

Review of polymer materials with low dielectric constant

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Abstract

One of the exciting and promising developments in material science today is the design and synthesis of novel low-dielectric-constant polymer materials, which are found to have potential applications in the field of ultralarge-scale integration, capacitors and other electronic circuits as insulating and/or dielectric materials. In this article the new polymer dielectric materials reported in recent years are reviewed, including aromatic (heteroaromatic) polymers, silicon-containing polymers, fluorinated polymers, porous polymers, etc. In summarizing the review, the development, potential applications and future directions of polymer materials with low dielectric constant are discussed.

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Keywords: polymeric dielectric materials; low dielectric constant; ultralarge-scale integration; electronic circuits

INTRODUCTION

With the development of ultralarge-scale integrated circuits, the feature sizes of integrated circuits have decreased to about 180 nm or even smaller.^{1–3} Consequently, reduction in the electrical resistance induced by interaction between interconnect lines, time delay caused by wire capacitance, crosstalk and power dissipation have become bottleneck problems limiting the progress of high-speed, low power cost and multi-functional integrated circuits.^{4–6} For this reason, three major technological advances have been made in recent years to meet the ever increasing requirements for the electrical performance of on-chip wiring. First, copper has replaced aluminium as the new interconnect metal of choice, with the introduction of damascene processing. Second, simulations and optimizations of the effects of the dimensional sizes between layers and lines, technology and materials on the thermal and electrical properties have been made. Third, alternatives for SiO₂ with a lower dielectric constant (*k*) are being developed and introduced as the dielectric between layers and lines.^{7–11} However, besides a low dielectric constant, any materials used to replace SiO₂ as dielectrics must satisfy other requirements,^{12–16} which include: (1) high thermal stability, being stable at temperatures above 400 °C; (2) high mechanical strength; (3) low ionic concentration; (4) breakdown field above 2 MV cm^{−1}; (5) low moisture absorption; (6) ease of damascene processing or etching; (7) low thermal swelling coefficient or film stress; (8) good adhesion to various substrates; and (9) reactive inertness towards metals at high temperature. Among the broad variety of accessible alternatives, polymers have been some of the most widely studied materials due to their outstanding and promising mechanical and physicochemical properties. Advantage can be taken of the unique combination of excellent chemical inertness, good mechanical properties, thermal stability, electrical properties, safety, weather resistance, formability and easy shaping.

There are two main methods to obtain polymer materials with low dielectric constant. First, the atoms involved in preparing dielectric polymers can be chosen such as to decrease the molecular polarizability. The choice of precursor with atoms

that have appropriate electronegativity and bonding them in an appropriate configuration can reduce the molecular polarizability to low values; for example, incorporation of fluorine atoms in an Si–O backbone forming Si–F is a good approach to lower the dielectric constant of polymers. In addition, incorporation of more C–C building blocks with low polarizability in the polymer backbone can also decrease the dielectric constant. Second, it is clear from the polarization mechanism^{17,18} that lower density configurations of dielectric materials correspond to lower density of components that contribute to the molecular polarizability. Accordingly, another method that can be used to lower the dielectric constant is to lower the density of polymer films. One of the most attractive approaches to attain low-dielectric-constant polymers is to introduce free volume in the form of porosity. Since the dielectric constant of air is 1, introducing porosity^{19,20} to a low-*k* film can reduce the dielectric constant and the density of the film at the same time. Also, the degree of reduction is dependent on the percentage porosity of the film. Another important approach to obtain low-*k* polymers is incorporating space-occupying groups such as methyl, ethyl and phenyl to increase the free volume in the polymer structure.

In the following, an overview is given of molecular design, chemical structures, related properties and future development directions of polymeric dielectric materials.

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AROMATIC (HETEROAROMATIC) POLYMERIC DIELECTRIC MATERIALS

Polyimides

The main strategies used to lower dielectric constants in polyimides (PIs) are: (1) incorporating diamine and dianhydride reactants which minimize polarizability; (2) incorporating diamine and dianhydride reactants which impart a high degree of free volume; and (3) incorporating fluorine atoms into the molecular structures of PIs. Recently, Deligöz *et al.* developed a novel crosslinked PI, which is very promising for electrical applications, obtained by imidization of crosslinked poly(amic acid).²¹ The dielectric constant and dielectric loss of the novel crosslinked PI films were found to be frequency and temperature dependent. Also, they showed good thermal stability, excellent solvent resistance, low dielectric constant, low moisture absorption and stability in a variety of frequency regions. The molecular design and synthetic route of the crosslinked PIs is shown in Fig. 1.

To improve the processability of rigid aromatic polymers without loss of heat resistance, Behniafar and Habibian²² synthesized new thermally stable poly(ester-imide)s derived from 2,2'-bis(4-trimellitimidophenoxy)biphenyl, 2,2'-bis(4-trimellitimidophenoxy)-1,1'-binaphthyl and various aromatic dihydroxy compounds in the presence of pyridine and lithium chloride. The synthesized polymers showed good solubility in common organic solvents owing to the presence of the bulky and twisted biphenyl and binaphthyl units in the polymer backbone. Moreover, a new family of wholly aromatic poly(urea-ether-imide)s possessing binaphthylene twisted rings was prepared by diphenyl azidophosphate-activated one-pot polyaddition reaction of a pre-formed imide heterocyclic ring-containing dicarboxylic acid, 2,2'-bis(4-trimellitimidophenoxy)-1,1'-binaphthyl, with various kinds of aromatic diamines.²³ All of the resulting polymers exhibited excellent solubility in common polar solvents such as *N*-methyl-2-pyrrolidone, dimethylsulfoxide, *N,N*-dimethylformamide and *N,N*-dimethylacetamide. The polymers showed glass transition temperatures (T_g) in the range 274–302 °C depending on the structure of the aromatic diamine component, and increasing T_g corresponded to an increase in the rigidity and bulkiness of the diamine monomer moiety.

Polynitriles

Polynitriles synthesized by plasma polymerization are an emerging class of polymers for dielectrics due to their good adhesion to substrates, thermal stability and especially low dielectric constant after introduction of large occupying groups in their backbones. Zhao *et al.*²⁴ prepared plasma-polymerized 4-biphenylcarbonitrile (PPBPCN) thin films. A uniform and defect-free conjugated polynitrile thin film with a dielectric constant of about 2.5 was achieved when a low discharge power of 25 W was used during film formation. Measurements also show that the dielectric constant of PPBPCN thin films decreases with frequency and increases with temperature (Figs 2 and 3).

