogen and the degradation temperature is from about 450°C to 490°C . This phenomenon is as same as the sol-gel MTES/TEOS degradation behavior in

which organic methyl groups can only be burnt-off in air (Chapter 5). Siew^[202] also pointed out that PAMAM-COONa dendrimer could not be removed in nitrogen, but only in air. Other researchers who studied the porous low- k materials using surfactant as porogen also found that the surfactant polymers can only be pyrolyzed in air^[179, 201, 203, 210].

Since the sacrificial polymer can only be pyrolyzed effectively in air ambient, it is necessary to anneal the hybrid films under air to obtain the porous films. The properties of the HMSQ films cured in nitrogen and in air have been compared in last chapter and it has been demonstrated that there are no significant differences in dielectric properties between the two types of the films. The HMSQ begins to cure in air at about 350°C, which is below the decomposition temperature 450°C of PAMAM porogen. The strength of the HMSQ matrix increases with the curing and the PAMAM porogens are frozen in the matrix before thermolysis. This point is very important to prevent pore collapse.

7.4 Effect of PAMAM Concentration on the Properties of Porous PAMAM/HMSQ Films

The porous PAMAM/HMSQ films were obtained by curing the HMSQ matrix and degradation of the PAMAM porogen in air. The experimental procedures have been described in Chapter 3. The annealing temperature was 490°C because the PAMAM derivatives were almost completely decomposed at this temperature (Figure 7.4). Further increasing the annealing temperature would only cause more loss of organic species (Figure 7.5) which is not beneficial to the dielectric properties. The PAMAM porogen concentration was found to have a profound influence on the thermal, structural, dielectric as well as mechanical properties of the films. In this section, the PAMAM loading was varied from 0 to 20 wt%. It can be seen from the following discussions that ultra-low- k films can be obtained with 20 wt% of PAMAM. Although the further increase in PAMAM concentration can lead to lower dielectric constant, the electrical properties (such as leakage current density), mechanical properties (such as elastic modulus and hardness) and structural properties (such as pore size) are compromised. Therefore, the highest sacrificial polymer concentration was limited to 20 wt%.

7.4.1 Thermal properties of the films

Figure 7.7 shows the thermal decomposition profiles of the PAMAM/HMSQ hybrids with different weight ratios of PAMAM in the HMSQ.

(a) TGA

(b) DTA

Figure 7.7 TGA/DTA data of the PAMAM/HMSQ films with different PAMAM concentrations

Two stages of weight-loss behavior are found from TGA data for PAMAM/HMSQ hybrids regardless of the PAMAM contents. The weight loss from 350°C to 460°C is due to the curing of HMSQ and loss of organic species as discussed in last chapter. Both the weight loss in TGA and exothermic peak in DTA for HMSQ are much higher. This is because the experiments were conducted with concentrated HMSQ and much diluted HMSQ/PAMAM derivative hybrid as described in Chapter 3. The weight-loss from 460°C to 490°C is due to the degradation of PAMAM derivative. The percentage of the weight-loss increases with increasing PAMAM fraction. Moreover, the exothermic peaks in the DTA curves also increase in height with PAMAM loading. Table 7.2 lists the percentage of weight-loss for the hybrids with different ratios of PAMAM and HMSQ from 460°C to 490°C.

Table 7.2 TGA weight-loss of the PAMAM/HMSQ samples from 460°C to 490°C

PAMAM Loading (wt%)	0	5	10	15	20
Weight-Loss (%)	1.3	6.9	11.4	20.7	28.9

The amount of weight-loss increases with the increasing concentration of PAMAM as expected. The weight-loss for the film with PAMAM/HMSQ = 20 : 80 is about 4.2 times of that of the film with PAMAM/HMSQ = 5 : 95 in the temperature range of 460°C – 490°C, being consistent with the PAMAM concentration.

It is noted that the weight-loss percentage of the PAMAM/HMSQ hybrid obtained is all higher than the PAMAM loading. For example, the weight-loss is 11.4% for the 10 wt% PAMAM film and 28.9% for the 20 wt% PAMAM film. The reason is that the voids are contributed by the decomposition of the organic groups of PAMAM/TPIC derivatives instead of PAMAM molecules.

7.4.2 Hydrophobicity of the films

FTIR spectra for the films with different concentrations of PAMAM after 490°C annealing are shown in Figure 7.8. The spectra are quite similar for all the films. The

existence of organic groups presented by the peaks centered at 1277 cm^{-1} (Si-C) and 2975 cm^{-1} (C-H) suggests the hydrophobicity of the films. No hydroxyl groups and absorbed water are found in the FTIR spectra after the films undergo thermal treatment at 490°C .

The hydrophobicity of the films was evaluated by the contact angle of a water droplet on the surface of the films. Figure 7.9 shows the images of the measured water droplet on the surface of the films. Figure 7.10 plots the contact angle of the films with different concentrations of PAMAM.

Figure 7.8 FTIR spectra of the films with different ratios of PAMAM and HMSQ

Figure 7.9 Optical images of a water droplet on the templated films

Figure 7.10 Contact angle of the films as a function of PAMAM concentration

The contact angles of the films are all greater than 100° indicating the hydrophobic nature of the templated films. The contact angle is about 103° for the HMSQ film and 104.7° for the PAMAM/HMSQ film with 20 wt% PAMAM fraction.

7.4.3 Structural properties of the films

The density and porosity of HMSQ and PAMAM/HMSQ films were determined by SXR analysis. Figure 7.11 shows the SXR curves for samples with different PAMAM : HMSQ ratios presented as the logarithm of the reflectivity versus incident angle.

Figure 7.11 SXR curves of the porous PAMAM/HMSQ films with different PAMAM loadings

If the film density is less than the substrate, the X-rays will first penetrate the film. When the incidence angle exceeds the film critical angle, the reflectivity falls sharply due to the absorption in the film until they are totally externally reflected at the film – substrate interface. When the incidence angle exceeds the larger substrate critical angle, the X rays penetrate the substrate and the reflectivity falls further.

Clearly, two critical angles arising from the dielectric material and the silicon substrate are observed in both the HMSQ and PAMAM/HMSQ reflectivity data. The first critical angle is due to the dielectric thin film and the second angle is due to the silicon

substrate, which is about 0.21° independent of the PAMAM concentrations. The density of the films is proportional to the film stoichiometry and the film critical angle (Equation (3.14)). The elements in the films are Si, O, C and H. Since the hydrogen concentration is very low in the final films (Figure 7.8), it can be assumed that $\frac{\sum X_j M_j}{\sum X_j Z_j} = 2$. Similar to the analysis of the sol-gel MTES/TEOS SXR curves, the film density can be calculated according to Equation (5.4). The porosity of the PAMAM/HMSQ films can be obtained by comparing its film density to the dense HMSQ film density (Equation (3.13)). Table 7.3 gives the calculation results.

Table 7.3 SXR data of the films with different PAMAM concentrations

PAMAM Fraction (wt%)	0	5	10	15	20
Film Critical Angle ($^\circ$)	0.183	0.172	0.163	0.155	0.147
Film Mass Density (g/cm ³)	1.59	1.41	1.26	1.14	1.03
Porosity of the Film (%)	0	11.26	20.66	28.16	35.47

As expected, the density of the films decreases and the porosity of the films increases with the PAMAM porogen concentration. The porosity obtained from SXR analysis is consistent with the TGA analysis results.

