Chapter 3

Low Dielectric Materials for Microelectronics

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/51499

1. Introduction

Over the past half century, low dielectric materials have been intensively researched by ceramic and polymer scientists. However, these materials possess a vast myriad of electrical, thermal, chemical, and mechanical properties that are just as crucial as the name that classifies them. Therefore, in many cases, the applications of low dielectric constant materials are dictated by these other properties, and the choice of low dielectric material may have a tremendous effect on a device's performance and lifetime.

In the field of microelectronics, many of the early low dielectric materials have been satisfactory in covering the required properties. But as the microelectronics industry continuously boomed through the 21st century, more and more advanced processes and materials have been in demand. Since the invention of microprocessor, the number of active devices on a chip has been exponentially increasing, approximately doubling every year, famously forecast by Gordon Moore in 1965. All of this is driven by the need for optimal electrical and functional performance.

Figure 1 shows the shrinking of the device dimensions over signal delay value. And while the total capacitance can be traded for resistance and vice versa by changing the geometry of the wire cross-section, the RC will always increase for future nodes. In other words, in order to enhance performance, decreasing the device size, as well as decreasing the interconnecting wire distance, gate and interconnect signals delay is the main challenge for ceramic and polymer scientists to overcome. In another approach to solve this RC delay problem, researchers have already changed the aluminum line to Cu line, which has lower resistance. But due to limitations in metal lines being applicable for use, research of low dielectric materials are continually being pursued today. The main challenge for researchers in the microelectronic industry is not to develop materials with the lowest dielectric constant, but to find materials that satisfy all of the electrical, thermal, chemical, and mechanical properties required for optimal device performance.

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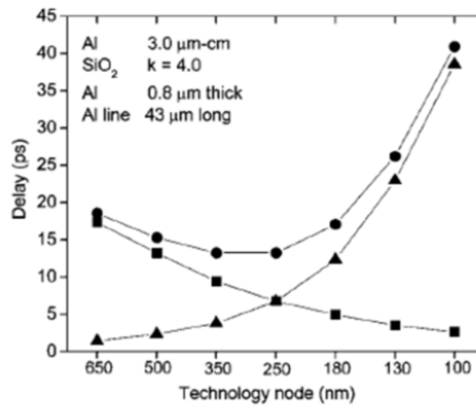

ITRS Technology Trend Targets (including PIDS 2011 roadmap flash and DRAM trend driver proposals)

	Year of Production	'09	'10	'11	'12	'13	'14	'15	'16	'17	'18	'19	'20	'21	'22	'23	'24	'25
2010 ORTC	Flash 1/2 Pitch (nm) (un-contacted Poly)(f) [A]	32	38	28	25	23	20	18	15.9	14.2	12.6	11.3	10.0	8.9	8.0	7.1	6.3	N/A
2010 PIDS Projection based on survey data	Flash 1/2 Pitch (nm) (un-contacted Poly)(f) [B]	N/A	26	24	22	20	19	18	16	14	13	12	11	9	8	8	8	N/A
2010 WAS	DRAM 1/2 Pitch (nm) (contacted) [C]	52	45	40	36	32	28	25	22.5	20.0	17.9	15.9	14.2	12.6	11.3	10.0	8.9	N/A
2010 PIDS Projection based on survey data	DRAM 1/2 Pitch (nm) (contacted) [D]	N/A	42	36	31	28	25	24.0	21.0	18.0	16.0	14.0	13.0	12.0	10.0	9.0	8.0	N/A
	MPU/ASIC Metal 1 (M1) 1/2 Pitch (nm)	54	45	38	32	27	24	21	18.9	16.9	15.0	13.4	11.9	10.6	9.5	8.4	7.5	N/A
	MPU Printed Gate Length (GLph)(nm)	47	41	35	31	28	25	22	19.8	17.7	15.7	14.0	12.5	11.1	9.9	8.8	7.9	N/A
	MPU Physical Gate Length (GLph)(nm)	29	27	24	22	20	18	17	15.3	14.0	12.8	11.7	10.7	9.7	8.9	8.1	7.4	N/A
	ASIC/Low Operating Power Printed Gate Length (nm)	54	47	41	35	31	25	22	19.8	17.7	15.7	14.0	12.5	11.1	9.9	8.8	7.9	N/A
	ASIC/Low Operating Power Physical Gate Length (nm)	32	29	27	24	22	18	17	15.3	14.0	12.8	11.7	10.7	9.7	8.9	8.1	7.4	N/A
	ASIC/Low Standby Power Physical Gate Length (nm)	38	32	29	27	22	18	17	15.3	14.0	12.8	11.7	10.7	9.7	8.9	8.1	7.4	N/A
	MPU Etch Ratio Glpr/Glph (nm)	1.6409	1.5296	1.4588	1.4237	1.3895	1.3561	1.3235	1.2917	1.2607	1.2304	1.2008	1.1720	1.1438	1.1163	1.0895	1.0633	N/A