SiLK resin

SiLK resin contains neither fluorine nor silicon. It is highly aromatic, and it has an isotropic k with very high thermal stability. Thus, it is considered as a promising low- k material, and promises new levels of chip performance – faster, smaller devices with reduced crosstalk and power consumption. Tseng *et al.*²⁵ studied the dielectric anisotropy of SiLK films in an integrated Cu–SiLK system. The out-of-plane dielectric constant,

measured with a metal–insulator–metal structure, was 2.65; the in-plane dielectric constant, evaluated with a comb and serpentine interdigitated structure, was 2.75. An estimate of the gross dielectric constant was made on the basis of the in-plane and out-of-plane dielectric constants. The dielectric anisotropy of SiLK, –3.77%, is attributed to the molecular polarization and should fade away at high frequencies ($>10^{10}$ Hz). The low dielectric constant renders SiLK a good candidate to replace SiO₂ for low-dielectric-constant materials. However, copper passivated with SiLK exhibits larger leakage current, higher thermal impedance and shorter electromigration lifetime than when passivated with SiO₂. Hence, there is a reliability concern for the integrated Cu–SiLK system.

To improve the adhesion of SiLK resin to underlying and top layers, the influence of plasma treatment on SiLK films has been studied. The density of the SiLK films does not change significantly under various plasma treatments such as O₂, H₂/N₂, O₂/N₂, CH₂F₂/Ar₂ and CF₄/O₂. However, the surface and the interface between SiLK resin and transition layer become rougher due to the treatments, accompanied also by a thickness decrease. Such roughening is more severe for oxygen plasma treatment. Hence, it is reasonable to conclude that oxidation of the surface plays a major role in surface roughness change.²⁶ Gonda *et al.* measured the viscoelastic properties for modeling the thermomechanical behavior of thin films of SiLK resin for microelectronic applications using nanoindentation and substrate curvature techniques.²⁷ The films showed nonlinear stress versus temperature curves under the conditions of a constant Poisson's ratio of 0.4 and constant coefficient of thermal expansion of 60 ppm K^{–1}.

Benzocyclobutene resins

Benzocyclobutene (BCB) resins, developed by Dow Company, are a promising class of materials for dielectrics. The BCB group (**1**) is a tautomer of the *ortho*-xylylidene group (**2**), the actual reactive species in BCB resins during curing. This group can undergo a variety of reactions, including Diels–Alder cycloaddition reactions and free radical addition or combination; in addition, no low-molecular-weight byproduct will be formed during the reactions.²⁸ The *ortho*-xylylidene structure **2** has a biradical character **3** to a considerable extent. Figure 4 shows the mesomeric structures of the BCB group and Fig. 5 shows the reactions of BCB.

The curing of BCB can be performed at 250 °C for 10 min, and it requires an inert atmosphere. Ouaknine *et al.* have developed a new approach for low-temperature curing and annealing of BCB using rapid thermal processing.²⁹ The properties of the BCB resins can be adjusted by variation of the chemical structure to a wide extent. By introducing organo-silane groups into the chemical structure, the properties of BCB can be enhanced greatly. Furthermore, fully cured BCB films are highly resistant to most chemicals, which make them difficult to remove. Once a film has been completely cured, plasma etching is usually the only viable means of removing it.³⁰ A piranha bath (H₂O₂/H₂SO₄) or fuming nitric acid bath will remove fully cured BCB, but metals and underlying device structures will generally not tolerate this aggressive cleaning agent, so this is only useful for test wafers.

Poly(binaphthylene ether) and polydiphenyl

Tsuchiya *et al.*³¹ synthesized a thermally stable polymer with a low dielectric constant using oxidative coupling polymerization of 2,2'-bis(1-naphthoxy)-1,1'-binaphthyl with FeCl₃ as an oxidant. Figure 6 shows the synthetic route to poly(binaphthylene ether). The dielectric constant of the obtained poly(binaphthylene ether)

