

High-temperature polymers for advanced microelectronics

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Abstract

Several series of aromatic polyethers and polybenzoxazoles with high thermal stability and low dielectric constant were prepared and characterized. The polyethers were synthesized by nucleophilic aromatic displacement of fluorine with phenoxides. In order to avoid strongly polar groups such as carbonyl and sulfone, trifluoromethyl groups were used to activate the fluorine for displacement. An additional benefit of the presence of the trifluoromethyl groups is the decreased dielectric constant, which fluorinated materials exhibit. This is attributed to two factors: the strong electronegativity of fluorine, resulting in very low polarizability of the C–F bonds, and the larger radius of a fluorine atom in comparison with a hydrogen atom, resulting in increased free volume.

Trifluoromethyl substituted terphenyl and quadriphenyl poly(arylether)s prepared in this study exhibit decomposition temperatures far in excess of 500 °C, even in air, dielectric constants below three, and mechanical properties comparable to engineering plastics such as polycarbonate and high-performance thermoplastics such as PEEK.

Poly(benzoxazole)s were prepared with and without fluorine substituents. Since most of the poly(benzoxazole)s were insoluble, they were prepared via soluble poly(hydroxyamide) precursors, which were converted to the final polymers by thermal treatment. These materials had dielectric constants as low as 2.69 and also decomposition temperatures far above 500 °C in air.

1. Introduction

The continuing need for higher memory capacity of RAM chips and higher integration density of CPUs has reached a state where conventional materials used to fabricate the microelectronics devices can no longer fulfill all requirements [1–6]. This is especially true for the materials used to fabricate the interconnect structures (the ‘wiring’) on the chips. One of the problems is the

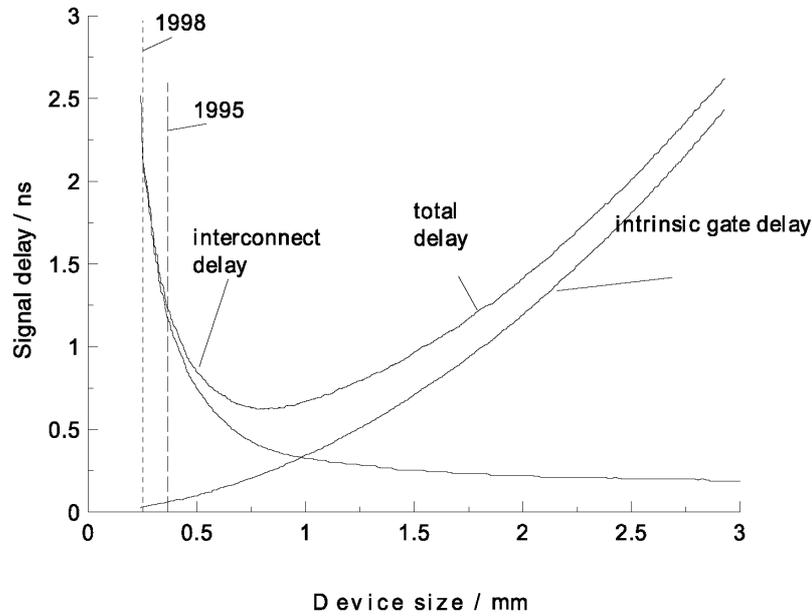


Figure 1. Signal delay as a function of device size.

need for an insulating material to separate the electrically conducting metal lines (interlayer dielectric (ILD) or intermetal dielectric (IMD)). Typically, silicon dioxide is used for this purpose [7]; it has a dielectric constant of $\epsilon \approx 4$ [7, 8], and its high thermal stability, low coefficient of thermal expansion, well known adhesion characteristics, and processing compatibility made it the ideal material. However, for further advancement in integration density, an insulating material with a lower dielectric constant is needed. In a simplified model [4], the signal delay time τ between two devices can be expressed as

$$\tau = RC = 2\rho\epsilon\epsilon_0 \left[\frac{4L^2}{P^2} + \frac{L^2}{T^2} \right] \quad (1)$$

where τ is the signal delay time, R is the total capacitance, C is the total resistance, ρ is the specific resistance of the conductor, ϵ is the dielectric constant of the insulator, ϵ_0 is the dielectric constant of vacuum, and L , T and P are the length, thickness, and pitch ($= 2 \times$ distance) of the conductor lines.