In addition, it can also be seen from Figure 7.11 and Figure 6.5 that the oscillation behavior beyond the second critical angle is different for the HMSQ and PAMAM/HMSQ films. The Kiessig oscillations, which result from the constructive and destructive interference between X-rays reflected from the air/film and film/silicon interfaces, is present in the HMSQ SXR curve only. Relative to the HMSQ film, not only does the oscillation in the PAMAM/HMSQ hybrid films disappear but also the specular reflectivity drops more quickly beyond critical angle. As discussed in the literature^[21], 212], this phenomenon indicates that the surface roughness of the PAMAM/HMSQ films

is increased compared to the HMSQ film. It should be pointed out that the roughness of the films measured by SXR is actually different from that measured by real space methods such as AFM. The information obtained from SXR measurements is generated from larger sampling volumes. The X-ray beam width is 1 mm – 5 mm with a height of 100 μm . At very small angles of incidence, the footprint on the sample is 1 mm – 5 mm by 1 cm – 2 cm. This is particularly significant when comparing roughness from SXR to AFM, where the area probed is typically only 0.1 μm^2 – 1 μm^2 . Thus the SXR experiments provide complementary information on a “global” scale.

The morphology of the films was studied using AFM and TEM. AFM images obtained for the HMSQ film and 15 wt% loading of PAMAM/HMSQ film are presented in Figure 7.12 and Figure 7.13, respectively.

The image was processed by flatten only to remove the spot noise. The gray scale shows the vertical profile of the sample with the light regions being the highest points and darkest regions being lowest. Both AFM images reveal a uniform microstructure. For the HMSQ film, the surface is flat and no obvious pores can be seen. By contrast, for the PAMAM/HMSQ film, the pores can be seen clearly as small well-defined dark areas. The pores are not interconnected and the pore size is about 10 nm in diameter.

Figure 7.12 AFM image of the HMSQ film

Figure 7.13 AFM image of the PAMAM/HMSQ film with 15 wt% of PAMAM

Figure 7.14 shows a plan-view TEM image of the film with PAMAM : HMSQ = 15 : 85 after decomposition of the sacrificial material. The lighter (less electron density) regions in the image correspond to the pores.

Figure 7.14 TEM observation for the PAMAM/HMSQ film with 15 wt% of PAMAM

The TEM result also reveals a rather uniform structure as the AFM microstructure. The pores are clearly visible as light areas in the TEM image; they are nearly spherical in

shape and are in closed form. When pore dimensions obtained from AFM and TEM observations are compared, it is found that the pore dimension obtained by AFM is slightly larger, about 10 nm in diameter versus 7 nm – 8 nm from TEM observation. This difference underlines the uncertainty in pore definition on AFM images.

AFM has the tremendous advantage of operation in air with no sample preparation. However, care has to be taken in the use of AFM for determination of pore sizes as the measured pore dimensions may be a result of convolution of tip and pore shape on the recorded profiles, which can become complex if the tip and surface pore sizes are comparable ^[213]. The relation is illustrated by two simplified pore structures and an idealized tip in Figure 7.15 ^[214].

Figure 7.15 Interaction between tip and pore structure ^[214]

Model (a) is an ideal pore membrane. Model (b) is a funnel-shaped pore with rounded corners and is closer to the reality. For both models, pores with diameter smaller and larger than the radius of the scanning tip are discussed. The AFM-trace represents a convolution between the tip shape and pore shape. It does not pose any problem to determine the actual pore size from the AFM-trace for the pore structure A, while in the case of structure B the AFM can only measure the maximum pore size at the very top of the surface. In other words, in the case of funnel-shaped pores, the tip can be prevented

from deeply penetrating into the apertures. Therefore, the measured average values are much higher than the expected pore diameter.

In addition, surface roughness should be taken into consideration when deducing average pore diameters from AFM images ^[215]. For rough surfaces of films where the pores apertures are located between nodular structures there is a possibility to make their localization more elusive.

In our work, the tip dimension of AFM is approximately 20 nm – in the same order of the pore sizes. So it is possible that the pore sizes are overestimated by the AFM observation. The conclusion that AFM tends to give higher values for pore dimensions than measured by electron microscopy was also reported by Kim *et al.* ^[216].

The plan-view of TEM images for films with PAMAM : HMSQ ratios of 5 : 95, 10 : 90 and 20 : 80 are shown in Figure 7.16.

(a) PAMAM = 5 wt%

(b) PAMAM = 10 wt%

(c) PAMAM = 20 wt%

Figure 7.16 TEM observation for the PAMAM/HMSQ films
with different amount of PAMAM

The TEM images present a uniform microstructure even at higher loading of PAMAM. It seems the proper mixing and chemical bonding at the molecular level between PAMAM template and HMSQ matrix are achieved. So the phase separation and agglomeration of the polymer are minimized.

The pore diameter of the films as a function of porogen loading level is a critical parameter. From TEM observations, the pore sizes of PAMAM/HMSQ films are about 3 nm – 5 nm for 5 wt% and 10 wt% PAMAM fractions, about 7 nm – 8 nm for 15 wt% PAMAM concentration and about 9 nm – 10 nm for 20 wt% PAMAM loading. The pore size becomes larger at higher PAMAM concentrations. Miller *et al.* [217] pointed out that the phase separation of the porogen from the matrix process proceeded by a nucleation and growth mechanism so the pores become larger as the porogen loading level increases. Moreover, an increase in the pore size at a certain level of sacrificial material content can also result from the interconnection of domains and/or pores. The dimension of the G2 PAMAM molecule is 2.9 nm [111]. So a certain degree of percolation of pores may occur for the films with 15 wt% and 20 wt% of PAMAM fractions. When the percolation happens, the mesopores start to merge with or connect to the surrounding pores, leading to a bigger pore size. It can be seen from Table 7.3, the porosities of these two films are as high as 28.16% and 35.47%, respectively, due to the pyrolysis of PAMAM/TPIC derivative. Usually the percolation threshold occurs at approximately 25% porosity in the silsesquioxane films [218].

7.4.4 Pore arrangement

XRD was used to examine whether the pores are arranged in order in the films. Figure 7.17 shows the XRD results for the films with different fractions of PAMAM.

Figure 7.17 XRD patterns of the templated films with different PAMAM fractions

No obvious peaks appear for all the samples, suggesting that the pores are arranged randomly in the films. This result agrees with AFM and TEM observations.

7.4.5 Optical and dielectric properties of the films

The refractive index and corresponding porosity derived from Lorentz-Lorenz relationship for the PAMAM/HMSQ films are shown in Figure 7.18.

Figure 7.18 Refractive index and corresponding porosity of the PAMAM/HMSQ films as a function of PAMAM loading

The results for the refractive index show a reduction from 1.35 for the HMSQ film to 1.29 for the 10 : 90 of PAMAM : HMSQ film and to 1.21 for the film with 20 wt% of PAMAM. The porosity derived from the refractive index increases gradually with PAMAM porogen fraction. The PAMAM/HMSQ film with 20 wt% loading of porogen contains 38.2% pores. The results are in good agreement with the porosity data obtained from the SXR evaluations.

The measured capacitance and conductance of the films with different HMSQ and PAMAM ratios are shown in Figures 7.19 and 7.20, respectively. The sequence of the curves is not very meaningful as the measured capacitance and conductance do not take the film thickness into consideration.

Figure 7.19 Measured capacitance for the different PAMAM/HMSQ films

Figure 7.20 Measured conductance for the different PAMAM/HMSQ films

The capacitance of the film is almost linear because of the heavily doped n^+ wafer substrate used. A RTS noise due to the defects or charged carriers in the films is also

observed in the conductance versus voltage curves, similar to the sol-gel derived dielectric films.