Figure 1. Calculated gate and interconnect dely as a function of technology node according to the National Technology Roadmap for Semiconductores(NTRS) in 1997 (top): ■gate delay; ▲interconnect delay (Al and SiO_2); ● sum of delays (Al and SiO_2) and ITRS technology trend targets (bottom)

2. Definition of dielectric constant

Dielectric constant k (also called relative permittivity εr) is the ratio of the permittivity of a substance to that of free space. A material containing polar components, such as polar chemical bonds, which are presented as electric dipoles in Figure 2, has an elevated dielectric constant, in which the electrical dipoles align under an external electric field. This alignment of dipoles adds to the electric field. As a result, a capacitor with a dielectric medium of higher k will hold more electric charge at the same applied voltage or, in other words, its capacitance will be higher. The dipole formation is a result of electronic polarization (displacement of electrons), distortion polarization (displacement of ions), or orientation polarization (displacement of molecules) in an alternating electric field. These phenomena have characteristic dependencies on the frequency of the alternating electric field, giving rise to a change in the real and imaginary part of the dielectric constant between the microwave, ultraviolet, and optical frequency range.

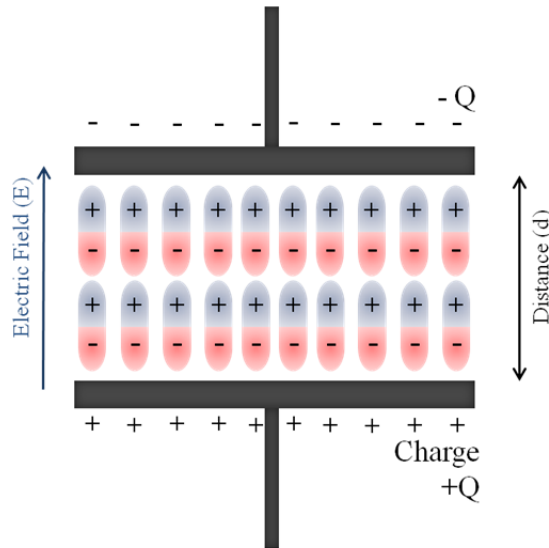

Figure 2. Schematic illustration of a capacitor.

3. Property requirements of low dielectric material

Dielectric materials must meet stringent material property requirements for successful integration into the interconnect structures. These requirements are based on electrical properties, thermal stability, thermomechanical and thermal stress properties, and chemical stability. The desired electrical properties can be outlined as low dielectric constant, low dielectric loss and leakage current, and high breakdown voltage. As RC delay and crosstalk are primarily determined by the dielectric constant, in a typical CVD SiO_2 film, the dielectric constant is around 4. And although many polymeric materials satisfy these electrical criteria, the dimensional stability, thermal and chemical stability, mechanical strength, and thermal conductivity of polymers are inferior to those of SiO_2.

Electrical	Chemical	Mechanical	Thermal
Dielectirc constant Anisotropy Low dissipation Low leakage current Low charge trapping High electric-field strength High reliability	Chemical resistance Etch selectivity Low moisture uptake Low solubility in H_2O Low gas permeability High purity No metal corrosion Long storage life Enviromentally safe	Thickness uniformly Good adhesion Low stress High hardness Low shrinkage Crack resistance High tensile modulus	High thermal stability Low coefficient of thermal expansion Low thermal weight loss High thermal conductivity

Table 1. Property Requirements of Low-k Dielectrics

In the fabrication of the multilevel structures, as many as 10 to 15 temperature treatments are repeated at elevated temperatures exceeding 400-425°C. This inherent processing of inter-dielectric (ILD) materials makes thermal stability a key prerequisite of low dielectric materials in microelectronics. Not only is the thermal stability in terms of degradation key, but the insensitivity to thermal history may be just as important. For example, changes in the crystallinity and/or crystalline phases during these thermal cycles may cause changes in the electrical and/or mechanical properties, making the material dependent on its thermal history. Other problems seldom seen in thermal processing include outgassing of volatile solvents and/or decomposition products which may cause poisoning, delamination, blistering, or cracking in the ILD.

Another thermomechanical concern of ILD materials is its coefficient of thermal expansion (CTE). The extensive thermal cycling of microelectronics may also cause stresses in the interconnect structure if there is a CTE mismatch between the ILD material and the metal or substrate. These stresses invariably cause delamination if adhesion is poor. And while adhesion promoters may be added to enhance wetting and chemical bonding at the interface between the ILD and substrate, this is mostly undesired from manufacturing point of view, as it adds unnecessary processing steps. Also, if the adhesion promoter thermally degrades, it may lead to adhesion failures or create a leakage path.

