ISTANBUL UNIVERSITY ENGINEERING FACULTY
JOURNAL OF ELECTRICAL & ELECTRONICS
YEAR : 2002 (359-367)
VOLUME : 2
NUMBER : 1

A STUDY ON DIELECTRIC MODELING OF A NEW SYNTHESIZED POLYIMIDE

YENÝ SENTEZLENEN BÝR POLÝÝMÝDÝN DÝELEKTRÝK MODELÝ ÜZERÝNE BÝR ÇALIÞMA

Ayten KUNTMAN[1] **Hakan KUNTMAN** [2]

[1]Ýstanbul University, Faculty of Engineering, Department of Electrical and Electronics Engineering, Avcýlar, 34850, Istanbul-Turkey
[2]Istanbul Technical University, Faculty of Electrical and Electronics Engineering, Department of Electronics and Communication Engineering, 80626, Maslak, Istanbul, Turkey,
[1]Phone: +90-212-591 19 98-1298, Fax: +90-212-591 19 97,
[2]Phone: +90-212-285 36 47, Fax: +90-212-285 35 65,

[1]E-Mail:akuntman@istanbul.edu.tr [2]E-Mail:kuntman@ehb.itu.edu.tr

ABSTRACT

Polyimides (PI) have desirable properties for use in the electrical and electronics industry because they are a group of excellent high temperature heat-resistant organic polymers and have good planarization capability, excellent chemical resistance, low relative permitivity and electrical insulating properties. A dielectric model for PI is required to understand the degradation due to various stresses such as high temperature and high humidity. In this study, manufacturing a metal-polyimide-metal (MIM) structure and performing measurements on this MIM structure, changes observed in the complex permittivity of PI due to high temperature and humidity (RH) aging are modeled using a Debye-type function.

Key Words: *Dielectrics, Electrical Materials*

ÖZET

Polimerler elektrik ve elektronik endüstrisinde elektriksel yalýtkanlýk özellikleri nedeniyle yaygýn olarak kullanýlýrlar. Özellikle poliimidler (PI), düþük dielektrik sabiti deðeri, yüksek ýsýl dayanýklýk nedeniyle dielektrik ve izolatör olarak mikroelektronik ve sensor endüstrisinde yaygýn bir kullaným alaný bulmaktadýr. Bu çalýþmada yeni sentez edilen bir poliimidin dielektrik özellikleri Debye modeli ile belirlenmiþtir. Bu amaçla MIM yapýsýnda kapasiteler oluþturulmuþ ,bu yapý üzerinde yapýlan ölçümlerden yararlanýlarak sýcaklýk ve nem etkilerine baðlý olarak ortaya çýkan kapasite deðiþimleri önerilen model yardýmýyla hesaplanmýþtýr.

Anahtar Kelimeler: *Dielektrikler, Elektriksel Malzemeler*

1. INTRODUCTION

Polymers as a dielectric material play a significant role in achieving the current state-of-the art in microelectronics [1-18]. Polymeric insulators also are increasingly being used in both the distribution and transmission voltage [19-28]. Especially, polyimides (PI), cyclic-chain polymers, have desirable properties for use in the microelectronics industry because they are a group of excellent high temperature heat-resistant organic polymers and have good planarization capability, excellent chemical resistance, low relative permitivity and electrical insulating properties. The long-term reliability of PI must be understood to insure optimal used in microelectronic and sensor applications. Recently, several papers have reported the use of polyimide for multilevel interconnect systems [1-4,6-7,10].

In previous works, the dielectric properties of a recently reported new polyimide material [1-2,4] suitable for microelectronics applications have been investigated. Using this specific polyimide, a metal-polyimide-silicon (MIS) structure was manufactured to demonstrate the dielectric properties of the material. Furthermore an electrical model of this MIS structure was proposed in a recent work [1].