The corresponding dielectric constant and dissipation factor of the films are obtained from the above two graphs (Equations (3.20) and (3.21)) and shown in Figure 7.21.

Figure 7.21 Dependence of dielectric properties of the PAMAM/HMSQ films on PAMAM concentration

The dielectric constant of the films shows a monotonic decrease with PAMAM concentration, as the porosity of the films is proportional to the PAMAM porogen fraction. The k value reduces from 2.71 for the nonporous HMSQ film to 2.45 for the porous film of PAMAM : HMSQ = 10 : 90 and to $k = 2.06$ for the film containing 20 wt % of PAMAM.

The dissipation factor, on the other hand, increases with PAMAM loading. The dissipation factor is a measure of the energy required to align dipoles and to move trace ions. The increase in dissipation factor implies that the trace ions increase in amount with increasing PAMAM concentration. This phenomenon may be caused from incomplete thermolysis of the template molecules as well as the porous nature of the films.

7.4.6 Electrical properties of the films

The I - V property of the PAMAM/HMSQ films is displayed in Figure 7.22.

Figure 7.22 I - V characterization of the films with different PAMAM concentrations

All the I - V curves show no sign of breakdown up to 40 V regardless of the PAMAM fractions. As seen in Figure 7.23 of leakage current density versus applied field, which excludes the effect of film thickness, all the films have very high breakdown fields. The breakdown field is above 1.4 MV/cm even for the film with 20 wt% of PAMAM.

Figure 7.23 J - E characterization of the mesoporous PAMAM/HMSQ films

Usually, the dielectric constant is dependent on the porosity of the film and not on the pore structure ^[219]. However, the dielectric breakdown strength, which becomes very important for low-*k* thin films at higher circuit packing density, may be adversely affected by the pore structure: interconnected pores will make the dielectric more susceptible to moisture and metal diffusion, resulting in inferior electrical properties. The high breakdown strength of PAMAM/HMSQ films indicates that there are not significant open porosity in the films. The interconnection of the pores at higher PAMAM fractions only results in the merging of the pores in a certain degree.

Figure 7.24 gives the effect of PAMAM fraction on the leakage current density of the films at 1 MV/cm.

Figure 7.24 Leakage current density of the PAMAM/HMSQ films versus PAMAM fraction (at 1 MV/cm)

The leakage current density for the PAMAM/HMSQ films is greater than that for HMSQ film and increases with increasing PAMAM concentration. This phenomenon is consistent with dissipation factor experimental data. Fortunately, the increase is insignificant and all the PAMAM/HMSQ films exhibit leakage current density on the 10^{-7} A/cm² order at 1 MV/cm.

In order to understand better about the leakage behavior of the films, the nature of the carrier transport in the low- k silsesquioxane polymer is studied in terms of Frenkel-Poole and Schottky emission. Figure 7.25 shows the $\ln J - E^{1/2}$ curves for the films with different PAMAM fractions.

Figure 7.25 $\ln J$ versus $E^{1/2}$ for the films with different PAMAM loadings

The $\ln J$ exhibits a linear relationship with $E^{1/2}$ for the films with different PAMAM loadings in the mid applied field of 0.4 MV/cm to 1.4 MV/cm. As discussed in Chapter 5, the linear variations of the current correspond either to Schottky emission or to Frenkel-Poole mechanism (Equations (5.6) and (5.8)). The Schottky emission process is thermionic emission across the metal – insulator interface or the insulator – semiconductor interface are responsible for carrier transport. The Frenkel-Poole emission is due to field-enhanced thermal excitation of trapped electrons into the conduction band. The deviation of conduction mechanism from Schottky and Frenkel-Poole emission at low electrical field is due to the effect of ohmic conduction^[183]. In order to define the prominent conduction mechanism, $\beta_{theory,Sc}$ and $\beta_{theory,FP}$ as described in Chapter 5 (Equations (5.5b) and (5.7b)) are calculated from the experimental dielectric constant and compared to the β_{slope} obtained from the slope of the $\ln J - E^{1/2}$ curve. These results for

the HMSQ films incorporated with different fractions of PAMAM are tabulated in Table 7.4.

Table 7.4 Comparison of β_{slope} to $\beta_{theory,Sc}$ and $\beta_{theory,FP}$ for the PAMAM/HMSQ films

PAMAM Fraction (wt%)	Experimental Dielectric Constant	β_{slope} ($\text{Jm}^{1/2}/\text{V}^{1/2}$)	$\beta_{theory,Sc}$ ($\text{Jm}^{1/2}/\text{V}^{1/2}$)	$\beta_{theory,FP}$ ($= 2 \beta_{theory,Sc}$) ($\text{Jm}^{1/2}/\text{V}^{1/2}$)
0	2.706	2.98×10^{-24}	3.70×10^{-24}	7.39×10^{-24}
5	2.652	2.54×10^{-24}	3.73×10^{-24}	7.47×10^{-24}
10	2.447	2.63×10^{-24}	3.89×10^{-24}	7.77×10^{-24}
15	2.205	3.21×10^{-24}	4.09×10^{-24}	8.19×10^{-24}
20	2.058	2.95×10^{-24}	4.24×10^{-24}	8.48×10^{-24}

β_{slope} is closer to $\beta_{theory,Sc}$ than $\beta_{theory,FP}$ for all the films. So the conduction mechanism of the PAMAM/HMSQ films with different PAMAM fractions is Schottky emission dominated in the mid applied field (0.4 MV/cm to 1.4 MV/cm), just as same as the sol-gel derived low- k films. The assumption that the PAMAM/HMSQ films have Schottky conduction mechanism is as same as that of SiLKTM [220] low- k films measured at temperatures ranging from 50°C to 200°C using aluminum as electrode, but different from that of HSQ [221] low- k films measured at temperatures ranging from 425°C to 500°C using copper as electrode.

7.4.7 Mechanical properties of the films

The elastic modulus and hardness of the films were determined with a nanoindenter. A typical experimental load – depth curve is shown in Figure 7.26.

Figure 7.26 An experimental indentation curve for the film with 5 wt% of PAMAM

Figure 7.27 and 7.28 depict, respectively, the dependence of the reduced elastic modulus and hardness of the templated films on the ratio of contact depth/film thickness. The ratio of the contact depth (h_c) and the film thickness (t) is used instead of the contact depth to get rid of the influence of the film thickness.

Figure 7.27 Reduced elastic modulus of the films as a function of h_c/t

Figure 7.28 Hardness of the films as a function of h_c/t

The observed increase of the reduced modulus with contact depth is due to the influence of the hard silicon substrate, as expected for a thin film. Reliable data should be extracted at low contact depth where this influence is minimal. The same behavior is also observed for $H(h_c/t)$ curves, although the increasing trend is shifted to slightly larger depths due to the smaller spatial extent of the plastic as compared to the elastic deformation field.

Figure 7.29 shows the dependence of the mechanical properties of the films on the PAMAM concentration.

Figure 7.29 Elastic modulus and hardness of the films as a function of PAMAM loading

The hardness of the films is obtained directly from the experimental curve, while the elastic modulus of the samples is derived from the Equation (3.25) and a Poisson's ratio of 0.22 is assumed^[149].