While the intrinsic signal delay (gate delay), caused by the transistor itself, decreases with decreasing device size, the total signal delay shows a different behaviour. The total signal delay has to account for the delay caused by the wiring in addition to the intrinsic gate delay. Decreasing the size of the devices also means decreasing the distance of the conducting interconnects. As the conductors get closer and closer, they start to ‘see’ each other: capacitive resistance, induction (cross-talk), and other phenomena are observed. This leads to an increase in RC as the lines get closer and closer. The resulting dependence of the total signal delay time on the device size is shown in figure 1 [3, 9].

From the plot in figure 1 it is obvious that a solution must be found. Equation (1) shows three possible approaches: utilization of a conductor with lower specific resistance ρ , changes in the geometry of the interconnect scheme, and utilization of an insulator with a lower dielectric constant ϵ . Copper has been used since 1998, instead of aluminium, as a conductor. The specific resistance of copper is approximately 37% lower than that of aluminium [7, 10, 11],

resulting in a proportional decrease of the signal delay. Further improvements will certainly be possible by changing the layout of the interconnect scheme, but this requires significant redesign of the chips. Thus, introducing an interconnect dielectric with a significantly lower dielectric constant than SiO₂ is an attractive option.

Many polymers have been proposed for this application [3–7,12]. The list includes polyimides (fluorinated and non-fluorinated), poly(arylether)s (fluorinated and non-fluorinated), heteroaromatic polymers, poly(silsesquioxane)s, poly(perfluorocyclobutane)s, poly(benzocyclobutene)s, poly(norbornene), poly(xylylene)s (fluorinated and non-fluorinated), poly(naphthalene)s (fluorinated and non-fluorinated), amorphous hydro- and fluorocarbon layers from plasma deposition techniques, poly(tetrafluoroethylene) and amorphous derivatives thereof, and many others. All of these polymers have their specific benefits and drawbacks. The most severe problems are insufficient thermal stability for processing, insufficiently high water uptake, low adhesion, and too high dielectric constant.

We chose poly(arylene ether)s and poly(benzoxazole)s with or without fluorine substituents for our work in order to overcome the problem of low thermal stability and still maintain sufficiently low dielectric constants.

2. Requirements for interconnect dielectric materials

Aside from the low dielectric constant, there is a long list of properties which are important if a material is to be used as interconnect dielectric [1, 5, 13]. These requirements are mostly related to the processing conditions and issues related to integration of the material into existing manufacturing processes and equipment. The most important are:

- dielectric constant below three, preferably below 2.5;
- water uptake far below 1%, preferably below 0.1%;
- thermal stability up to 400 °C, preferably 450 °C for several hours;
- sufficient adhesion to Si, SiO₂, Al, Cu, TiN, and other oxides and nitrides.

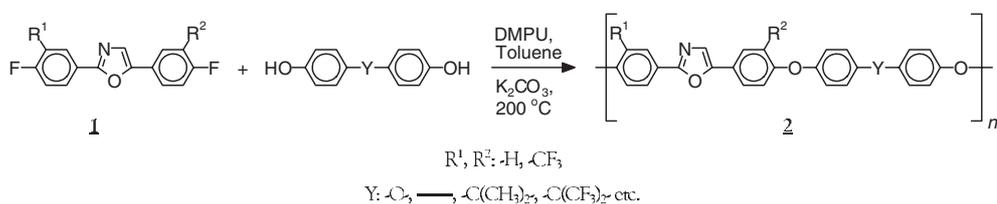
In addition, their plasma etching behaviour, purity, mechanical properties, coefficient of thermal expansion, local and global planarization, and other properties have to be considered [1, 5, 13].

3. Selection of monomer and polymer structures

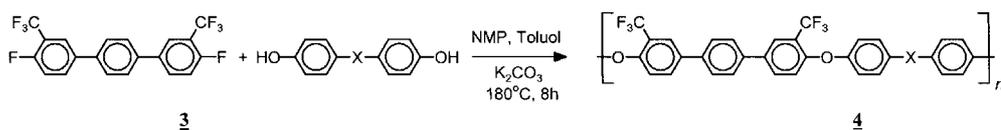
In order to achieve a polymer structure with a low dielectric constant, repeating units with low polarity and low polarizability have to be used. This also decreases water uptake. Incorporation of fluorine substituents or perfluoroalkyl side chains is also known to result in low dielectric constants because of the low polarity and low polarizability of the C–F bond, caused by the strong electronegativity of fluorine. Another approach is to increase the free volume of the polymer by the introduction of bulky groups. Free volume does not contribute to the dielectric constant.