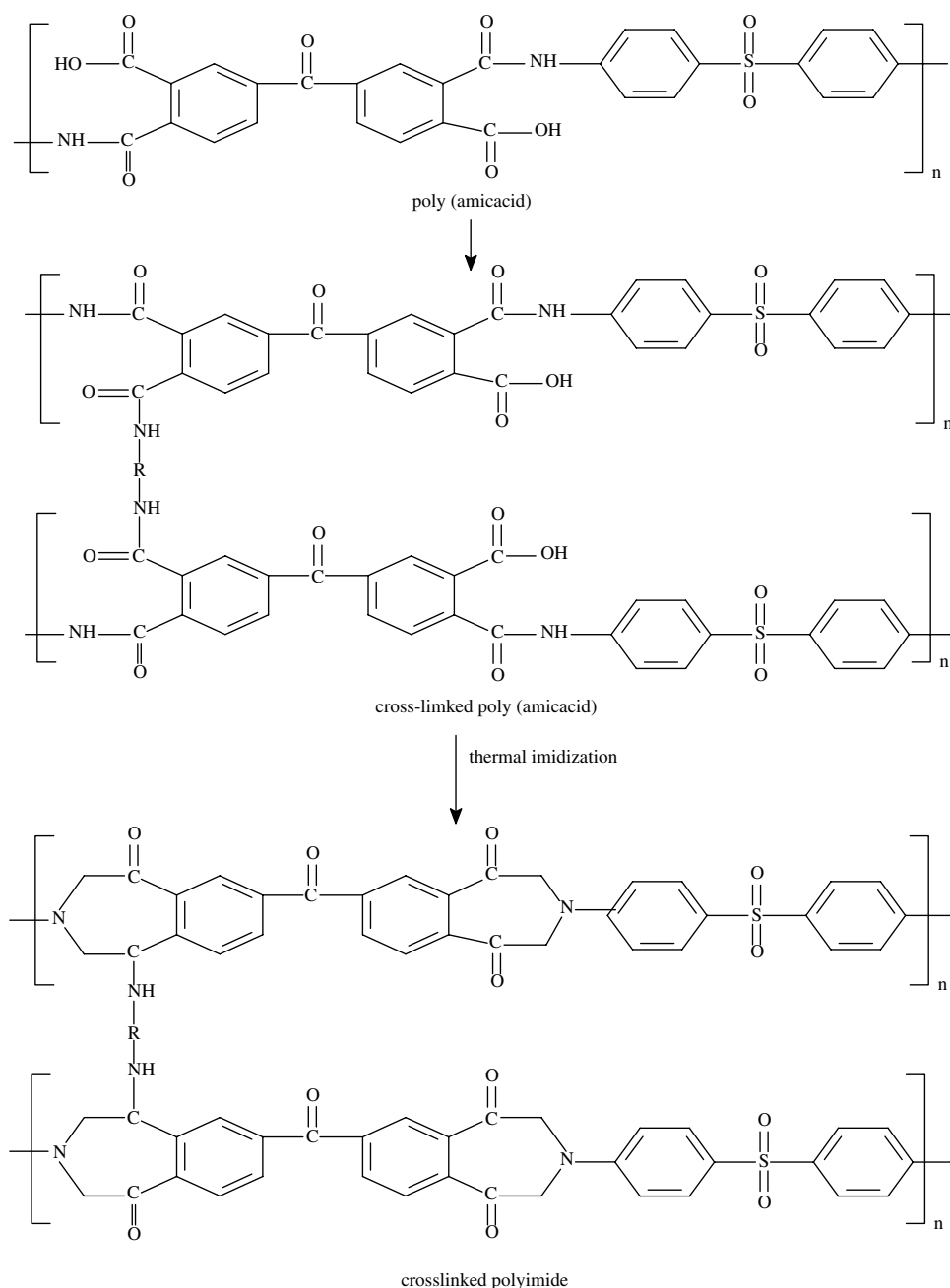


Figure 1. Synthesis route of crosslinked PI.

at 1 MHz was directly measured from the capacitance as 2.50, and the modulus and hardness of it were determined as 9.8 and 0.42 GPa, respectively.

A novel thermally stable and low-dielectric poly(2-naphthol) containing an adamantyl unit has been developed.³² It was easily prepared by oxidative coupling polymerization of (1,3-adamantyl)bis(2-naphthol) with CuCl(OH)tetramethylethylenediamine as a catalyst. The polymerization produced a region-controlled polymer with a number-average molecular weight of 10 500 Da and a molecular weight distribution of 4.1. The 5% weight loss temperature of the polymer was 480 °C and no glass transition temperature was observed. The dielectric constants of the polymer estimated from the refractive index and capacitance were 2.92 and 2.96, respectively.

Polyquinolines

Polyquinolines, which are non-polar, often exhibit very high thermal stabilities with decomposition temperatures up to 600 °C even in air. Thus by incorporating functionalized quinoline rings into polymer backbones, desired polymers with high performance can be obtained.

Recently, Zhao *et al.*³³ have prepared high-quality, low-dielectric-constant, plasma-polymerized 1-cyanoisoquinoline (PP-CIQ) thin film with a roughness of 0.53 nm by the plasma polymerization technique using 1-cyanoisoquinoline as precursor. PPCIQ thin film deposited at 15 W gives a low dielectric constant of 2.62, probably resulting from a reduction of the density of the film due to the higher retention of the aromatic rings (space-occupying groups), which might be a potential candidate

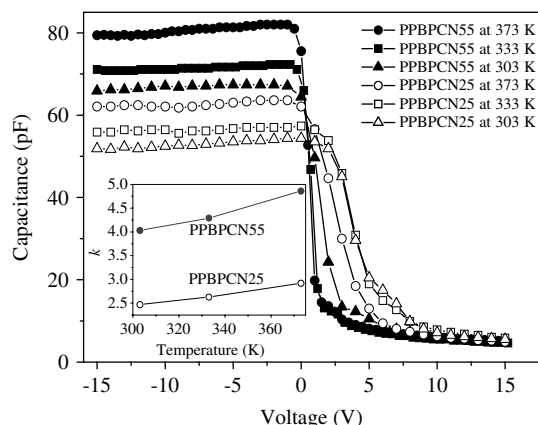


Figure 2. Capacitance–voltage curves of PPBPCN thin films measured at 1 MHz at various temperatures. Inset: effect of measured temperature on dielectric constant of PPBPCN thin films.

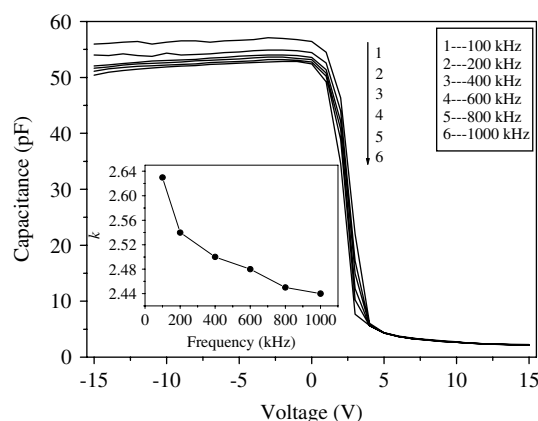


Figure 3. Capacitance–voltage curves of PPBPCN thin films measured at 298 K. Inset: variation of dielectric constant of PPBPCN thin film as a function of measured frequency.

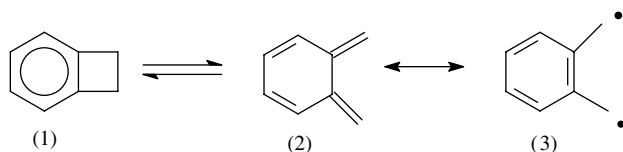


Figure 4. Mesomeric structures of the BCB group.

for use as in intermetallic dielectrics in microelectronics. Furthermore, the variation of dielectric constant with frequency in the range from 100 kHz to 1 MHz and the variation of the dielectric loss factor ($\tan \delta$) as a function of frequency were also investigated, and the corresponding results are shown in Figs 7 and 8, respectively. From the results, it is clear that, in the frequency range mentioned above, there is an increase in dielectric constant with a decrease in frequency while the dielectric loss factor increases with an increase in frequency.