Adhesion is determined by chemical bonding at the metal/ILD interface and the mechanical interaction between the metal and ILD. Thus, ideal ILDs should have good mechanical properties such as a large Young's modulus (E), tensile strength, and elongation-at-break. And although it is uncertain what constitutes sufficient mechanical strength for successful integration into a manufacturable process, the elongation-at-break should be as large as possible to sustain the deformation and impart crack resistance, even at elevated temperatures. Also, a high modulus retention at elevated temperatures, E(T), is required for the ILD to maintain its structural integrity and dimensional stability during subsequent processing steps. Related to E(T) is the glass transition temperature, Tg. Since exceeding the Tg causes a large decrease in the modulus and yield stress in amorphous, non-crosslinked polymers, a Tg greater or equal to the highest processing temperature is desired. For example, residual compressive stresses in capping layers can cause buckling and delamination of the capping films due to the compliance of an ILD above its Tg [1,2]. Buckling has also been observed in capping layers deposited below the ILD's Tg if the capping film is highly compressive [3].

Other processing concerns include chemical resistance to the solvents and etchants commonly used during chip fabrication, chemical interaction with the metal lines causing corrosion, and moisture uptake. Moisture is a primary concern because even trace amounts can have a detrimental impact on the dielectric constant. The ILDs should also be free of trace metal contaminants, have long shelf-lives, and, preferably, not require refrigeration. Metal contamination, which can compromise the device and provide a leakage path between lines, is often a problem for polymers synthesized using metal catalysts. Other processing requirements include the ability to pattern and etch the film, etch selectivity to resists, good thickness uniformity, gap-fill in submicron trenches, and planarization.

The long-term reliability of chips fabricated using low-k materials must also be evaluated. Electromigration and stress voiding are primary failure mechanisms in integrated circuits [4-6] and these are reliability concerns when replacing SiO_2 with an alternative ILD that has thermal and mechanical properties inferior to those of SiO_2.

4. Design of low dielectric material

There are two strategies for designing a low dielectric material: decreasing dipole strength or the number of dipoles (Fig. 4) or a combination of both. In the first strategy, materials with chemical bonds of lower polarizability than Si-O or lower density would be used. Today, the microelectronics industry has already moved to certain low-k materials, where some silica Si-O bonds have been replaced with less polar Si-F or Si-C bonds. A more elementary reduction of the polarizability can be attained by utilizing all nonpolar bonds, such as C-C or C-H, as in the case of organic polymers.

Bond	Polarizability ($Å^3$)	Average bond energy (Kcal/mole)
C - C	0.531	83
C - F	0.555	116
C - O	0.584	84
C - H	0.652	99
O - H	0.706	102
C=O	1.020	176
C=C	1.643	146
C≡C	2.036	200
C≡N	2.239	213

[a] Reference [7].
[b] Reference [8]

Table 2. Electronic polarizability[a] and bond enthalpieds[b]

The second strategy involves decreasing the number of dipoles within the ILD material by effectively decreasing the density of a material. This can be achieved by increasing the free volume through rearranging the material structure or introducing porosity. Porosity can be constitutive or subtractive. Constitutive porosity refers to the self-organization of a material. After manufacturing, such a material is porous without any additional treatment. Constitutive porosity is relatively low (usually less than 15%) and pore sizes are ~ 1 nm in diameter. According to International Union of Pure and Applied Chemistry (IUPAC) classification[9], pores less than 2 nm are denoted 'micropores'. Subtractive porosity involves selective removal of part of the material. This can be achieved via an artificially added ingredient (e.g. a thermally degradable substance called a 'porogen', which is removed by annealing to leave behind pores) or by selective etching (e.g. Si-O bonds in SiOCH materials removed by HF).

5. Utilization of low dielectric materials in microelectronics

A particularly difficult challenge for low dielectric materials development has been to obtain the combination of low dielectric constant and good thermal and mechanical stability. Generally, the types of chemical structures that imbue structural stability are those having strong individual bonds and a high density of such bonds. However, the strongest bonds often are the most polarizable, and increasing the bond density gives a similar increase in polarization. For example, the rigidity and thermal stability of SiO_2 is in part due to the dense (2.2–2.4 g/cc) chemical network. Unfortunately, the high bond and material density in SiO2 lead to a large atomic polarizability, and therefore a high dielectric constant. Organic polymeric materials often have a lower dielectric constant due to the lower material density (<1.0 g/cc) and lower individual bond polarizabilities.

In this part, the relationship between molecular structure and low dielectric properties is discussed with consideration of factors such chemical bond, density, and polarizability.

5.1. Linear structure

Linear structured materials have been actively researched for various microelectronic applications. In the early stages of microelectronics development, IBM implemented a polyimide-based material in microchips based on its good thermal, mechanical, chemical, and electrical properties. However, as required properties have become stricter because of narrowing interconnect line distance, polyimide-based materials have been unable to satisfy device performance with the main reason due to its high water absorption. Despite its superior properties, it became apparent that a linear polymeric structure was unfeasible for application as more high performance devices were being demanded.