In earlier projects we prepared poly(arylether oxazole)s **2** (scheme 1) from monomers **1** and various bisphenols [14, 15].

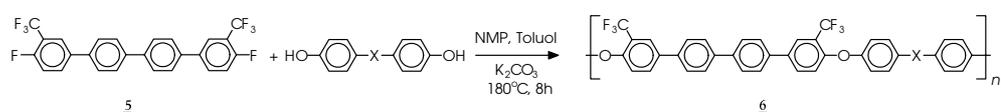
Polymer **2a** with R¹ = R² = –CF₃ and Y = –C(CF₃)₂– exhibited a dielectric constant of $\epsilon = 2.8$ in preliminary measurements. However, the decomposition temperatures of the polymers **2** are not as high as desired. 10% weight loss in dynamic thermogravimetry in air occurs at temperatures between 430 and 490 °C [14, 15]. Also, higher glass transition temperatures are desirable. The T_g of **2a** is 205 °C [14, 15]. Since the fabrication of the interconnects on a microchip requires repeated heating from room temperature to 400 or



Scheme 1. Poly(arylether oxazole)s **2** [14, 15].



Scheme 2. Terphenyl polymers **4**.



Scheme 3. Quadriphenyl polymers **6**.

450 °C [5], and the materials properties (such as coefficient of thermal expansion) undergo a step change at the glass transition, this transition should be as high as possible, preferably above 400 °C.

Therefore, we modified the structures of polymers **2** in order to increase the thermal stability and the glass transition temperatures while keeping the dielectric constant as low as possible. Two approaches were pursued. The first was exchange of the slightly polar oxazole rings for non-polar phenyl rings in order to further decrease ϵ and at the same time increase the glass transition temperature due to introduction of a more linear, rigid structure. The second approach was the replacement of the single oxazole rings by the more thermally stable fused benzoxazole system. Both polymer classes will be described in the following sections.

4. Polymers

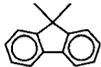
4.1. Terphenyl polymers

Scheme 2 shows the structure of polymers **4** prepared from monomer **3** and various bisphenols. These polymers are derived from polymers **2** by replacement of the oxazole ring by a 1,4-phenylene group. The synthesis of monomer **3** and the details of the polymerization are described in [16, 17]. Table 1 summarizes some of the properties of these polymers.

While the thermal stabilities of polymers **4** with decomposition temperatures in excess of 500 °C are quite sufficient, the glass transition temperatures are not. In fact, for polymers **4a** and **4b** the values of T_g are even lower than for the corresponding oxazole polymers **2**. This may be due to the fact that the oxazole ring is slightly polar, resulting in attractive interaction in the oxazole polymers **2**, which is absent in the terphenyl polymers **4**.

Mechanical properties were determined by DMTA and stress–strain measurements on thin films [16, 17]. The results are shown in table 2. The values for the tensile modulus, especially for the fluorene based polymer **4d**, indicate rather stiff materials, with moderate values for

Table 1. Properties of terphenyl polymers **4** [16, 17].

Polymer	–X–	T_g (°C)	\bar{M}_n^a (g mol ⁻¹)	\bar{M}_w^a (g mol ⁻¹)	T_d^b (°C)
4a	–C(CH ₃) ₂ –	174	32 100	61 300	464
4b	–C(CF ₃) ₂ –	190	14 700	39 700	500
4c	—	209	21 200	62 100	514
4d		234	44 600	71 600	530

^a GPC in THF, using a calibration with polystyrene standards.

^b 5% weight loss in air, 20 K min⁻¹.

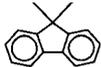
Table 2. Mechanical properties of the terphenyl polymers **4** [16, 17].