Polynorbornenes

Vinyl polynorbornene (PNB) has good physical characteristics, such as high thermal stability, high glass transition temperature, low moisture absorption and low dielectric constant (2.2), which make it attractive for electronic applications. However, its poor solubility

in common organic solvents, mechanical brittleness and poor adhesion property present serious drawbacks in terms of potential applications. Thus, many efforts have been made to overcome these shortcomings while maintaining the thermal stability and other useful properties.

In recent years, much work has been done on the copolymerization of norbornene with α -olefins and/or by incorporation of functional pendant groups into the polycyclic backbone. The latter has attracted much attention for it can provide a versatile way to optimize the properties of the resulting polymers by incorporating various pendant substituents. Many kinds of functional groups have been introduced in PNB as pendant chains, such as alkoxysilyl, alkyl and ester groups, substantially enhancing the adhesion to surfaces, elongation-at-break and solubility in common organic solvents to some extent. However, these modifiers have a tendency to degrade the thermal stability and dielectric properties. To balance these properties, Liu *et al.*³⁴ have prepared a set of functionalized PNBs with various substituted pendant imide groups (*N*-substituted imide groups were adamantyl, cyclohexyl, tolyl and phenyl) via a vinylic pathway using di-*L*-chloro-bis(6-methoxybicyclo[2.2.1]hept-2-ene-endo-5*r*,2*p*)-palladium catalyst as a means of developing materials of low dielectric constant which exhibit good thermal stability, better than that of unsubstituted PNB, and are characterized by low k values between 2.26 and 2.53. The bulky adamantyl moieties in the side chain of the polymer are favorable to achieve low k values. The glass transition temperature was determined as 257.3, 276.2 and 320.6 °C for polyphenyl-*N*-substituted-exo-norbornene-5,6-dicarboximides, polycyclohexyl-*N*-substituted-exo-norbornene-5,6-dicarboximides and polytolyl-*N*-substituted-exo-norbornene-5,6-dicarboximides, respectively. At the same time, all of the polynadimides obtained were highly soluble in chloroform.

SILICON-CONTAINING POLYMERIC DIELECTRIC MATERIALS

Polysilsesquioxanes, with a formula of $(\text{RSiO}_{3/2})_n$, where R can represent hydrogen, alkyl, aryl or other organic groups with functional derivatives, have been extensively studied because of their outstanding thermal, chemical, mechanical and electronic properties. Applications of silsesquioxane-related materials as types of dielectric materials, additives and pre-ceramics have been demonstrated recently. Poly(hydrogen silsesquioxane) (PHSSQ) and polymethylsilsesquioxane (PMSSQ) have been recognized as low-dielectric-constant materials for deep submicrometer integrated circuit processes.^{35–37} The chemical structures of PHSSQ and PMSSQ contain both Si–O–Si cages and network structures. The physical properties of PHSSQ and PMSSQ, such as the refractive index and dielectric constant, can be varied through the ratio of the cage to the network structure by varying the curing process including a curing atmosphere of nitrogen and of air. It is reported that the cage/network ratio of prepared PHSSQ films decreased with increasing curing temperatures, resulting in an increase of refractive index or dielectric constant.³⁸ In addition, various post-treatments, such as thermal oxygen, thermal N_2O and oxygen plasma, carried out on a cured PMSSQ film can modify the physical properties, thermal stability and dielectric constant of the film.³⁹

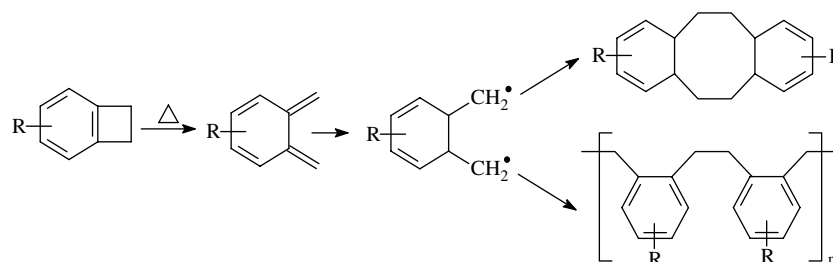


Figure 5. Synthesis reactions of BCB.

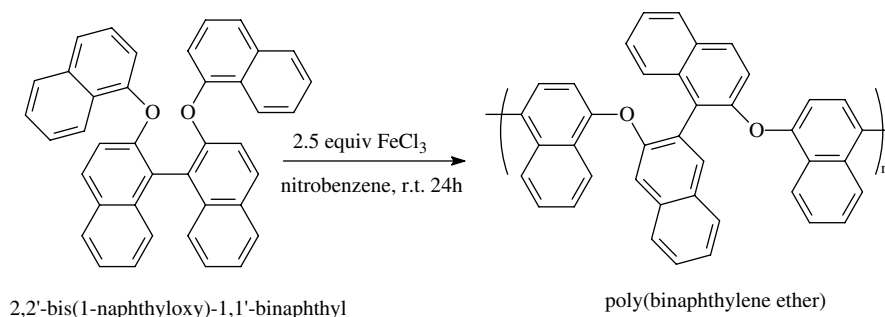


Figure 6. Synthetic route of poly(binaphthylene ether).

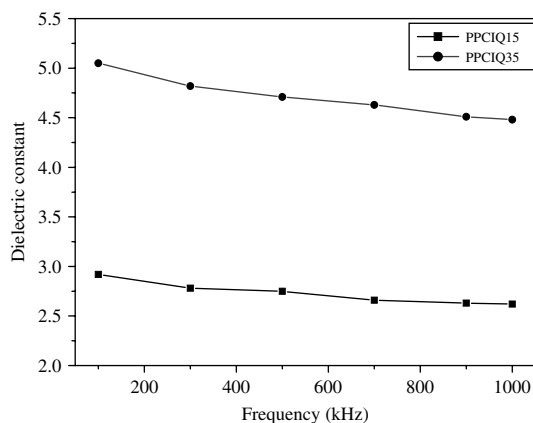


Figure 7. Variation of dielectric constant of PPCIQ thin films as a function of frequency.