However, linear polymeric structures have given polymer scientists invaluable clues into the possible molecular content of low dielectric materials. According to the definition of a dielectric, the material density has a direct relationship with respect to its dielectric constant. Linear polymers occupy a free volume, derived from large steric hindrance compared to single small molecules. For this reason, linear structured materials such as organic polymers, polyethylene and polypropylene show quite low density (0.8~0.9), and thus low dielectric value (2.1~2.6). Unfortunately, these organic polymers suffer from critical disadvantages such as thermal instability such as low glass transition temperature and low degradation temperature.

Therefore, many scientists turned to polymeric materials having an aromatic moiety. This chemical structure showed enhanced thermal properties and was expected to have a low density due its rigid molecular structure. The high polarizability of these materials due to their relatively high dipole moment was expected to compensate for the inherently large free volume. Some of the various aromatic, linear polymers are outlined below.

5.1.1. Polyimides (PIs)

Excellent thermomechanical properties can be obtained by incorporating a very stiff polymer. The classic example of a stiff polymer chain is aromatic polyimides, which have a

rigid backbone due to the many aryl and imide rings along the chain. These structural characteristics give rise to excellent mechanical and thermal properties in the form high modulus (8–10 GPa) and high Tg (350 to 400°C) [10]. However, the rigid chain structure causes the PI chains to align preferentially parallel to the substrate, especially when deposited as thin films, which results in anisotropic properties [11-18]. For example, while the out-of-plane k value of BPDA-PDA is 3.1, the more important in-plane value is >3.5 [14].

The thermomechanical properties are likewise anisotropic. For instance, the CTE of thin films of rigid PIs is often <10 ppm/°C in the plane of the film, but can be more than ten times larger in the out-of-plane direction [14]. Another drawback to PIs is that they absorb water effectively owing to the carbonyl groups, which raises the dielectric constant further. The release of this water during processing can cause blistering of overlying layers [19].

Some of the drawbacks mentioned above can be ameliorated by tailoring the chemical structure of the PI. The k value and water adsorption can be lowered by incorporating fluorine into the material, while the anisotropy can be reduced by introducing single bonds between rings, making the chain less rigid. For example, PMDA-TFMOB-6FDA-PDA, which utilizes both of these design strategies, has an out-of-plane k=2.64 [20] and absorbs less moisture than unfluorinated PIs such as BPDA-PDA [10]. However, the in-plane k value is still >3.0, and the water uptake, although reduced, is significant enough to cause blistering in overlying layers during integration [19].

5.1.2. Poly (aryl ethers) (PAE)

The utilization of spin-on PAE materials results from attempts to balance the dielectric and thermomechanical properties. The aryl rings in these materials provide better thermomechanical properties than do PIs, but the flexible aryl linkages allow bending of the chains, which results in a more isotropic material than is obtained for PIs.

Additionally, the lack of polar groups, such as carbonyl, results in a lower k value and lower water uptake than the PIs. Fluorinated versions of PAEs had a k value of 2.4 [21]. However, because of concerns about fluorine corrosion, the fluorine was removed from later versions of the material. The nonfluorinated PAEs typically have a k of 2.8–2.9, whereas typical values for the modulus and CTE are 2.0 GPa and 50-60 ppm/°C, respectively. Resistance to thermal decomposition can be quite good for PAEs as weight losses of only <2% over 8 h at 425°C have been reported. One drawback of uncrosslinked PAEs is that they have a relatively low Tg of <275°C, which is lower than many of the thermal treatment temperatures of microelectronic devices.

5.1.3. Polynorbornene

Polynorbornene [22] is a pure hydrocarbon polymer without any polar or polarizable groups. Known for their high thermal stability among organic polymers (Tg ~365°C) and low dielectric constant [23] (~2.2), polynorbornenes are soluble in common organic solvents

despite its rigid backbond due to the randomly coiled nature of the polymer chains and lack of polar interactions.