Clearly, the introduction of subtractive porosity into the films results in a drastic decrease in the hardness and elastic modulus of the PAMAM/HMSQ films. The average elastic modulus is reduced from 9.8 GPa for the HMSQ film to 4.9 GPa for the film with 10 wt% of PAMAM in the HMSQ and 2.5 GPa for the film with 20 wt% of PAMAM in the HMSQ. A similar behavior is observed for the hardness, where the values are reduced from 1.21 GPa for the HMSQ film to 0.71 and to 0.39 GPa for the 10 : 90 and 20 : 80 of PAMAM : HMSQ films, respectively. The results that the increasing porosity compromises the mechanical properties of the films agree well with literature^[60, 222, 223].

An almost linear weakening of elastic modulus and hardness due to the introduction of porosity is observed as shown in Figure 7.30.

Figure 7.30 Hardness of the templated films against the elastic modulus

7.5 Effect of Aging Time on the Properties of the Films

When the films are exposed to atmosphere, they may absorb moisture and the properties of the films may be changed over time. The magnitude of the change depends greatly on the surface hydrophobicity and the pore structure of the films. If the surface of

the films are hydrophobic and the pores are in closed form, they do not easily absorb moisture from atmosphere and the properties of the films change little over the time.

In this work, the templated mesoporous films were aged in room ambient – about 25°C and 75% humidity to monitor the moisture uptake. The dielectric constant and dissipation factor of the film with 20 wt% of PAMAM loading as a function of the aging time is presented in Figure 7.31.

Figure 7.31 Dielectric properties of the templated film as a function of aging time

The dielectric constant and dissipation factor of the templated film are almost independent of aging time during the experimental period of nearly two months. The dielectric constant and dissipation factor of the film are about 2.058 and 0.0256 after the fabrication, and they are remained about 2.07 and 0.0279 after 51 days aging.

The leakage current of the films is usually more sensitive to the aging conditions than the dielectric constant^[219]. The comparison of the leakage current of the templated film before and after aging is shown in Figure 7.32.

Figure 7.32 Comparison of the leakage current density of the templated film before and after aging

The leakage current density of the film is about 5.07×10^{-7} A/cm² at 1 MV/cm one month after fabrication comparing to 4.48×10^{-7} A/cm² of just fabrication. So the leakage current density is almost unchanged for the PAMAM/HMSQ films after one month of aging.

Figure 7.33 shows the FTIR spectra of the films measured two months after fabrication.

Figure 7.33 FTIR spectra of the films with different PAMAM fractions measured two months after fabrication

In comparison with the FTIR spectra of the films obtained just after the synthesis (Figure 7.8), no obvious hydroxyl peaks are observed indicating that there is no significant moisture uptake for the PAMAM templated films during the experimental period.

Two conclusions can be drawn based on the aging experimental results. Firstly, the surface of the films is hydrophobic, in good agreement of contact angle measurement (Figures 7.9 and 7.10), so they are resistant to moisture attack. Secondly, the pores in the PAMAM/HMSQ films are in closed form. Even though the pores merge at the higher PAMAM loadings, the resultant bigger pores are still in the closed form.

7.6 Summary

Templated dielectric films are successfully prepared by linking covalently a sacrificial polymer (PAMAM) to a host polymer (HMSQ) via a coupling agent. Films with the porogen fraction up to 20 wt% in the HMSQ matrix have been fabricated without agglomeration or phase separation of the sacrificial polymer, affirming the effectiveness of the coupling agent.

The degradation study of the porogen template in different atmospheres indicates that the PAMAM thermolysis is more effective in air than in nitrogen. The thermal removal of the porogen occurs at a temperature higher than the curing temperature of the HMSQ matrix, so the original template structure is remained and nanosized voids are formed within the films.

The physical, structural, dielectric and mechanical properties of the porous PAMAM/HMSQ films are studied as a function of the sacrificial polymer concentration. The film density and porosity are evaluated by SXR and a reflectometer. The results show that the density of the films monotonically decreases and the porosity increases with increasing PAMAM concentration. The film with 20 wt% of PAMAM has density of 1.03 g/cm³ and porosity of 35.5%. AFM and TEM micrographs provide information about the structure of the hybrid films. The pores are of nearly spherical geometry and in closed form. Pore sizes increase with PAMAM concentration. Nevertheless, the average pore diameter of the film with 20 wt% of PAMAM is still less than 10 nm. The XRD patterns show that pores are randomly arranged in the templated films.

The dielectric constant of the PAMAM/HMSQ films reduces remarkably comparing with that of the HMSQ film. A low dielectric constant of about 2.06 can be obtained with 20 wt% PAMAM concentration and the leakage current density is on the 10^{-7} A/cm² order at 1 MV/cm. The dielectric constants and the leakage current density change little even after the films have been aged for about two months at room ambient. This is attributed to the hydrophobic nature of the film surface and also indicates that although the pores merge at higher PAMAM fractions, the pores are still in the closed form.

The conduction mechanism of leakage current of the films is studied at room temperature and found that the carries in the films with different PAMAM loadings have Schottky conduction mechanism in the electrical field of 0.4 MV/cm to 1.4 MV/cm.

The mechanical properties of the films are determined by nanoindentation. Both the elastic modulus and hardness decrease with increasing PAMAM concentration, implying that the introduction of the porosity deteriorates the mechanical properties. The elastic modulus and hardness reduce from 9.8 GPa and 1.21 GPa for the HMSQ film to 2.5 GPa and 0.39 GPa, respectively, for the film with 20 wt% of PAMAM.

These results, along with the structural parameters of the films demonstrate a possibility to prepare interconnect dielectric films with controllable pore size and porosity using the sacrificial polymer approach.

**CHAPTER 8 COMPARISON OF THE LOW DIELECTRIC CONSTANT FILMS
PREPARED BY SOL-GEL AND TEMPLATE METHODS**

In the previous chapters, low dielectric constant organosilicate films have been prepared by the sol-gel and porogen template methods. Their properties have also been investigated systematically. In this chapter, the synthesis process and properties of these two types of films will be briefly compared.

8.1 Comparison of the Synthesis Process

In the fabrication of sol-gel derived low-*k* films, two types of precursors are used: TEOS catalyzed by an acid and MTES catalyzed by a base. The acid catalysis produces a dense film. On the other hand, base catalysis produces a film with highly porosity. Thus, a composite structure with highly porous structure embedded into a dense matrix is fabricated by employing acid and base two-step catalysis. The MTES catalyzed by the base can be regarded as a porogen in the broadest sense.

In the template approach, HMSQ is used as a matrix and PAMAM dendrimer is used as a template or porogen. By controlling the weight percentage of the porogen, morphology with domains of the thermally labile block surrounded by the thermally stable HMSQ matrix is obtained. In the subsequent processing steps, the films are heated to cure the HMSQ matrix and decompose the porogen to volatile products. These products diffuse out of the HMSQ matrix to yield the desired porous nanostructure.

The steps involved in the sol-gel and template processes are tabulated in Table 8.1.

Table 8.1 Comparison of the fabrication process for the sol-gel and templated films

Sol-Gel Process	Template Process
1. Spin on 2. Bake 3. HMDS surface modification 4. Heat-treatment to dry the film and remove hydroxyl groups 5. Further dehydroxylation	1. Spin on 2. Bake 3. Heat-treatment to cure HSMQ and to pyrolyze PAMAM

Comparing the two approaches, the process to synthesize the templated films is simpler than the sol-gel method. The sol-gel films have to undergo surface modifications in the subsequent steps to eliminate the surface silanol groups generated in the hydrolysis of the precursors. In contrast, the templated films are prepared in a single step.