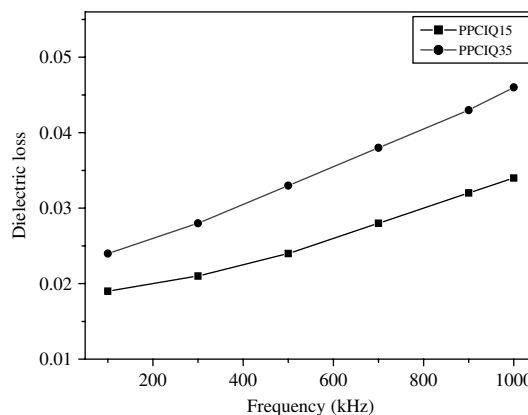


Figure 8. Dielectric loss factor ($\tan \delta$) of PPCIQ thin films as a function of frequency.

FLUORINATED POLYMERS

It is well known that the incorporation of fluorinated substituents into polymers decreases the dielectric constant due to the small dipole and the low polarizability of the C–F bond. At the same time, an additional positive effect of reduced moisture absorption due to the non-polar character of fluorocarbon groups can be achieved. Thus, fluoropolymers are attractive in the development of dielectric materials with high thermal and oxidative stability, chemical resistance and low moisture absorption.

Fluorinated polyimides

Fluorination is one of the methods used to decrease the dielectric constants of PIs. The incorporation of fluorine increases in the fractional free volume of PIs, and the electronic polarizability of the fluorinated PIs decreases due to the low polarizability of the fluorine atom. The dielectric constant is strongly influenced by the fluorine content; the dielectric constant decreases as

the fluorine content increases. This can be attributed to the following three effects: changes in hydrophobicity; changes in free volume; and changes in total polarizability. The most common method to obtain fluorinated PIs is via the reaction of fluorinated diamines and fluorinated dianhydrides. Figures 9 and 10 show examples of molecular design and synthetic routes of novel fluorinated monomers.^{40–42} Table 1 gives the properties of novel fluorinated PIs.

The high thermal stability combined with chemical resistance and excellent electrical and mechanical properties of fluorinated PIs make them attractive as versatile high-performance materials for electrics. However, most of them encounter processing difficulties because of their low solubility⁴³ in common organic solvents and high melting or softening temperatures, which limit some of their applications. To extend the utility of PIs, much effort has been devoted to making processable PIs based on new dianhydrides and diamines with the purpose of obtaining certain advantageous properties. Solubilization of PIs has been targeted

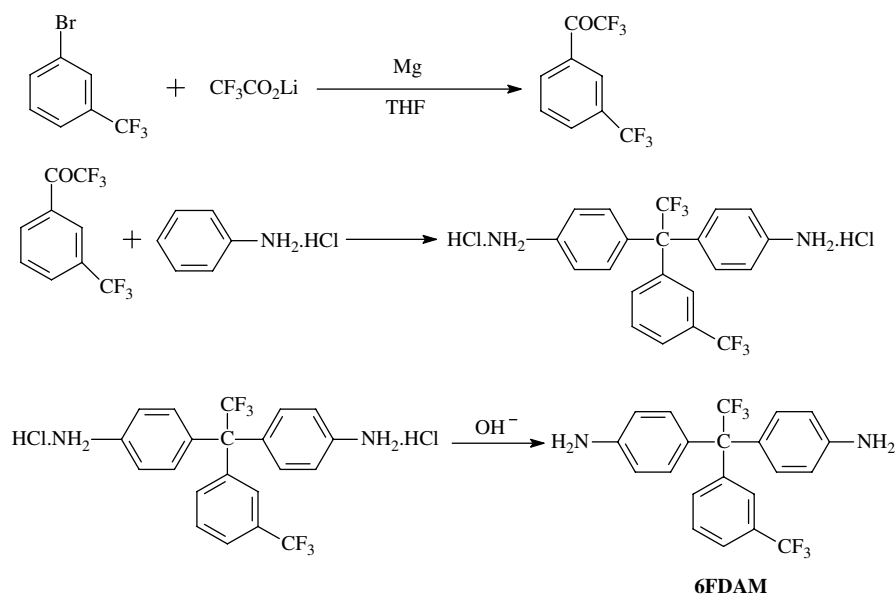


Figure 9. Synthetic route of 1,10-bis(4-aminophenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FDAM). (THF: tetrahydrofuran).

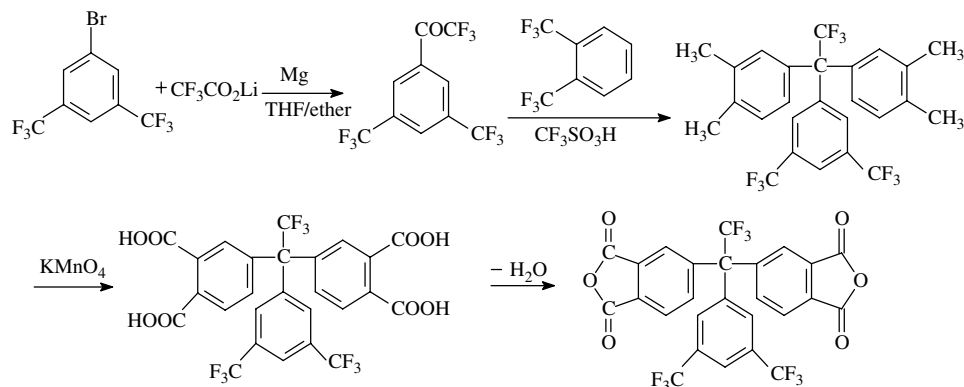


Figure 10. Synthetic route of 4,4'-[2,2,2-trifluoro-1-(3,5-difluoromethylphenyl)ethyldiene] diphthalic anhydride (9FDA). (THF: tetrahydrofuran).

by several means, such as the introduction of flexible linkages, bulky substituents and bulky units within the polymer backbone and the use of non-coplanar or alicyclic monomers. The main concept behind all these approaches is the reduction of several types of polymer chain–chain interactions, of chain packing and of charge transfer electronic polarization interactions.