This combination of properties makes polynorbornene an interesting candidate for ILD/IMD use. However, polynorbornenes exhibit insufficient adhesion to substrates with polar surfaces such as Si, oxides or metals and its rigid backbone results in a rather brittle material. To overcome these shortcomings, a copolymer with alkoxysilyl and aikyi side groups at the norbornane rings in the backbone of polynorbornene was developed by BFGoodrich (Avatre[). [23,24] The alkoxysilyl groups enhance adhesion to surfaces with hydroxyl groups and increase the relative mobility of the polymer chains, and hence the elongation at break of thin films [23]. However, the dielectric constant increases from 2.2 of the unsubstitituted polymer to 2.67 with an aikoxysilyl content of 20% [23]. Copolymers from alkoxysilyl norbornene and alkylnorbornene derivatives show improved elongation-at-break and reduced dielectric constant [23] of E = 2.56. The glass transition temperatures and thermal stabilities of these materials are reduced compared to non-functionalized polynorbornene [25,26]

5.1.4. Polytetrafluoroethylene (PTFE)

Proposals to use fluorinated organic materials like PTFE are aimed toward minimizing the dielectric constant using the bonds of lowest polarizability. PTFE, which consists of singly bonded carbon chains saturated with fluorine atoms, has one of the lowest k values (<1.9) of any nonporous material, and is normally deposited by spin-on films [27]. One drawback of PTFE is that the flexible and uncrosslinked chain structure limits the thermomechanical stability of the material. For example, one PTFE material evaluated in our laboratory was found to have a low yield stress (12 MPa), low elastic modulus (0.5 GPa), low softening temperature (<250°C), and high thermal expansion coefficient (CTE) (>100 ppm/°C). Together these factors can cause buckling or wrinkling of the film during process integration. A second issue for PTFE, which is a concern for all fluorine-containing materials, is the potential release of fluorine atoms that can cause corrosion of metals or other reliability problems in the interconnect structure.

5.1.5. Polysilsesquioxane

While research of linear, rigid, organic polymers have centered on lowering the density and enhancing thermal and mechanical properties [28,29], many of these materials tend to have elevated dielectric constants and decreased processability because the main frame of these polymers are composed of aromatics, double, and triple bonds, which can be readily polarized or have weak thermal stability.

Polysilsesquioxanes $(RSiO_{3/2})_n$ comprise a class of polymers that exhibit unique physical properties different from those of purely organic or inorganic compounds [30]. The various structures of polysilsesquioxanes, including ladder-like polysilsesquioxanes with double stranded backbones, cage-type polyhedral oligomeric silsesquioxanes (POSS), and sol-gel

processed random branched structures have shown many inherent advantageous properties such as high thermal stability, low dielectric constant, good mechanical properties, and chemical resistance. Such properties have made polysilsesquioxanes a material of interest for polymer and ceramic scientists in the microelectronics industry.

In particular, polymethylsilsesquioxanes are of particular interest, as these materials exhibit low loss at high temperatures exceeding 500°C. However, to approach the favorable properties of polysilsesquioxanes in a reproducible manner, a regular structure with high molecular weight, such as ladder-structures, is to be favorable. This rigid ladder backbone with high molecular weight would support lower dielectric constants stemming from increase of inter-molecular space and high mechanical strength, as well as minimizing shrinkage during the ILD process. This material had 6.3 GPa of modulus and 2.7 of dielectric constant without curing process. [31]

5.2. Branched structures

In polymer chemistry, polymer branching induces a lower profile of material density without significant changes of in chemical properties. Because of this, many researchers have investigated polymer geometries such as graft and hyper branched structure for application as low dielectric material.

Branched polymers are advantageous in that through chemical modification of the side or end groups can give unique functionality that could not be realized by composites of two or three different materials. Also, the chemical bonding between the two components may offset one or more deficient property of the singular component.

5.2.1. Graft Polymers

Graft copolymers are a special type of branched copolymer in which the side chains are structurally distinct from the main chain. The Figure (3) depicts a special case where the main chain and side chains are composed of distinct homopolymers.

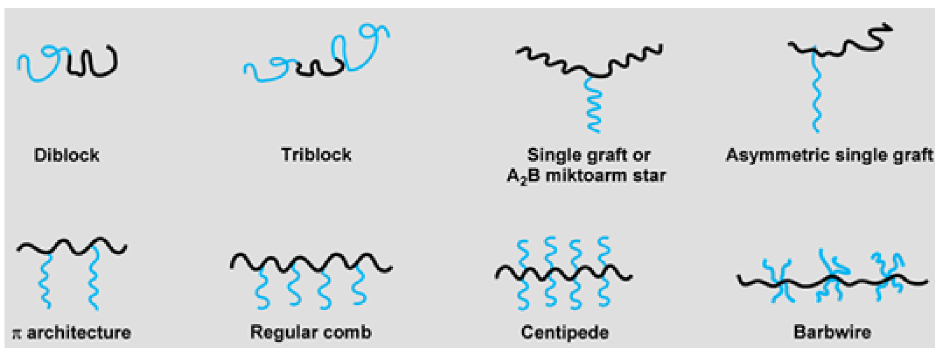

Figure 3. Special cases of grafted polymer

Kung-Hwa wei et al. reported a polyimide grafted polyhedral oligomeric silsesquioxane (POSS). They presented the dielectric constants and densities of the POSS/polyimide nanocomposites (figure 4). The dielectric constants of the POSS/polyimide nanocomposites decreased as the amount of POSS increased. The maximum reduction in the dielectric constant of POSS/polyimide nanocomposites was found to be about 29%, compared to 16 mol% POSS/polyimide to pure polyimide (*k*) 2.32 vs 3.26. However, these graft polymers exhibited a slightly lower glass transition temperature about 40°C and increased thermal expansion efficient (CTE) from 31.9 ppm/K to 57.1 ppm/K after the grafting of POSS. [32]