8.2 Comparison of the Material Properties

Regarding the dielectric properties, both types of films can yield dielectric constant around 2.0. However, the sol-gel films require a higher level of porosity to reach this dielectric constant due to the higher k value of the matrix (Figure 8.1).

Figure 8.1 Relationship between the porosity and dielectric constant of the films

The porosity for films with k about 2.0 is 61.4% and 35.5% (from XRR) for the sol-gel and templated films, respectively. About one-third more pore volume has to be present for the sol-gel film to achieve the same ultra-low- k value. This is because the matrix material for sol-gel films is silica that has a dielectric constant of 4.0; the matrix material for templated films is HMSQ resin and its dielectric constant is 2.7. The insertion of the cage structure with Si-H and Si-CH₃ groups results in HMSQ having a lower density and polarizability, leading to a lower dielectric constant of HMSQ than

SiO₂. Hence the HMSQ based films can reach the same dielectric level at lower porosity than the sol-gel films.

When the two types of films are aged in an ambient environment, the dielectric constant of the templated film is almost independent of aging time during the experimental period of nearly two months. However, the dielectric constant of the sol-gel film increases with aging time (Figure 8.2).

Figure 8.2 Dielectric constant of the sol-gel and templated films as a function of aging time

The different aging behavior of the two kinds of films is mainly resulted from the different pore structure of the films. The templated films have a closed pore structure whilst the sol-gel films consist of closed pores and open pores.

Although the sol-gel films possess higher porosity, their mechanical properties are better than the templated films. Figure 8.3 and 8.4 gives the relationship between the elastic modulus, hardness and the porosity of the films.

Figure 8.3 Comparison of the elastic modulus of the sol-gel and templated films

Figure 8.4 Comparison of the hardness of the sol-gel and templated films

The elastic modulus and hardness of the templated films are much lower than that of the sol-gel films at the same porosity level. The main reason may be attributed to the difference in the mechanical properties of the matrix. The silsesquioxanes have a much lower elastic modulus and hardness than silica due to their cage structure with some pendant organic groups. The same trends have also been found in the literature ^[223 – 228].

Nevertheless, higher elastic modulus and hardness are found for present samples compared to the literature values. For example, Maex *et al.* ^[229] reported an elastic modulus of about 1.2 GPa and hardness of 0.1 GPa for a MSQ-based material with the porogen level of 34%. In comparison, our PAMAM/HMSQ film with 20 wt% of PAMAM and porosity of 35.5% has an elastic modulus of 2.5 GPa and hardness of 0.39 GPa. The mechanical properties are improved when more cage structure converts to network structure and more organic groups pyrolyze in air. In addition, although the templated films have lower mechanical properties than the sol-gel films for the same porosity, they have similar mechanical properties for films with the same dielectric constant due to the much lower porosity of the templated films.

The main properties of the films prepared by the sol-gel and templated methods are compared in Table 8.2.

Table 8.2 Comparison of materials properties of the sol-gel and templated films

Material Property	Sol-Gel Film (MTES/TEOS = 1.0, mole)	Templated Film (PAMAM/HMSQ=20/80, weight)
Refractive Index (at 632.8 nm)	1.18	1.21
Density (g/cm ³) (SXR)	0.84	1.03
Porosity (%) (SXR)	61.4	35.5
Pore Connectivity (N ₂ adsorption, SXR TEM, aging experiments)	Closed pores + open pores	Closed pores
Average Pore Size (nm) (TEM)	5	9.5
Pore Arrangement (XRD)	Random	Random
Lowest Dielectric Constant (after fabrication)	1.89	2.06
Change of Dielectric Constant (%) (one month after fabrication*)	32.27%	0.97%
Leakage Current Density at 1 MV/cm (A/cm ²) (after fabrication)	1.9×10^{-6}	4.51×10^{-7}
Leakage Current Density at 1 MV/cm (A/cm ²) (one month after fabrication*)	6.02×10^{-6}	5.07×10^{-7}
Young's Modulus (GPa)	5.8	2.5
Hardness (GPa)	0.74	0.39

* aging condition: 25°C and relative humidity = 75%.

CHAPTER 9 PRELIMINARY STUDY OF COPPER INTERACTION WITH THE SOL-GEL LOW DIELECTRIC CONSTANT FILMS

Very large scale integration of devices necessitates the use of multilayer metallization structures on the chip level and for packaging. The traditional Al and SiO₂ interconnect materials are being replaced by alternative materials to meet the needs of device miniaturization. Low-*k* materials were introduced recently to replace SiO₂ as the insulating layer. Prior to that copper has been used since 1997 as the conductor material for interconnect metallization to replace Al due to its low bulk resistivity and high reliability against electromigration^[230 – 232]. However, the transition from the Al/SiO₂ scheme to Cu/low-*k* scheme has brought about many integration challenges. The important reliability concerns include the interface of the low-*k* materials with the adjacent Cu metal layers. If copper cannot adhere well to the dielectrics and tends to diffuse into the dielectrics, a diffusion barrier will be needed to prevent significantly increased interlevel leakage current, inadequate field isolation and transistor degradation. Many barrier metals between Cu and the underlying Si or dielectric have been studied^[233 – 235]. There is still, however, a lack of conclusive data in terms of the extent of Cu concentration that a device can withstand before failure. In this chapter, the diffusion of copper in sol-gel organosilicate films will be studied. The investigation on templated organosilicate films is not reported due to the shortage of the HMSQ material.

9.1 Experiment

The samples for investigating interaction of sol-gel low-*k* films with Cu layer were made by first depositing the sol-gel film on a heavily doped n-type silicon wafer, using MTES and TEOS as precursors. The experimental procedures were the same as described in Chapter 3.

Copper was deposited in an e-beam evaporator with base vacuum in the evaporation chamber of 4×10^{-6} Torr (5.333×10^{-4} Pa). A pure, semiconductor grade Cu slug with purity of 99.999% was used as the source material. The current and voltage were about 0.04 A and 7 kV, respectively, resulting in a deposition rate of 5 – 6 nm/min. The deposited Cu films were 200 nm thick.

In order to study the thermal stability of the interface between the film and the metal, the samples have to be heated to an elevated temperature in a vacuum^[236, 237] or nitrogen^[238 – 240] environment to ensure that the exposed Cu electrodes do not oxidize during heating. In this work, the annealing experiments were conducted in a rapid thermal processor (RTP, JIPELEC) at 200°C and 450°C for 30 minutes, respectively. A nitrogen purge was present during the temperature ramp, annealing and cooling periods. RTP is used instead of tube furnace because RTP is pre-evacuated before the chamber is filled with nitrogen. As a result, the residual air or oxygen content in the chamber can be kept at lower level.

Tape tests were carried out to evaluate the adhesion of copper to the films. An optical microscope (Olympus BX-60) was used to examine the copper surface before and after the tape test.

The capacitance of the films was determined using a Keithley CV Analyzer at 1 MHz. The dielectric constant was calculated from the capacitance – voltage (C - V) plots of the Cu capacitors. The leakage current was measured with a precision semiconductor parameter analyzer (HP 4155A). The evaluation of both dielectric constant and leakage current of the films was conducted in ambient conditions.