In the present study, a metal-polyimide-metal (MIM) structure was manufactured; performing measurements on this MIM structure, changes observed in the complex permittivity of PI due to high temperature and humidity (RH) aging are modeled using a Debye-type function. A dielectric model is required to understand the degradation due to various stresses such as high temperature and high humidity so that the implications for long-term reliability can be understood. The dielectric properties of PI after exposure to high temperature are determined experimentally from the measurements performed on the MIM structure. The capacitance and the dissipation factor of the PI are calculated for different temperature and frequency values using the modified Debye model.

2. EXPERIMENTAL

Realization of MIM Capacitors with spin-on technology and electrical measurements:

The polyimide was synthesized following the synthesis of 4,4'-bis(3-aminophenoxy) diphenyl sulfone (DAPDS), by nucleophilic aromatic substitution of 4,4'-dichlorodiphenyl sulfone with m-aminophenol, DAPDS/pyromellitic dianhydride (PMDA)[2]. The test devices used in this study are *parallel* plate capacitors using PI film as the insulator. It was furthermore shown that the new polyimide material exhibits good adhesion as patterned on metal, fills small gaps, is patternable, and provides small capacity at low temperature as a stand-alone polyimide [6-7]. Synthesized polyamic acid was spun at appropriate 2500-6500(cycle/sec) spin speeds, for 40 s to achieve 840-to 1400 nm film thickness on the 100 p-type silicon wafer. The polyamic acid film cast on the silicon wafer was pre-baked 30 min at 130^0C in air, and then it was cured 2 h at 180^0C in nitrogen environment for imidization. The thickness of PI films was measured with a Nanometrics (210xP scanning UV). The polyimide films were covered with aluminum by evaporation, and the films were prebaked before they were covered with the photoresist needed for the patterning process. Consequently, aluminum film was patterned. A metal insulator metal (MIM) structure is formed like a sandwich structure. The area forming the capacitor in this pattern is $7.85x10^{-3}cm^2$. The thickness of PI is 1.13um.

Dielectric and C-V characteristics were determined on these simple ring-dot MIM structures .The C-V characteristics and dielectric properties were measured using a Keithley 590 CV analyzer. Capacitors have values of 56 pF and 50 pF for 100KHz and 1MHz at 25C, respectively.

Breakdown voltage was determined by using a HP 4145 A semiconductor parameter analyzer as 6 to $7x10^5$ V/cm.

The behavior of the MIM capacitances is investigated at low and high frequencies for different temperature ranges (25, 100, 200, 250 C) and humidity.

The polyimide capacitance is calculated similar to MOS oxide capacitance as follows

$$C_{PI} = Ae_{PI} / t_{PI}(1x10^{-19}) \qquad (1)$$

where C_{PI} is the polyimide capacitance (pF), A is the gate area (cm^2), ε_{PI} is the permittivity of polyimide (F/cm), t_{PI} is the polyimide thickness (nm).

Using this equation, ε_{PI} was determined for polyimide films with thickness ranging from 0.8

to 1.4µm for the optimum cure condition by measuring capacitance vs. gate voltage at specific temperatures (room temperature, 100, 200, and 250^0 C).