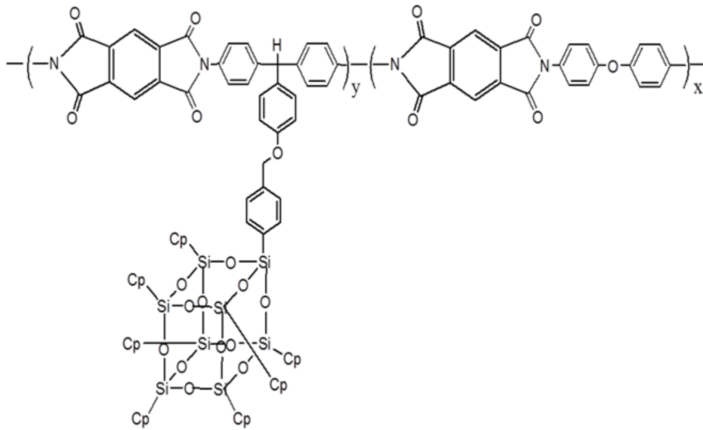

Figure 4. POSS/polyimide nanocomposites by grafted method

Another researcher studied about polyimide with grafted POSS structure. By introducing a polymerizable methyl methacryl functional groups to POSS and subsequent free-radical graft polymerization to an ozone treated polyimide, POSS grafted polyimide structures were obtained. Copolymers with dielectric constants approaching 2.2 could be achieved in the PI-*g*-PMA-POSS film containing 23.5 mol % MA-POSS. In this approach, POSS content could be easily tuned by the grafting ratio of MA-POSS.[33]

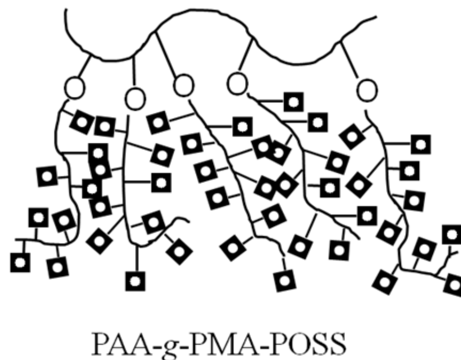

Figure 5. Synthesis of PI-*g*-PMA-POSS for low dielectrics

5.2.2. *Hyperbranched Polymer*

Hyperbranched polymers are densely branched structures with large number of reactive groups. They are polymerized from monomers with mixed reactivities, commonly denoted A2B or A3B monomers, thus giving branched structures with exponential growth, in both end-group functionalities and molecular weights.

One property often mentioned of hyperbranched polymers is the non-Newtonian relationship between viscosities and molecular weight, where hyperbranched polymers showed *low viscosities* at *high molecular weights.* For coating applications, this should be highly interesting in terms of microelectronics, where they may be used as an aid in critical patterning applications for **back**-**end**-of-line (BEOL) inter-level dielectric (**ILD**) materials.

Jitendra et al. showed that dense hyperbranched carbosiloxane (HBCSO) thin films have better mechanical properties than traditional organosilicates.[34] These materials are obtained by sol-gel processing of methane-bridged hyperbranched polycarbosilanes (HBPCSs), with the incorporated methane bridges being reminiscent of the systems described above (Figure 6). For example, Young's moduli of 17-22 GPa are obtained for films with dielectric constants ranging from 2.6 to 3.1. These materials have excellent electrical properties, breakdown voltages higher than 5 MV/ cm, and leakage currents <10^{-8} A/cm2 measured at 2 MV.

It was also shown that the HBPCS structure is of considerable importance in determining the properties of the thin films generated after sol-gel processing.

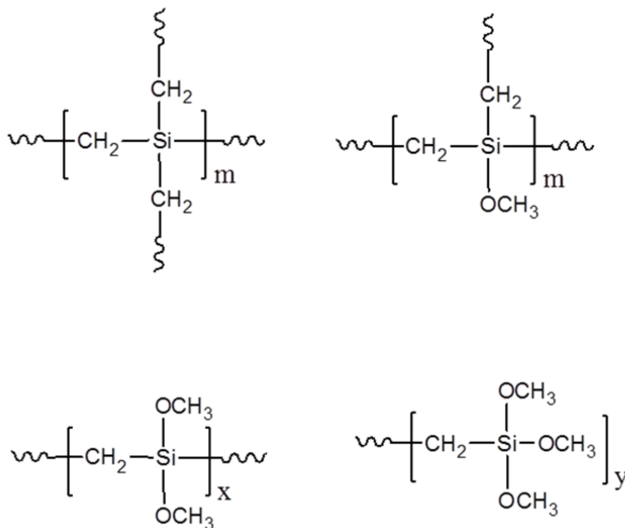

Figure 6. Chemical repeat units found in HBPCS precursors.