9.2 Preliminary Study of Copper Diffusion to the Sol-Gel Films

9.2.1 Adhesion of copper to the sol-gel low- k films

One of the main integration problems is the metal compatibility with the low- k material. Typically, the low- k material is in contact directly with the metal barrier (such as tantalum nitride, TaN) or possibly to the copper metallization in the damascene structure. If the films are incompatible with copper or the barrier layer, another layer has to be deposited to promote the adhesion. Maisonobe^[241] investigated the adhesion of CVD copper to SiLKTM (Dow Chemicals) low- k films and found that copper was delaminated over the surface of the wafer after annealing for 30 min at 250°C and totally removed after maintaining for 1 hr at 450°C.

In this work, it is found that the e-beam evaporated copper shows no visible change when directly deposited on sol-gel organosilicate films, even for the film annealed at

450°C for 30 minutes. Figure 9.1 shows the micrographs of the copper before and after tape tests for as deposited and annealed copper capacitors.

Figure 9.1 Optical images of the copper electrodes before and after tape tests (magnification 300x)

The tape tests reveal that the copper has a better adhesion on the sol-gel films after annealing. The as-deposited copper electrodes are totally or partially removed by the tape. However, the copper electrodes annealed at 200°C and 450°C are still adhered well to the film surfaces after the tape tests. The common phenomenon of adhesion failure of the metal such as delamination copper over wafer surface or peeling of copper is not found in the annealed Cu/organosilicate film system. It seems that more stable interface between copper and sol-gel film is formed at higher temperatures. Since, for semiconductor applications of Cu interconnects and our SiO₂ based ILD, the target processing temperature is 450°C, the stability at 450°C may indicate the possibility that an adhesion promoting layer, which results in an increase in the effective dielectric constant, can be avoided.

9.2.2 Effect of annealing temperature

Figure 9.2 shows the dielectric constant at 1 MHz of copper/low-*k* film/*n*⁺ Si quasi MIM capacitors subjected to different temperatures. Additional insight into the diffusion of copper is gained by measuring the *I-V* characteristics. Figure 9.3 shows the leakage current density of the as-deposited and annealed Cu capacitors at applied field of 1 MV/cm.

Figure 9.2 Effect of annealing temperature on the dielectric constant of the capacitors with copper upper electrode and MTES/TEOS dielectrics

Figure 9.3 Effect of annealing temperature on the leakage current density of the copper capacitors

In general, Cu atoms have a higher driving force to diffuse into the bulk of low- k films at higher temperature. It can be seen from Figures 9.2 and 9.3, both the dielectric constant and leakage current density of the annealed films keep the same profiles as do the as-deposited samples. No significant increase in the dielectric constant and leakage current is observed for the 200°C and 450°C annealed Cu capacitors. In other words, the C - V and I - V behaviors are unaffected by the thermal treatments.

In order to elucidate the leakage mechanisms, plots of leakage current density J versus applied field E and $\ln J$ against $E^{1/2}$ for the Cu/film/ n^+ Si capacitors annealed at 450°C are given in Figures 9.4 and 9.5.

Figure 9.4 Leakage current density of the copper capacitors with different fractions of MTES annealed at 450°C

Figure 9.5 $\ln J$ versus $E^{1/2}$ plot of the Cu/film/ n^+ Si capacitors annealed at 450°C

The leakage current densities of the films with different MTES fractions are found to be linearly related to the square root of the applied electric field. Thus the carriers transport corresponds either to Schottky emission or to Frenkel-Poole type conduction mechanism. To see which mechanism is the dominant one, the theoretical $\beta_{theory,Sc}$

$\beta_{theory,FP}$ and experimental β_{slope} as described in Chapter 5 are extracted and compared. Table 9.1 lists the results.

Table 9.1 Values of the dielectric constant and constant β at 25°C for the film with Cu as electrodes after 450°C annealing

MTES/TEOS (molar ratio)	Experimental Dielectric Constant	β_{slope} ($\text{Jm}^{1/2}/\text{V}^{1/2}$)	$\beta_{theory,Sc}$ ($\text{Jm}^{1/2}/\text{V}^{1/2}$)	$\beta_{theory,FP}$ ($= 2 \beta_{theory,Sc}$) ($\text{Jm}^{1/2}/\text{V}^{1/2}$)
0.5	2.25	3.72×10^{-24}	4.05×10^{-24}	8.11×10^{-24}
0.67	2.17	3.49×10^{-24}	4.13×10^{-24}	8.25×10^{-24}
1.0	2.20	3.65×10^{-24}	4.01×10^{-24}	8.02×10^{-24}
2.0	2.05	4.09×10^{-24}	4.26×10^{-24}	8.52×10^{-24}
4.0	2.09	2.37×10^{-24}	4.21×10^{-24}	8.41×10^{-24}

Just like the sol-gel films using Au/Ti as electrodes, the β_{slope} is closer to $\beta_{theory,Sc}$ than $\beta_{theory,FP}$ for the films with MTES/TEOS = 4.0, 2.0, 1.0, 0.67 and 0.5. In other words, the conduction for all the films are dominated by the electrode – limited field-assisted Schottky mechanism in the mid electric field (0.09 MV/cm – 1.1 MV/cm).

9.2.3 Effect of porosity of the films

Both the dielectric constant and leakage current density of the films vary with MTES fractions as seen in Figures 9.2 and 9.3. As discussed in Chapter 5, the higher MTES concentration leads to higher porosity of the MTES/TEOS films. So the dielectric constant of the films with Cu electrodes decreases with MTES/TEOS ratio. On the other hand, the leakage current of the films with Cu electrodes increases with porosity. However, this increase is not caused by the copper diffusion, but the more porous nature of the films at higher MTES content as discussed in Chapter 5. Comparing Figure 9.3 to Figure 5.12 using Au/Ti as electrode, it can be seen that the current density of Cu capacitors are similar or even a little lower than that in Au/Ti capacitors. For example, for the film with equal moles of MTES and TEOS, the leakage current density at 1 MV/cm is 8.52×10^{-7} and 1.90×10^{-6} A/cm² for Cu and Au/Ti capacitor, respectively. The result of

Cu capacitors having similar leakage current as Au capacitors is similar to Loke's ^[238], but different from Rogojevic's ^[182] who found that the leakage current density of copper capacitor is one or two orders lower than that of Al or Au capacitor.

These results indicate that the direct deposition of copper on sol-gel films does not induce a dramatic diffusion of the as-deposited or annealed copper into the sol-gel films, even for the film with MTES/TEOS of 4.0 which has porosity as high as 73%. Although the free volume of sol-gel film may facilitate the interstitial migration of Cu ions, the copper does not diffuse into the films. Compared to literature, Jain *et al.* ^[242] found that Cu did not diffuse into highly porous (up to 90%) silica xerogel films after annealing in N₂ or vacuum environment up to 450°C for 11 hr, as determined by RBS. Fisher *et al.* ^[236] also found that copper did not diffuse into sol-gel organosilicate films after 500°C anneal for 30 minutes.

This is an important result because copper has a high diffusivity in thermal SiO₂ and requires a diffusion barrier between the copper and dielectric layer ^[243 – 245]. However, the addition of the barrier layer will inevitably increase the effective dielectric constant of the stack as barrier layer usually has a higher dielectric constant. Although the backbone of the sol-gel films is also silica, the material shows fundamentally different behavior from that of solid SiO₂. Rogojevic *et al.* ^[182] attributed this phenomenon to the more stable interface between Cu and xerogels than that of Cu and thermal SiO₂ based on the Rutherford backscattering spectroscopy (RBS) and SEM studies. Moreover, it is speculated that the incorporation of MTES precursor and surface modification of the sol-gel films by -Si(CH₃)₃ groups can significantly affect the interfacial properties and inhibit the copper diffusion.