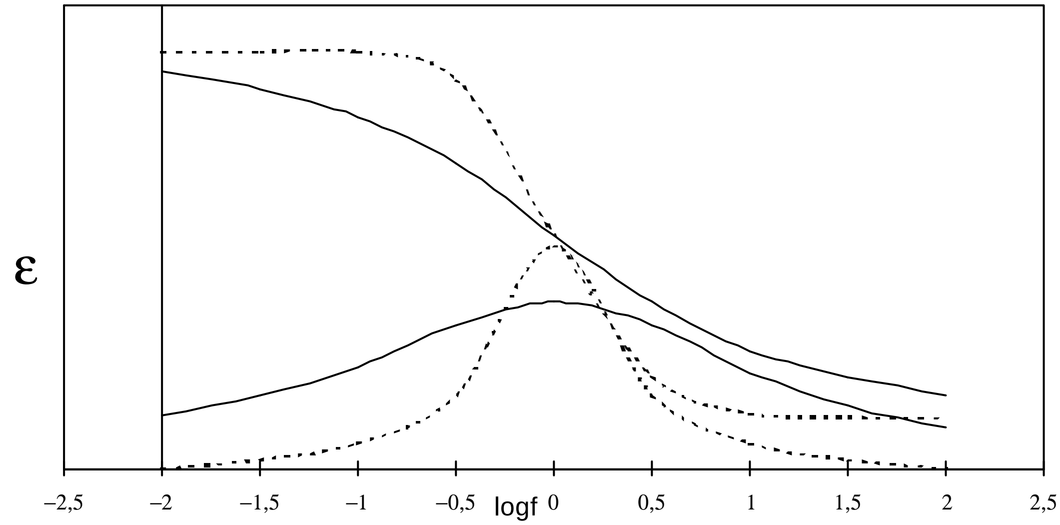

Figure 1: The characteristic differences between polymeric systems and the Debye equation reported by K. S. Cole and Cole [18].
………… Debye equation, _________ Polymeric systems.

Dielectric Modeling:
The classic Debye behavior for the complex permittivity as a function of frequency is illustrated by the solid curves in Figure 1. For most polymer, however, the values for ε'(ω) and ε"(ω) deviate widely from the Debye equation. Cole et al. report that there are three characteristic differences between polymeric systems and the model system exhibiting the classic Debye behavior [31-32].

The circuit model is given Figure 2. R_1 and C_1 represent the relaxation time for the low frequency behavior of capacitance and loss. G_0 is a variable conductance representing the effects of aging on the loss. In this modified Debye model, the real and imaginary parts of the complex permittivity are:

$$e' = \sum_{j=0}^{1} e_u + \frac{(e_l - e_u)_j}{1 + w^2 t_j^2} \qquad (2)$$

$$e'' = \frac{s_{dc}}{w} + \sum_{j=0}^{1} e_u + \frac{(e_l - e_u)_j w t_j}{1 + w^2 t_j^2} \qquad (3)$$

where ε_1 is the low frequency or static permittivity, ε_u is the permittivity in the high frequency limit and τ is the characteristic time constant or dielectric relaxation time.

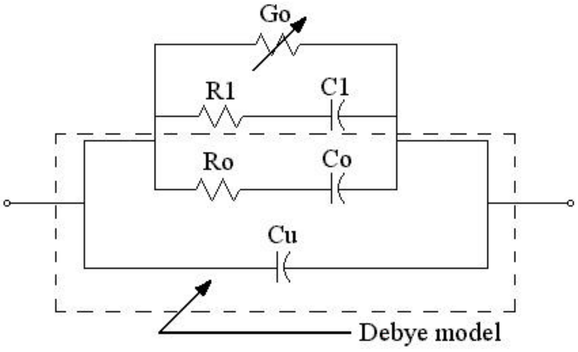

Figure 2: The modified Debye model equivalent circuit

The lumped parameter circuit model can be interpreted as a complex capacitor, and its equivalent admittance then be derived as follows:

$$Y(w) = jw(C^{'} + C^{''})$$

$$C(w)^{'} = \sum_{j=0}^{1} C_u + \frac{C_j}{1+w^2 t_j^2} \qquad (4a)$$

$$C^{''}(w) = \frac{G_O}{w} + \sum_{j=0}^{1} e_u + \frac{C_j w t_j}{1+w^2 t_j^2} \qquad (4b)$$

where $\tau_j = R_j C_j$, j= 0 , 1.
By comparing Equations 2,3 with Equation 4, we obtain the following duality:

$$\begin{array}{lcl} Cu & \longleftrightarrow & \varepsilon_u \\ C_j & \longleftrightarrow & (\varepsilon_1\text{-}\varepsilon_u)j \\ G_0 & \longleftrightarrow & \sigma dc \\ R_j & \longleftrightarrow & \tau j / Cj \end{array} \qquad (5)$$

where C_u is the capacitance at high frequency and ε_u represents the high frequency permittivity. The quantity (ε_l-ε_u) is called the relaxation strength and varies with the product of the concentration of dipoles and the square of their dipole moment. G_0 is the variable conductance.