5.3. Network structure of low dielectric materials

In defining the different types of network structure materials for low dielectric constant applications in microelectronics, two classifications may exist. One is organic networks based on elemental carbon including amorphous carbon (diamond-like-carbon(DLC)) [35,36] and interpenetrating polymer network (IPN). The other is inorganic networks based on silicon oxide bonds such as amorphous SiO_2 and mesoporous crystalline silicon oxide.

Intuitively, network structures have excellent thermal stabilities and mechanical properties, and chemical resistance, but have relatively high density which is a factor in elevated dielectric constants. Because of this, dielectric constant and mechanical properties should be carefully controlled and careful consideration of its crystalline structure, as crystalline structures tend to be easily polarized.

5.3.1. Organic Network

When compared with linear structured polymers, network polymers have significant advantages in thermal stability with increasing glass transition temperature and complying CTEs. Dielectric materials for microelectronics needed to have high Tg temperature up to 400°C and endurance of repeated thermal cycling, creating the thermal mismatches which can lead to flow, delamination, adhesive failure, etc. Examples or organic network materials are discussed below.

5.3.1.1. Diamond-like carbon [DLC]

Amorphous diamond-like carbon [DLC], which can be prepared by chemical vapor deposition [CVD] method, [35,36] are metastable materials composed of sp2, sp3, and even sp1 hybridized carbon atoms with hydrogen concentrations, *CH*, ranging from 1% to 50%, with the composition being primarily determined by the nature of the precursor and the corresponding deposition conditions.

These sp^3 bonds can occur not only with crystals - in other words, in solids with long-range order - but also in amorphous solids where the atoms are in a random arrangement. In this case, there will only be bonding between a few individual atoms and not in a long-range order extending over a large number of atoms. The bond types have a considerable influence on the material properties of amorphous carbon films. If the sp^2 type is predominant the film will be softer, if the sp^3 type is predominant the film will be harder.

Under the right conditions, it is possible to deposit DLC films with compressive stress, spanning values from 200-800 MPa, and dielectric constants approaching 2.7.[36, 37]

5.3.1.2. SiLK and BCB resins

A very promising class of network polymers has been developed by Dow under the name 'Silk'. The formulations presumably consist of a mixture of monomeric and/or oligomeric

aromatic starting compounds, which contain ortho-bisethinyl or -phenylethinyl groups [38]. The materials exhibit k values on the order of 2.6-2.7, with decomposition temperatures in excess of 500°C, no softening up to 490°C, good gap fill properties down to below 0.1 um, a maximum water uptake of 0.25%, and a coefficient of thermal expansion 4s of 66 ppm/K.

Benzocyclobutene (BCB) resins were developed by Dow in the 1980's [39], with a silicon-containing derivative for microelectronics applications, and are commercially available under the name 'Cyclotene'. BCB resins with imide structures can be extremely tough, and the dielectric constant of cured films from this monomer is 2.6-2.7, with thermal stability up to 375°C and water adsorption of only 0.2% [40,42].

5.3.2. Inorganic network

Inorganic networks mainly consist of ceramics or amorphous silica. In various materials for microelectronics, the silicon oxides play a major role due to its low polarizability, superior thermal and mechanical properties. In addition, tunable microspores can be made to reduce the dielectric constant through control of microstructure under special conditions.

5.3.2.1. Ordered Mesoporous Materials

Microporous zeolite thin films were first investigated by Yan and co-workers. [43] These films offer good thermal stability (i.e. no pore collapse or unidirectional shrinkage) and inter-particle mechanical strength. They can be prepared via a simple spin-on method [43,44] or by in situ growth. [44,45] With simple spin-on methods a dispersion of small zeolite particles are prepared and cast onto a surface. The porosity originates from the interparticle porosity within the zeolite nanoparticles and the intra-particle porosity owing to the packing of the near-spherical nanoparticles in thin film format.

5.3.2.2. Network polysilsesquioxane

Some of the most promising materials for dielectric materials are poly(silsesquioxanes). Most common are polymethylsilsesquioxane (MSQ), e.g. Accuspin T-18 from Allied Signal [46], or poly(hydridosiLsesquioxane) (HSQ), e.g. FOx from Dow Corning [47]. Synthesis of these silsesquioxanes(MSQ and HSQ) have traditionally been through the sol-gel method, as its utility in being able to obtain highly cross-linked structures through acidic and or basic conditions has been well documented [48,49,50]. Dielectric constant values of around 2.6 can be achieved for HSQ and MSQ. But while MSQ exhibits this dielectric constant after curing at temperatures up to 450°C, HSQ must be cured at temperatures lower than 210°C [51]. Curing of HSQ at temperatures of 250°C or above results in dielectric constant around 3 or even higher 32°[51,52]. Gap fill and planarization properties are also acceptable and because of their chemical structure, which is closely related to SiO_2, polymethylsilsesquioxanes are also compatible with existing lithographic procedures.