9.3 Summary

This chapter initially studies the penetration of copper into the sol-gel derived low-*k* films with different porosities. The copper-insulator-n⁺ silicon capacitors are annealed at 200°C or 450°C for 30 minutes in nitrogen to study the thermal stability of the interface between the film and the metal. The tape tests reveal that annealed copper adheres better to the organosilicate films than the as-deposited one. The conduction mechanism analysis suggests that the leakage current of Cu capacitor measured at 25°C follows the Schottky emission for the films with MTES/TEOS of 4.0, 2.0, 1.0, 0.67 and 0.5. The

characterization of the films shows that the dielectric constant and leakage current for the as-deposited and annealed Cu/film capacitors are similar to that of Au/Ti/film capacitors. All of the experimental results indicate that there is no significant copper diffusion through the organosilicate films with different porosities under the experimental conditions. The interface stability at 450°C suggests that an adhesion promoting layer and diffusion barrier with higher dielectric constants perhaps can be avoided for the sol-gel derived low- k films.

CHAPTER 10 CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORK

10.1 Conclusions

Multilevel interconnect technology beyond the 130 nm generation requires interlayer dielectric materials with much lower dielectric constant than the traditional SiO_2 to reduce the parasitic capacitance between the metal wires, and thus reduce the RC delay, cross-talk noise and power dissipation of the circuits. Since few existing materials have dielectric constant less than 2.0, the strategy of incorporation of voids into dielectric materials has emerged as the leading approach. In this work, two techniques to prepare porous films from spin-on solutions: (i) sol-gel approach to construct a constitutive porous network and (ii) porogen template method to construct a subtractive porous network, have been employed to synthesize organosilicate films with low dielectric constant.

Two types of precursors, organic MTES and inorganic TEOS, catalyzed by base and acid respectively, have been used to fabricate the sol-gel films. The introduction of organic ligands into the SiO_2 network not only changes the mechanism of film drying so that crack-free films can be obtained but also renders the films hydrophobic. Additional HMDS surface modification and air, nitrogen two-step annealing progressively cause the film surface to contain fewer silanol groups and to become more hydrophobic. Therefore, the moisture uptake by the films is prevented and the dielectric constant and leakage current density of the films can be kept low.

The acid/base two-step catalysis with different mechanisms of hydrolysis and condensation controls the microstructure of the sol-gel films. The base catalyzed MTES precursor produces highly porous structure while the acid catalyzed TEOS tends to produce dense films. By controlling the fraction of MTES and TEOS, a structure of pores embedded in the dense films is formed. It is found from the SXR and nitrogen adsorption porosimetry evaluations that the pores in the films consist of open and closed pores. The total porosity, percentage of closed pores and the pore size of the films increase with increasing concentration of MTES. When the MTES/TEOS molar ratio increases from 0.5 to 4.0, the total porosity is varied from about 53% to 73% with closed

pores of about 26% to 59% and the pore size changes from about 2.5 nm to 7 nm. The pores are arranged randomly in the films based on the XRD measurements.

The dielectric constant of the sol-gel films has been found to decrease with MTES fraction or porosity. An ultra-low dielectric constant of about 2.0 can be achieved with MTES/TEOS ratio ≥ 1.0 . The leakage current density of the films increases with MTES concentration. The leakage current density of the film with equal mole of MTES and TEOS, measured in ambient conditions, is about 1.9×10^{-6} A/cm² at 1 MV/cm.

The conduction mechanism for leakage current of films with different MTES contents has been investigated at room temperature and found that the carriers transport follows Schottky emission in the electric field of 0.09 MV/cm to 1.1 MV/cm.

The mechanical properties of the films are determined by nanoindentation and has been found that both elastic modulus and hardness of the films decrease with increasing concentration of MTES. The average elastic modulus and hardness are 5.8 GPa and 0.74 GPa for a film with MTES : TEOS = 1 : 1.

When the sol-gel films are aged in room ambient, their dielectric constant and leakage current will increase. The increase in the dielectric constant for the film of MTES/TEOS = 1.0 occurs mainly in the first few days and then the increment slows. The dielectric constant is still about 2.56 after two months aging consistent with the pore structure and hydrophobicity analysis. The increase in the leakage current is also not very significant and the increment decreases with increasing closed porosity. When the sol-gel films are subjected to the dry conditions such as desiccator, no obvious changes are observed for both dielectric constant and leakage current of the films.

The templated films have been prepared using HMSQ as a matrix material and PAMAM as a porogen template. A coupling agent is used to covalently bind the host and sacrificial materials together to achieve nanoscopic phase separation. Compared to the sol-gel films, the templated films can be synthesized in a single process.

The degradation behavior of the PAMAM template in different atmospheres has been studied. It is found that the PAMAM dendrimer thermolyzes more effectively in air than in nitrogen. The thermal and dielectric properties of HMSQ films cured in different atmospheres have also been investigated quantitatively from 25°C to 490°C. It is found that the curing of the HMSQ films both in nitrogen and in air is an exothermic process accompanying the loss of hydrogen and methyl groups, and there is a structural

transformation from cage to network structure during the curing. The differences in curing between the nitrogen- and air-cured films are: (1) HMSQ films starts to cure earlier in air than in nitrogen; (2) more small molecules are lost in air curing; and (3) the conversion from cage to network structure is higher for the air-cured films. However, in spite of the distinctions, the dielectric constant and leakage current of the films cured in air and in nitrogen are quite similar. The dielectric constants are about 2.64 and 2.71 for nitrogen- and air-cured HMSQ films, respectively and the leakage current densities for both films are of the order of 10^{-8} A/cm² at an applied field of 1 MV/cm after heat-treatment at 490°C. It is concluded from the study on PAMAM decomposition and HMSQ curing that it is beneficial to use air as the annealing gas in order to obtain porous PAMAM/HMSQ films.

The physical, structural, dielectric and mechanical properties of the porous PAMAM/HMSQ films cured in air have been investigated as a function of the PAMAM template concentration. The film density and porosity are evaluated by SXR and an optical reflectometer. The results show that the density of the films decreases and the porosity increases monotonically with increasing PAMAM concentration. The density and porosity for the film with 20 wt% PAMAM is 1.03 g/cm³ and 35.47%, respectively. The pores are not arranged in order in the films, similar to the sol-gel derived films. AFM and TEM micrographs provide information about the structure of the hybrid films and show pores of nearly spherical geometry with diameter less than 10 nm. Although the pores become larger at higher PAMAM fractions, there is no significant open porosity in the films.

The dielectric constant of PAMAM/HMSQ films decreases markedly with respect to that of the HMSQ film. And it yields the similar dielectric constant at much lower porosity comparing to the sol-gel films. An ultra-low dielectric constant of about 2.06 can be obtained with 20 wt% PAMAM loading and the leakage current density is on the order of 10^{-7} A/cm² at 1 MV/cm. The dielectric constant and the leakage current density change little even after two months aging at room ambient. This is attributed to the hydrophobic nature of the film surface and the closed pore structure. The conduction mechanism of leakage current of films with different PAMAM loadings is studied at room temperature. The carries in the films is Schottky emission dominated at the electrical field of 0.4 MV/cm to 1.4 MV/cm.

Both elastic modulus and hardness of the films, determined by nanoindentation, decrease with increasing PAMAM concentration. This implies that the introduction of the porosity weakens the mechanical properties. The elastic modulus and hardness for the film with 20 wt% of PAMAM are 2.5 GPa and 0.39 GPa, respectively.