3. RESULTS AND DISCUSSION

Capacitance values and dissipation factor of PI samples were calculated from Equations 3 and 4. The values of lumped circuit parameters were used for curve fitting at different temperature and RH values. Parameters for this circuit are given in Table 1.

Figure 3 shows the capacitance dependence of the specimens on frequency at 25, 100, 25, 200, and 25^{o}C, respectively. It is obvious from Figure 3 that the real part of the permittivity is almost equal to each other at 25 and 100^{o}C and can be assumed constant and independent of frequency, while the values at 200^{o}C are strongly dependent on frequency and become much higher at lower frequencies. Figure 4 shows the dependence of the dielectric dissipation factor of the specimen on the frequency at indicated temperatures. It can be easily observed from Figure 4 that the relationship between the dielectric dissipation factor and frequency is different for each temperature, although as a whole the dielectric dissipation factor values become higher with increasing frequency. It exhibits a minimum at 100 Hz. Below 100Hz; its values are slightly increased. Dissipation factor increases in the region beyond 100Hz. Its value reaches a maximum at 10^4. The temperature dependence of dielectric properties of PI between 25 and 200C permittivity values decreases with frequency whereas the dielectric dissipation factor value shows a peak at 100Hz.
The calculated capacitance and dissipation factor of the lumped parameter circuit model from Equation3 at humidity values are plotted in Figure 5 and 6.

It can be clearly observed from Figure 5 that the permittivity values remain almost constant at frequencies of MHz level.
We propose that the changes in dielectric behavior are due primarily to changes in the bulk PI after aging. These changes may be chemical or morphological in nature and may involve the redistribution of polar groups.
Since polyimide is an organic film, organic functional groups can be easily aligned during electrical stress creating the polarization effect [7]. The organic functional groups of the synthesized polyimide are SO2- (electron withdrawing) and -O- (electron donating). These groups can be aligned with applied electrical field.

Permanent dipole moments exist in some molecules by virtue of an asymmetrical arrangement of positively and negatively charged regions; such molecules are termed polar molecules or polar groups. Polarization is the alignment of permanent or induced atomic or molecular dipole moments with an externally applied electric field. There are three types of polarization electronic, ionic and orientation. Dielectric materials ordinarily exhibit at least one of these polarization types depending on the material and also the manner of the external field application [29-31].

Polyimide has a higher permittivity at 1 kHz because of the polar parts of its molecules responding to the field. But this contribution collapses at higher frequencies; molecular orientation can no longer keep up with the rapid oscillation of the field. Polymers, such as polystyrene, have no polar groups so its permittivity reflects the displacement of electrons relative to nuclei when a field is applied. Electrons, with their very low mass, can “keep up” with high frequencies so that ε is the same at 1kHz and 1MHz [32].

Table 1. The values of lumped circuit parameters used for curve fitting at different RH values

	Without RH	% 5 RH	% 65 RH
Go (1/Ω)	1.50E-10	1.70E-10	2.10E-10
Ro (Ω)	2.10E+04	1.30E+04	2.10E+03
Co (pF)	56	105	105
τo2 (sn)	-	0.53	138.3
Cu (pF)	50	100	100