Polymer	–X–	E'^a (GPa)	σ_B^b (MPa)	ϵ_B (%)
4a	–C(CH ₃) ₂ –	1.32	58	18
4b	–C(CF ₃) ₂ –	2.51	55	28
4c	—	1.77	70	7
4d	Fluorene	2.69	61	10

^a By DMTA with temperature sweeps at 1 and 10 Hz.

^b At 25 °C at 10% min⁻¹.

Table 3. Properties of the quadriphenyl polymers **6** [18].

Polymer	–X–	T_g (°C) DSC/DMTA	\bar{M}_n^a (g mol ⁻¹)	\bar{M}_w^a (g mol ⁻¹)	T_d^b (°C)
6a	–C(CH ₃) ₂ –	223/243	140 000	305 000	478
6b	–C(CF ₃) ₂ –	210/225	32 000	88 000	510
6c	—	257/268	39 300	94 400	549
6d		300/315	42 000	106 000	534

^a GPC in THF using a calibration with polystyrene standards.

^b 5% weight loss in air, 10 K min⁻¹.

elongation at break. Polymer **4b** with the hexafluoroisopropylidene group in the bisphenol unit is the most ductile material among these polymers.

4.2. Quadriphenyl polymers

In order to increase the glass transition temperatures, another 1,4-phenyl ring was introduced into the repeating unit. Thus, the quadriphenyl polymers **6** were prepared from monomer **5** (scheme 3). Table 3 shows some properties of these polymers [18].

The data in table 3 clearly indicate that the glass transition temperatures are strongly increased by replacement of the terphenyl groups by the quadriphenyl group. An increase of up to 60 °C is observed. Again, the thermal stabilities of the polymers are in excess of 500 °C, with the exception of the partly aliphatic, bisphenol-A-based polymer **6a**.

All polymers **6** exhibit excellent mechanical properties, with the quadriphenyl polymers **6** being superior to the terphenyl polymers **4** (compare tables 2 and 4). Table 4 shows the results of DMTA and stress–strain measurements [18]. The measurements were performed using thin films. Data for polycarbonate as an example for an engineering thermoplastic and for PEEKTM

Table 4. Mechanical properties of the quadriphenyl polymers **6** [18].

Polymer	-X-	E'^a (GPa)	σ_B^b (MPa)	ϵ_B (%)
Quadriphenyl				
6a	-C(CH ₃) ₂ -	2.62	65	130
6b	-C(CF ₃) ₂ -	2.59	65	78
6c	—	2.18	115	120
6d	Fluoren	2.04	75	76
Polycarbonate	—	2.4	72	120
PEEK	—	3.6	100	>50

^a By DMTA with temperature sweeps at 1 and 10 Hz.

^b At 25 °C at 10% min⁻¹.

Table 5. Dielectric constants of polymers **4**.

Polymer	-X-	$\epsilon_{\text{calc, free volume}}$	$\epsilon_{\text{calc, polarizability}}$	$\epsilon_{\text{measured}}$
4a	-C(CH ₃) ₂ -			3.0
4b	-C(CF ₃) ₂ -	2.57	2.67	2.9

as an example for a high-performance polymer are added for comparison. As can be seen, some of the quadriphenyl polymers **6** exhibit mechanical properties in the range of commercial engineering and high-performance polymers.

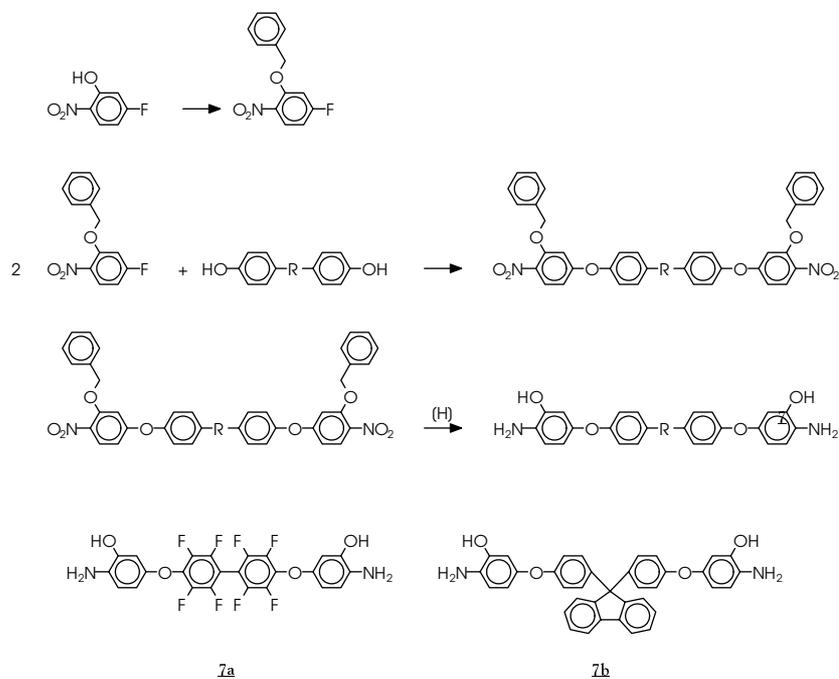
4.3. Dielectric constants of polymers **4** and **6**