Since surface modification of PIs by the use of ion beams and plasma treatment is considerably important in both technology and science, fluorination treatment on the surface of PIs has been utilized successfully to improve the dielectric properties of PI films. During the fluorination treatment, fluorine diffuses only slightly and slowly into the PI and then the diffusing fluorine atoms produce active radicals from the hydrocarbon backbone during the reaction time because of the highly electronegative character of fluorine atoms. The active radicals lead to the introduction of strong C–F covalent bonds in PI thin films.⁴⁴ The influence of atmospheric-pressure CHF₃/Ar plasma treatment on the surface dielectric properties of PI films at room temperature has been studied, and it was found that the fluorine-containing surface functional groups of the treated PI were increased with increased treatment time. Meanwhile, the fluorine groups led to a decrease of the surface free energy and dielectric constant of the PI films,

which can largely be attributed to the decrease of the deformation polarizability.⁴⁵

Fluorinated epoxy resins

Epoxy resins have been used as insulation materials for electric devices due to their good balance of properties such as excellent moisture, solvent and chemical resistance, low shrinkage after cure, superior electrical and mechanical properties and good adhesion to many substrates. In recent years, epoxy resins have found wide application in electronic packaging as epoxy molding compounds, electrically conductive silver pastes, die attach adhesives, etc.

To meet the requirements of advanced electronic packaging, much attention has been focused on developing novel epoxy resins with improved electrical insulating properties as well as enhanced thermal properties. As fluorination has become one of the most popular methods to decrease the dielectric constant of epoxy resins, increasing research has been concentrated on the investigation of fluorinated epoxy resins. Tao *et al.* synthesized a novel fluorinated epoxy resin using a four-step procedure.⁴⁶ The properties and the chemical structures as well as curing agents are given in Tables 2 and 3.

Table 1. Properties of fluorinated polyimides

Property	PMDA-6FDAM	6FDA-6FDAM	BTDA-6FDAM	ODPA-6FDAM	PMDA-ODA	9FDA-4,4'-ODA	9FDA-APB	9FDA-3,4'-ODA	9FDA-9FAPB
T_g (°C)	282	261	238	242	–	283.6	259.5	257.7	245.8
T_d (°C)	569	530	524	526	–	571.8	582.0	566.2	570.4
T_5 (°C)	547	543	535	536	–	536.8	546.4	536.4	546.2
T_{10} (°C)	583	562	563	562	–	562.5	578.2	563.4	573.5
D_s (kV mm ⁻¹)	92	122.6	98.6	110	178				
D_s^* (kV mm ⁻¹)	90.5	121.8	96.0	107.4	170				
ρ_v (Ω cm)	9.8×10^{15}	1.05×10^{16}	1.9×10^{15}	7.8×10^{15}	9.2×10^{15}	4.04×10^{15}	7.86×10^{16}	4.08×10^{16}	1.59×10^{17}
ρ_s (Ω)	4.18×10^{14}	6.71×10^{14}	1.23×10^{14}	3.85×10^{14}	5.6×10^{14}	4.08×10^{17}	3.26×10^{15}	4.57×10^{17}	1.39×10^{17}
ϵ_r	2.95	2.71	2.91	2.89	3.25	2.89	2.97	2.88	2.71
Tan δ	3.5×10^{-3}	2.8×10^{-3}	3.1×10^{-3}	2.9×10^{-3}	4.5×10^{-3}	1.4×10^{-3}	2.2×10^{-3}	1.3×10^{-3}	2.8×10^{-3}
λ_{cut} (nm)	375	330	360	340	420	357	343	336	330
T (%)	5	61	18	45	0				
Wa (%)	0.95	0.42	0.84	0.52	2.65	0.35	0.18	0.40	0.14
Elongation-at-break (%)	9.5	10.3	10.8	11.0	24.1	5	6.8	7.6	7.8
Tensile strength (MPa)	105	87.6	78.1	117	123	87.7	87.8	102.7	99.5
Young's modulus (GPa)	1.12	0.85	0.72	0.63	1.50	3.02	2.56	2.73	2.79

T_d : onset decomposition temperature; T_5 , T_{10} : decomposition temperatures at 5 and 10% weight loss, respectively; D_s : dielectric strength; D_s^* : dielectric strength after boiling in water for 6 h; ρ_v : volume resistivity; ρ_s : surface resistivity; ϵ_r : dielectric constant at 1 MHz, 25 °C; tan δ : dissipation factor; λ_{cut} : cutoff wavelength in UV-visible spectra; T : transparency of films at 400 nm; Wa: water adsorption; PMDA: pyromellitic dianhydride; 6FDA: 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane; BTDA: 3,3',4,4'-benzophenonetetracarboxylic dianhydride; ODPA: 4,4'-oxydiphthalic anhydride; ODA: 4,4'-oxydianiline.

Table 2. Properties of fluorinated epoxy resins

Property	BGTF-HMDA	BGTF-DDM	BADGE-HMDA	BADGE-DDM
T_g (°C)	175	170	164	187
R_W (%)	11.3	47.3	13.0	26.9
T_5 (°C)	382	370	380	374
T_{10} (°C)	402	395	399	395
ρ_v (Ω cm)	3.6×10^{16}	1.2×10^{16}	1.9×10^{16}	2.7×10^{16}
ρ_s (Ω)	2.2×10^{16}	2.8×10^{16}	4.9×10^{16}	4.5×10^{16}
ϵ_r	3.3	3.2	3.5	3.6
Tan δ	2.8×10^{-3}	2.1×10^{-3}	7.3×10^{-3}	6.9×10^{-3}
λ_{cut} (nm)	375	330	360	340
Flexural strength (MPa)	123	88	128	101
Flexural modulus (GPa)	2.88	2.79	2.67	2.17
Tensile strength (MPa)	76	56	65	53
Tensile modulus (GPa)	1.70	1.55	1.82	1.92

T_5 , T_{10} : decomposition temperatures at 5 and 10% weight loss, respectively; ρ_v : volume resistivity; ρ_s : surface resistivity; ϵ_r : dielectric constant at 1 MHz, 25 °C; tan δ : dissipation factor; λ_{cut} : cutoff wavelength in UV-visible spectra.

of over 1 GHz. A material with large tan δ creates an AC leakage current, which converts the dipole motion into heating of the material. Tsuchiya *et al.*⁴⁷ prepared a novel poly(binaphthylene ether) containing trifluoromethyl groups with low dielectric constant through oxidative coupling polymerization using 2,2'-bis(1-naphthoxy)-1,1'-binaphthyl as monomer and FeCl₃ as an oxidant. The polymer showed high thermal stability, good film processability, low refractive index of 1.582, low dielectric constant of 2.70 and low tan δ of 0.0025 at 20 GHz, all of which make it a good insulating material for future generations of microchips.