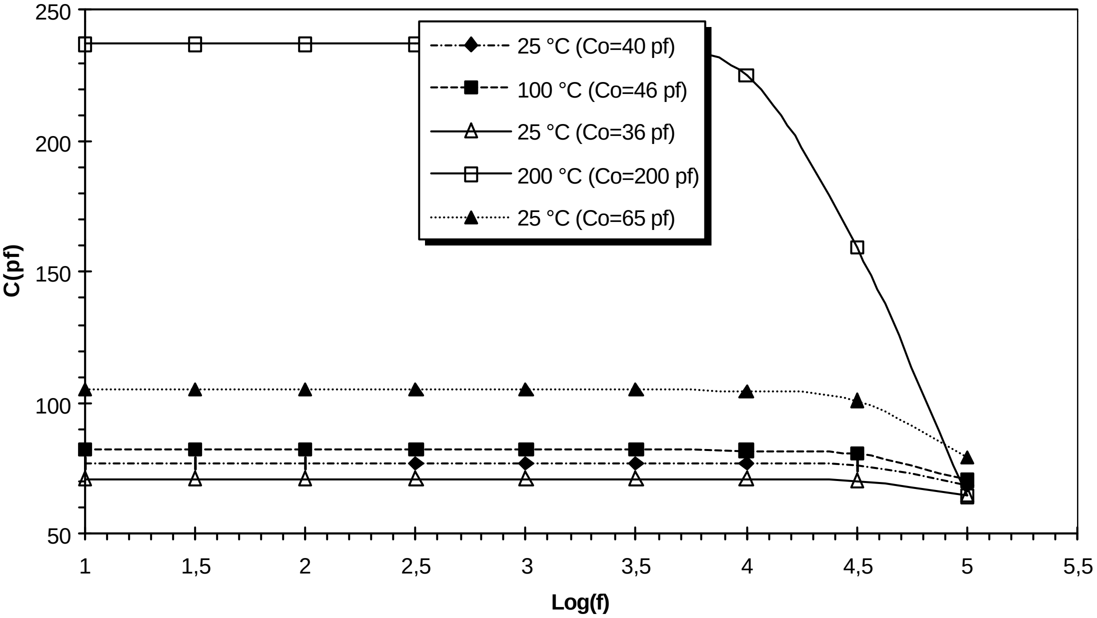

Figure 3: Calculated data for capacitance vs. frequency using Equation (3a) and (3a) for the aged capacitor at different temperature values.

Table 2. Dielectric properties for polar and non-polar polymer samples

Materials	T_g (^oC)			ε_r	
		1kHz < T_g	1MHz < T_g	1kHz > T_g	1MHz > T_g
*PS	105	2.5	2.5	2.5	-
**PI	267	3.5 (room temp) 4 (100^0C) unstable(200^0C)	3.1 (room temp.) 2.7(100^0C) 2.7 (200^0C)	unstable(250^0C)	2.3 (250^0C)

The characteristics obtained are similar to the results reported in the literature [21]. Low frequency permittivity values are calculated as 3.5, 4 to 5, 11 and 5 to 7.5 (increasing $E > 10^3$ V/cm) for temperatures 25, 100, 25, 200, 25 ^{0}C from Figure 3, respectively. Polarity dependent transport behavior occurs for $T>60^0$C and $E>10^3$V/cm for 1 kHz measurements [5]. The reason of this behavior can be the aligned polar groups in the PI or can be due to the residual carboxylic acid groups contained in their structure resulting from unimidized polyamic acid in PI. According to Sacher [35] these carboxylic acid groups -COOH are hydrogen bonded at room temperature however, since this bond energy is low, the concentration of unbonded acid groups increases rapidly with rising temperature. These groups than ionize, $COOH \rightarrow H^+ + COOH^-$, thereby providing free protons.

Close to and above glass transition temperature (T_g, 267°C for PI), PI has a further decrease of ε at high frequencies, but at low frequency and a temperature close to T_g, ε is increasing [34,35]. Table 2 shows the relation between the molecular structure and the dielectric properties for polar and nonpolar polymer samples.

Note that the shapes of the real and imaginary pars of the permittivity are in qualitative agreement with the observed behavior.