The measurements of the dielectric constants were performed between titanium layers: a titanium coated silicon wafer was spin coated with the polymer solution, the polymer was dried carefully, and circular titanium contact pads of various diameters were deposited on top of the polymer layer. This procedure excludes any contact problems. So far, only two polymers have been studied in this way. Table 5 shows the results.

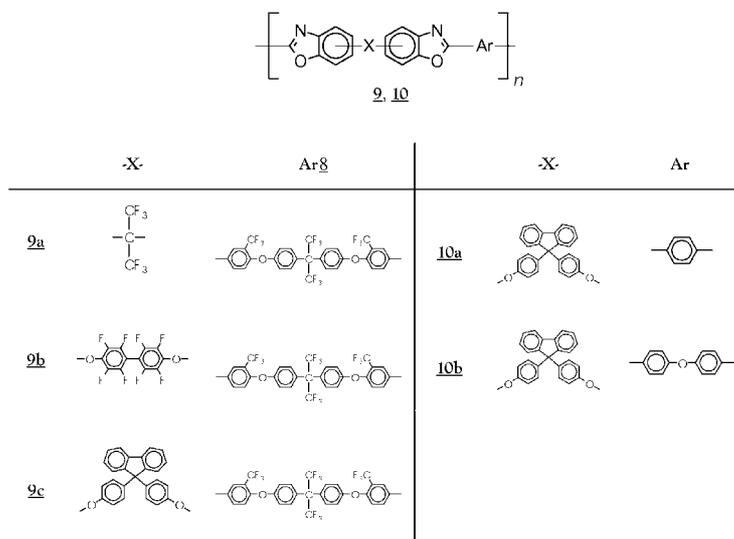
The values of the dielectric constants measured for both polymers **4a** and **4b** are surprisingly high, considering the absence of polar groups. Preliminary results had indicated lower values around 2.7 for **4b**. It is possible, that residual inorganic salt formed by the polycondensation reaction has not been removed thoroughly enough. In addition, the π -system of the terphenyl units may be polarizable to an extent where it contributes noticeably to the dielectric constant. However, a similar material without trifluoromethyl groups was prepared by Burgoyne *et al* [19]. The dielectric constant for this polymer is below 2.7, which indicates that the terphenyl group itself does not induce high dielectric constants.

4.4. Poly(benzoxazole)s

Polymers with benzoxazole groups are usually more thermally stable than comparable polymers with single oxazole rings. Poly(benzoxazole)s are often prepared via poly(hydroxyamide)s from bis(aminophenol)s and dicarboxylic acids, which are subsequently cyclized by thermal dehydration in a process which is comparable to polyimide synthesis. Aminophenols **7a** and **7b** were prepared as shown in scheme 4. The strategy is based on the nucleophilic substitution of fluorine in 4-fluoro-2-hydroxynitrobenzene by bisphenols. The hydroxy group must be protected and, finally (after the nucleophilic displacement reaction)

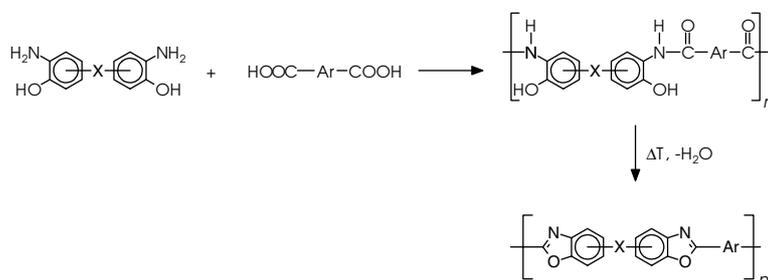


Scheme 4. General synthesis strategy for bis(aminophenols) **7**.