POROUS POLYMERS

Since few existing materials have dielectric constants less than 2.0, the strategy of incorporation of voids into dielectric materials has emerged as a leading approach for the reduction of dielectric constants. One practical technique is the introduction of nanometer-sized pores imposed by device minimum features into bulk materials. Pore size and distribution are crucial properties of porous dielectrics. The maximum pore size must be sufficiently smaller than the minimum feature size of device components. These materials are sometimes prepared through plasma-enhanced chemical vapor deposition (PECVD), mostly with a curing treatment, such as UV curing, thermal curing or UV-O₃ curing, being introduced. The structure and mechanical and electrical properties will change with a change of the treatment.^{48–53}

Fluorinated poly(binaphthylene ether)

Recently, high-temperature low- k materials with low dissipation factor (tan δ) have been in demand because of the rapid expansion into the market of electric devices that drive at a high frequency

Porous polyimides

Porous PIs with a low dielectric constant can be prepared using a templating method which relies on an organic group

Table 3. Chemical structures of epoxies and curing agents

Component	Abbreviation	Chemical structure
Epoxy	BGTF	
	BADGE	
Curing agent	HMPA	
	DDM	

occupying space until calcining, chemical oxidation, chemical rearrangements or hydrolysis eliminate the template. The pores remaining in the films are of size and shape roughly corresponding to those of the organic molecule. Nanoporous PI films prepared through the use of a hybrid poly(ethylene oxide) (PEO)–polyhedral oligomeric silsesquioxane (POSS) template and common PI derived from pyromellitic dianhydride and oxydianiline as polymer matrix have been reported.⁵⁴ Incorporation of oligomeric PEO chains into the silsesquioxane core significantly reduced PEO–POSS self-aggregation and enhanced its solubility in the poly(amic acid) matrix prior to imidization. Significant reductions in dielectric constant (from $k = 3.25$ to 2.25) for porous PI hybrid films with pore sizes in the range 10–40 nm have been achieved. These porous materials exhibit high thermal stability and good mechanical strength, and are promising candidates for use as next-generation low- k materials. A summary of the properties of PI nanoporous materials is given in Table 4.

Porous silicon-containing polymeric materials

Silsesquioxane films with low dielectric constant have been successfully synthesized by covalently binding a thermally decomposable porogen (polyamidoamine, PAMAM) to a host polymer (hydrogen methylsilsesquioxane) via a coupling agent.⁵⁵ PAMAM degraded more effectively in air than in nitrogen. A dielectric constant of about 2.06 was obtained with a pore size of less than 10 nm for a film with 20 wt% loading of the sacrificial polymer.

Meanwhile, low-dielectric-constant nanoporous PMSSQ prepared through the templating of an amphiphilic block copolymer, poly[styrene-*block*-(2-vinylpyridine)] (PS-*block*-P2VP), has been investigated.⁵⁶ Strong intermolecular hydrogen bonding occurs in the PMSSQ/PS-*block*-P2VP hybrid, preventing macrophase separation in the hybrid. The miscible hybrid and the narrow thermal decomposition of the PS-*block*-P2VP lead to uniform nanopores in the prepared films. Uniform pore morphology can be obtained from a modest porogen loading level. The refractive index and dielectric constant of the prepared nanoporous films could be tuned, by altering the loading ratio, to be in the ranges 1.361–1.139 and 2.359–1.509, respectively. Table 5 gives more detailed information on the nanoporous PMSSQ film properties. For each group, the

dielectric constant decreases with an increase of the templating material (PS-*block*-P2VP).

In order to improve the mechanical strength of porous low- k films prepared using a sol–gel method based on the self-organization of surfactant templates, Kohmura *et al.* developed a new 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) vapor annealing method. TMCTS molecules react with Si–OH groups on pore wall surfaces to form a polymer network which results in high hydrophobicity and reinforcement of the silica wall. This method can be used to recover plasma damages induced by etching and ashing in fabricating Cu/low- k interconnects.⁵⁷

Porous poly(vinylidene fluoride)

Poly(vinylidene fluoride), a technologically important polymer for its good mechanical strength, resistance to solvents, acids, bases and heat, and low smoke generation during fire events, shows a dielectric constant between 7 and 13 at room temperature at a measuring frequency of 1000 Hz which originates from the strong C–F dipoles.⁵⁸ In order to reduce the dielectric constant to below 2.0 for interlayer applications, Zhu *et al.*⁵⁹ successfully prepared porous low-dielectric-constant ($k = 1.5$ –2.5) poly(vinylidene fluoride) film, which possessed two compact surface layers and 0.5–1.5 μm internal cell structure, using a phase transformation technique.

OTHER POLYMERIC MATERIALS WITH LOW DIELECTRIC CONSTANT

Fabrication of organic–inorganic hybrid polymer thin films deposited by PECVD^{60–62} is another approach to low-dielectric-constant materials with favorable integrative properties. Bae *et al.*⁶² deposited hybrid films at radiofrequency power in the range 20–180 W by the PECVD method using organic precursors such as thiophene and tetraethoxysilane (TEOS) monomers. The dielectric constant obtained from the as-grown polymerized hybrid films was about 2.26 at a discharge power of 20 W. Lower refractive index and dielectric constant could be obtained at lower deposition power and annealing temperature due to decreased C–H and C–C bonding or increased Si–O structure in the films. Also, the as-grown transparent hybrid films had a higher crosslinking density

Table 4. Summary of properties of polyimide nanoporous materials

Sample	PEO-POSS in feed (wt%)	PEO-POSS in feed (mol%)	Softening temperature (°C)	5% weight loss temperature in air (°C)	Char yield in air (wt%)	Dielectric constant, <i>k</i>	Measured density (g cm ⁻³)
PI-0P	0	0	370	581	0	3.25	1.38
PI-2P	2	0.0007	368	578	0	2.88	1.31
PI-5P	5	0.0017	366	565	3	2.43	1.18
PI-10P	10	0.0034	360	558	5	2.25	1.09