The copper interaction with the sol-gel derived low- k films has been studied. Tape tests show that more stable interfaces between copper and the sol-gel film are formed after 200°C and 450°C annealing in nitrogen. The dielectric constant and leakage current of the as-deposited and annealed Cu capacitors are almost same as that of the Au/Ti capacitors. The conduction mechanism analysis suggests that the carriers of the Cu capacitors annealed at 450°C have the same transportation mechanism as that of the Au/Ti capacitors. For the films with MTES/TEOS of 4.0, 2.0, 1.0, 0.67 and 0.5, the conduction follows Schottky model. These results indicate that there is no significant Cu diffusion through the organosilicate films under the experimental conditions even for the film with porosity as high as 73%. The interface stability at 450°C suggests that an adhesion promoting layer and a diffusion barrier layer with higher dielectric constants perhaps can be avoided for the so-gel derived low- k films.

Sol-gel and templated films with controllable structural and dielectric properties have been successfully fabricated. The characterization of these two types of films shows that they are very promising materials for next generation Cu-interconnect technology.

10.2 Recommendation for Future Work

Although much work has been carried out systematically, there are still many research opportunities on this topic. The recommendations for the future work are described in the following:

1. Further characterize the properties of the sol-gel and templated films

With respect to the requirements for the low- k materials ^[13], more electrical, chemical, thermal and mechanical properties of the films should be evaluated such as the electric-field strength, chemical resistance, thermal conductivity, coefficient of thermal expansion and so on. Some research topics are presented below as a reference for future work.

The conduction mechanism of low- k films is necessary for understanding the intrinsic electrical properties such as leakage current of the films. The temperature dependent I - V measurement, which has not been carried out due to the lack of measurement facility, should be performed to supplement and confirm the conclusions obtained by room temperature I - V measurement. This is especially important for the sol-gel film with MTES/TEOS = 4.0 and for the templated film with 20 wt% of PAMAM as other mechanisms apart from Schottky emission may exist.

Percolation threshold in the porous films is an important pore structure property. It can be determined with positronium annihilation lifetime spectroscopy (PAL). Moreover, this technique can readily distinguish between open (interconnected) pores and closed (isolated) pores. Hence the pore structure obtained from PAL is more straightforward and evident than that from the nitrogen adsorption isotherm method which can only analyze bulk materials.

Thermal conductivity of the films, which can be used to estimate the power dissipation, is also very important. However, the methodology is challenging because most of the experimental methods developed for measuring thermal conductivity of bulk porous materials, such as the hot-wire technique ^[246, 247] are not applicable for thin dielectric films due to the lack of sensitivity and the large sample size requirement. Fortunately, a 3ω technique has recently been extended to thin films ^[248, 249] and has been successfully used in xerogel films ^[62].

2. Integration and reliability challenges

Building reliable Cu/low- k film interconnect is challenging for a number of reasons. The use of copper and low- k materials brings new issues, some of which have no material solution at present. A partial list of integration challenges include adhesion to underlayer or substrate, compatibility to hard mask, copper diffusion, etch selectivity, deep ultraviolet (DUV) photo resist poisoning, porous low- k voiding and damage due to etch, ash and/or cleans processes and side wall roughness in etched trenches. Furthermore, the effective k value of an integrated dielectric stack (k_{eff}) is determined by all the materials in that stack. The hard mask, CMP cap and etch-stop layers can all increase the k_{eff} . Consequently, selection of materials for these layers must consider their k values and the layer thickness should be minimized.

Although we have done some study on the interaction of copper with low- k films, there is still scope for future work. For example, the investigation of copper diffusion on templated films is not reported in this work due to the limited supply of HMSQ material. Moreover, the bias-temperature-stress (BTS) instrument, which is the more suitable technique for characterizing copper diffusion to the low- k materials, should be set up. In this measurement, Cu-insulator-Si capacitors are biased at elevated temperatures to accelerate Cu penetration from Cu gate electrodes into low- k insulators. Subsequent changes in the room temperature C - V characteristics of the capacitors are analyzed to extract the amounts of Cu that have diffused into the dielectrics. For additional insight into the Cu diffusion process, the C - V characterization should be supplemented by current – time (I - t), current – voltage (I - V) and dielectric time-to-failure (TTF) measurements during BTS, enabling a physical model to be formulated to explain the kinetics of Cu penetration. Additional work includes the effects of heating-cooling cycles and deposition methods of Cu (physical vapor deposition (PVD), electrochemical plating (ECP) and so on) on the interaction of Cu and low- k films.

Electromigration (EM) is another major reliability concern for on-chip interconnects. EM is the mass transport of a metal due to the momentum transfer between conducting electrons and diffusing metal atoms. It is a process of current-induced self-diffusion in metal lines, which can lead to a short between adjacent lines. EM has been extensively studied in Cu/oxide structures in the past several years. Compared with Al/oxide interconnects, Cu/low- k structures have distinct EM characteristics because the dual-damascene architecture has introduced different transport path, flux divergence and damage mechanisms^[250 – 253]. Multi-link statistical test structures with varying lengths of Cu/porous interconnect can be used to obtain the EM lifetime and failure mode^[254, 255].

3. Synthesis and characterization of ordered porous films

Ordered porous materials refer to the materials in which the pore arrangement is well-defined. Although it is not necessary for interconnect dielectrics with ordered pore structure, it is evident that the properties of the films and the integration process can be better controlled with well-defined pore structure. Ordered porous films can be formed by a template method – using supramolecular surfactant molecules which has the self-assembly function as structure directing agent^[256]. For instances, well-ordered hexagonal

mesoporous silica with pore size between 7.5 nm to 30 nm have been produced with amphiphilic block copolymers ^[83, 257] or nonionic oligomeric surfactants ^[258] as the organization directing agent. A critical step in this process is the thermal removal of the template polymer and retention of the original supramolecular structure.

We have done a preliminary study on the ordered porous organosilicate films using TEOS and MTES as precursors, PAMAM (G2) dendrimer as a structure directing agent. Some results are given below as a reference for the future work.

Figure 10.1 shows the effect of heat-treatment atmosphere on the arrangement of the voids.

Figure 10.1 XRD patterns of PAMAM directed sol-gel films

Only the film annealed in air shows XRD peak representing some extent of periodicity between voids. This is due to the effective removal of PAMAM molecules in air. The *d*-space is about 3.27 nm calculated according to Equation (3.19).

The ordered structure in the films may be destroyed if the MTES and TEOS molar ratio changes. Figure 10.2 shows the XRD pattern of the films with different molar ratios of precursors.

Figure 10.2 XRD patterns of the sol-gel films with different ratios of precursors

The increase in the TEOS concentration may result in more opened pores leading to a random structure.

The ordered porous films presented above are promising. Besides microelectronics, it can also be used in the fields of catalytic, medication, adsorbent, host for nanocluster synthesis, separation devices and optoelectronic devices.

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1. Suzhu Yu, Terence K. S. Wong, Xiao Hu and Jun Wei, Structural, Dielectric and Mechanical Properties of Mesoporous Silsesquioxane Films, *The 2nd International Conference on Technological Advances of Thin Films & Surface Coatings (ThinFilms 2004) and The 1st International Conference on Nanotechnology (Nanotech 2004)*, Singapore, 13-17 July (2004).
2. Suzhu Yu, Terence K. S. Wong, Xiao Hu and Jun Wei, Synthesis and Characterization Of Silsesquioxane Films with Nanometer Pores, *The 2nd International Conference on Technological Advances of Thin Films &*

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