Scheme 5. Partly fluorinated poly(benzoxazole)s **9** and non-fluorinated poly(benzoxazole)s **10**.

the nitro group must be reduced to an amino group. The use of a benzylether as a protecting group for the hydroxy group has the additional advantage of simultaneous deprotection of the hydroxyl group and reduction of the nitro group in one step. This strategy allows the use of any sufficiently nucleophilic bisphenol for the synthesis and thus opens up the path to a large number of bis(aminophenols).



Scheme 6. General preparation of poly(benzoxazole)s.

Table 6. Properties of the poly(benzoxazole)s **9** and **10**. In the table ‘n.d.’ denotes ‘not determined’.

Polymer	\bar{M}_n^a (g mol ⁻¹)	\bar{M}_w^a (g mol ⁻¹)	T_g (°C)	T_d (°C)	ϵ
9a	19 900	35 500	241	515	2.69
9b	17 500	37 600	208	505	2.8
9c	27 400	70 400	235	530	2.85
10a	n.d.	n.d.	295	540	2.8
10b	17 000	33 000	265	530	3.05

^a Of the poly(hydroxyamide) precursor.

^b 5% weight loss in air at a heating rate of 10 K min⁻¹.

In order to increase the fluorine content of the poly(benzoxazole)s, dicarboxylic acid **8** (scheme 5) was prepared from 4-fluoro-3-trifluoromethylbenzoic acid and 6F-bisphenol (2,2-bis(4'-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane), both among the few commercially available building blocks for construction of trifluoromethyl substituted compounds. Scheme 6 shows the general approach for the preparation of poly(benzoxazole)s.

The results of the characterization of the poly(benzoxazole)s **9** and **10** are presented in table 6. Molar masses of the poly(hydroxyamide) precursors were determined by GPC, since most of the poly(benzoxazole)s are not soluble in the fully cyclized form. All polymers **9** and **10** exhibit excellent thermal stability with decomposition temperatures far above 500 °C even in air. The glass transition temperatures are between 208 °C (**9b**) and 295 °C (**10a**).

The dielectric constants of the poly(benzoxazole)s were measured in the same way as described for the terphenyl polymers above. The results indicate lower values of ϵ with a higher degree of fluorination, as can be seen among polymers **9**. However, fluorinated polymers have been found to exhibit degradation with the formation of HF at high temperatures. This can not be tolerated in microchip fabrication because of the corrosive action of HF on silicon. Thus, non-fluorinated polymers may be preferred, provided their dielectric constants are sufficiently low. Polymer **10a** demonstrated that low values of ϵ can also be achieved without fluorination. The dielectric constant of **10a** with $\epsilon = 2.8$ is as low as that of the rather highly fluorinated polymer **9b** (table 6). Apparently, the bulky fluorenyl groups in the repeating unit of **10a** induce free volume to a sufficient extent to considerably reduce the dielectric constant. **10b** contains one ether linkage more than **10a**, which may be the explanation for the higher dielectric constant of **10b**.

5. Conclusion

Based on the fluorinated poly(arylether oxazole)s **2**, polymers with improved thermal stability, increased glass transition temperatures and decreased dielectric constant were prepared by

exchange of the oxazole rings by a phenyl or biphenyl group as well as benzoxazole based structures. Polymers **4**, **6**, **9**, and **10** exhibit decomposition temperatures far in excess of 500 °C in air. Glass transition temperatures up to 300 °C can be obtained. The poly(benzoxazole)s **9** and **10** are insoluble in the cyclized form. This requires processing via the poly(hydroxyamide)s, which are soluble in dipolar aprotic solvents. As a consequence, drying and thermal cyclodehydration of the precursor films results in insoluble films, allowing the use in multilayer interconnect structures. Further improvements of glass transition temperature and dielectric constant can be expected by increasing the number of bulky groups in the repeating units.

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