Table 5. Properties of prepared nanoporous PMSSQ films: P1, P2 and P3^a

Sample ^b	Loading (%)	Film thickness (Å)	<i>R_q</i> (nm) ^c	<i>n^d</i>	<i>k</i>	Δ <i>p</i> (%) ^e
PMSSQ	0	1788	0.294	1.361	2.359	0
P1-10	10	2178	0.755	1.347	2.267	3.5
P1-20	20	2512	0.888	1.313	2.138	12.2
P1-30	30	2824	1.210	1.284	2.039	19.7
P1-40	40	2891	0.900	1.238	1.843	31.9
P1-50	50	2941	1.481	1.179	1.715	48.0
P1-60	60	3045	1.471	1.139	1.506	59.3
P2-10	10	2866	0.661	1.339	2.341	5.6
P2-20	20	2901	0.611	1.314	2.182	12.0
P2-30	30	3376	0.864	1.294	1.988	17
P2-40	40	3351	0.685	1.242	1.981	30.7
P2-50	50	4145	0.744	1.217	1.758	37.6
P2-60	60	4119	1.073	1.154	1.603	54.9
P3-10	10	2954	0.346	1.328	2.269	8.3
P3-20	20	3196	0.439	1.301	2.170	15.3
P3-30	30	3886	0.436	1.279	2.111	21.0
P3-40	40	3735	0.621	1.222	2.084	36.2
P3-50	50	4073	0.656	1.207	1.810	40.3
P3-60	60	4332	0.633	1.141	1.527	58.7

^a P1, P2 and P3 are nanoporous PMSSQ thin films formed through templating of PS-*block*-P2VP I, II, and III respectively.

^b The number following P1, P2 or P3 is the weight percentage of PS-*block*-P2VP loading.

^c Root mean square roughness which shows the surface roughness of the material from AFM measurements.

^d Refractive index.

^e Porosity of nanoporous PMSSQ film relative to that of the parent PMSSQ thin film.

with increasing radiofrequency power. Organic–inorganic hybrid polymer thin films deposited on silicon substrates were also reported by Cho *et al.*⁶¹ using ethylcyclohexane and TEOS as precursors. The resulting films show a low dielectric constant of 1.83, with a leakage current density of 8–10 A cm⁻² at 1 MV cm⁻¹. The values of hardness and Young's modulus increased with an increase of TEOS bubbling ratio.

Low-*k* organic–inorganic hybrid dielectric films, based on a poly(methyl methacrylate)–poly(vinyl chloride) (PMMA–PVC) blend and silica powder functionalized on the surface with methylsiloxane groups (m-SiO₂), have also been prepared.⁶³ By dispersing m-SiO₂ into a [(PMMA)_{*x*}(PVC)_{*y*}] (*x*/*y* = 50/50 wt%) polymer blend, six [(PMMA)_{*x*}(PVC)_{*y*}]/(m-SiO₂)_{*z*} hybrid inorganic–organic materials were obtained, with *z* ranging from 0 to 38.3 wt% and *x* = *y* = (100 – *z*)/2. Transparent, homogeneous, crack-free films

were obtained using a solvent casting process from a tetrahydrofuran solution. The combination of m-SiO₂ oxoclusters with the [(PMMA)_{*x*}(PVC)_{*y*}] polymer blend yielded low-*k* composite films with acceptable electrical dispersion up to 1 MHz. In fact, films with 20 ≤ *z* ≤ 35 wt% had a *k* value lower than that of SiO₂ (*k* = 3.9) and tan δ < 0.05.

CONCLUSIONS

As we peer into the future requirements for dielectric materials, the challenges for polymer dielectric materials are definitely there, the focus being towards the synthesis of polymer dielectric materials suitable for fabricating transistors, capacitors and other devices on chips. Not only is the dielectric constant becoming smaller, but also the perfection requirements for polymer dielectric materials are becoming extremely rigorous. However, among all the polymer dielectric materials mentioned above, few have been found to satisfy all the requirements for modern integrated circuits because of various disadvantages. For example, most PIs cannot reach the demands for a *k* value between 2.9 and 3.5; some show a *k* value of 2.5, while *T_g* is always below 250 °C. Fluorinated polymers have inadequate thermal stability for use in current integration procedures. There are concerns for fluorine evolution at high temperatures, with the potentially resulting corrosion problems in microchips being considered too severe. The porous polymer dielectric materials also have many problems to be resolved, such as poor thermal conductivity and loss of inner structure which leads to undesired strength properties. Thus, there is much to do to overcome some of the limitations, and new approaches for overcoming these drawbacks and for improving the performance of low-dielectric-constant polymers have raised vital interest in researchers.

Based on the low-*k* polymer dielectric materials described in the literature so far, their future development will mainly focus on the following three areas. First, the search for more suitable polymer dielectric material with a dielectric constant *k* < 2.5 (for future chip generations, *k* will need to be less than 2.0) continues with unrelenting urgency, as the advancement of integration density appears to accelerate. Second, there is a need to improve their thermal stability. As reported, a high-temperature annealing at 400–450 °C is necessary to ensure void-free copper deposits during copper metallization; thus, polymer dielectric materials must be able to withstand these temperatures for several hours, and during this period, outgassing, shrinking, crack formation or any other damage must be avoided completely. Third, it is necessary to improve the adhesion of polymers to underlying and top layers, especially for the fluorocarbon polymer dielectric materials which exhibit only weak polymer–metal adhesion due to their low surface energy. Several approaches are used to improve

adhesion strength. Roughening of the surface leads to a larger surface for bonding and offers the opportunity for interlocking. Chemical bonding instead of physical interactions improves the adhesion strongly, but is difficult to achieve. In some cases, an adhesion promoter like γ -aminopropyltriethoxysilane is first deposited as a self-assembled monolayer on the metal surface before the deposition of the polymer layer takes place. However, it often remains unclear whether the adhesion of the polymer will withstand the manufacturing conditions, even if the material is described to exhibit good adhesion properties.

ACKNOWLEDGEMENTS

The project was sponsored by the Scientific Research Key Foundation for Returned Overseas Chinese Scholars, Ministry of Personnel of the People's Republic of China. This project was also supported by the Natural Science Foundation of Hebei Province (B2007000613) and by the Research Fund of Hebei University of Science and Technology.

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