Efforts to further decrease the dielectric constant without decreasing mechanical strength, POSS skeletons have been introduced in MSQ. To suppress the phase separation, incompletely condensed methyl functionalized POSS precursors have been used to form chemical bonds with oligomeric sol precursors. These incompletely condensed POSS moieties functioned as coupling agents while expanding the free volume of the final sol after curing which was accomplished to 4 GPa of modulus and 2.3 of dielectric constant. [53](figure 7).

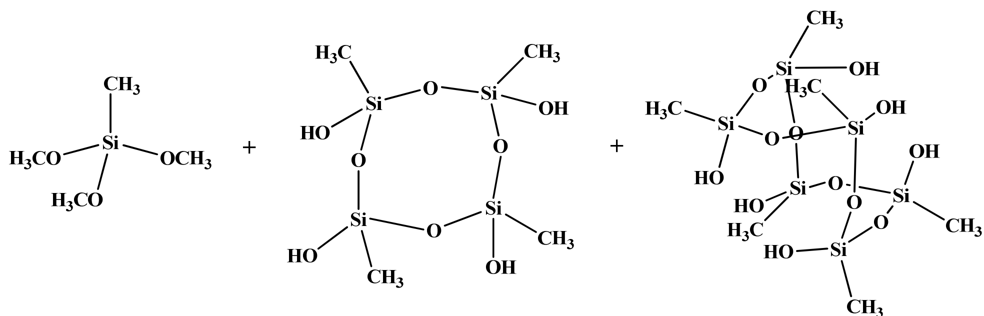

Figure 7. Introduction of POSS moiety by sol-gel method

5.4. Porous Network polymer by subtraction of porogen

Numerous methods of introducing subtractive porosity into spin-on deposited materials exist. Conventional methods of substractive porosity involve the addition of molecular or supramolecular particles called 'porogens' with tailored thermal stability to the dielectric precursor[54]. The stability of these particles is such that they are not affected by the coating drying step, and they are removed by pyrolysis during final film sintering or cure at temperatures typically in the range from 300 to 400 °C. An example of a material for which the pore size and porosity, or the pore size and porogen load can be controlled independently. [55] However, it should be noted that the use of porogens should only be applied to dense materials having a k less than 2.5 and modulus over 5 GPa in order for the final material to satisfy the required mechanical property.

In organic materials, the SilK matrix has been the only known material to provide the thermal and mechanical properties at temperature up to 500°C for use in combination with porogens. C.E. Mohler et al. [56] reported on porous SiLK dielectric film properties such as pore volume, porosity, size distribution, and showed a 2.2 dielectric constant at 30% load of porogens.

In comparison with organic porous dielectric material, inorganic porous dielectric materials have been more rigorously investigated because of their superior mechanical properties. Representative studies have used polymethylsilsesquioxane (PMSQ) as matrix for the

addition of various porogens such as the block copolymers, poly(styrerene-block-acrylic acid) [57], macromolecules of cyclodextrin [58], poly(caprolactone [59], and calix[4]arene [60].

Many of these studies with porogens have reported materials that have excellent mechanical and electrical properties, but lack in other practical aspects for application in microelectronics. When porogens are introduced into a matrix, critical problems may occur, such as thermal degradation products acting as a poison or contaminant within the matrix or interfacial adhesion problems. Therefore, use of porogens has yet to remain a difficult process for practical applications in microelectronics.

6. Conclusions

The search for materials with low dielectric constant in the microelectronics industry has and will continue feverishly into the future as the demand of faster processing speeds increases. Reduction of the dielectric constant of a material can be accomplished by selecting chemical bonds with low polarizability and introducing porosity. Integration of such materials into microelectronic circuits, however, poses a number of challenges, as the materials must meet strict requirements in terms of properties and reliability. The introduction of low-k materials in microelectronics research and development is a good example of how industrial needs drive new fundamental and applied research topics in science. Examples include pore structure characterization, deposition of thin films on porous substrates, mechanical properties of porous films, and conduction mechanisms in these materials. The substantial efforts made by materials and IC researchers to integrate the low-k films and continue historical device performance improvements have contributed to, and are still leading to, innovative fundamental and applied science.

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Acknowledgement

This work was financially supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea and Partially by a grant from Center for materials architecturing of Korea Institute of Science and Technology (KIST)

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