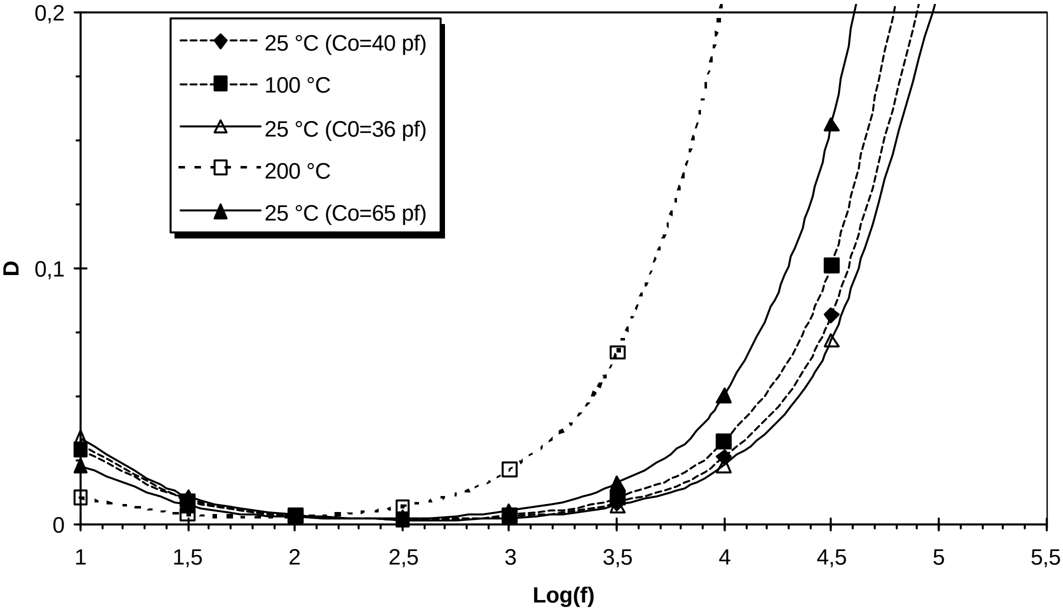

Figure 4: Calculated values of dielectric dissipation factor vs. frequency using Equation (3a) and (3a) for the aged capacitor at different temperature values.

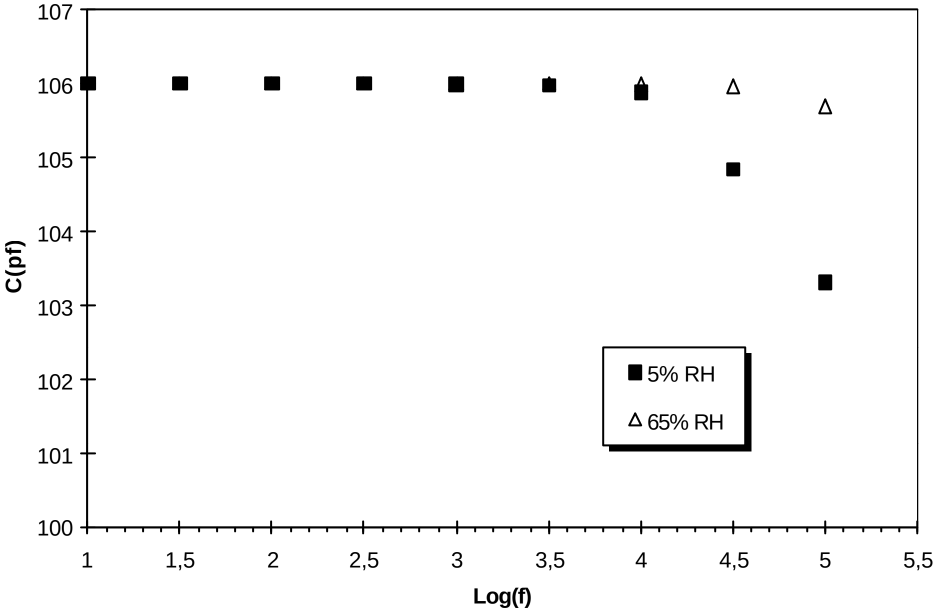

Figure 5: Calculated data for capacitance vs. frequency using Equation (3a) and (3a) for the aged capacitor at humidity values.

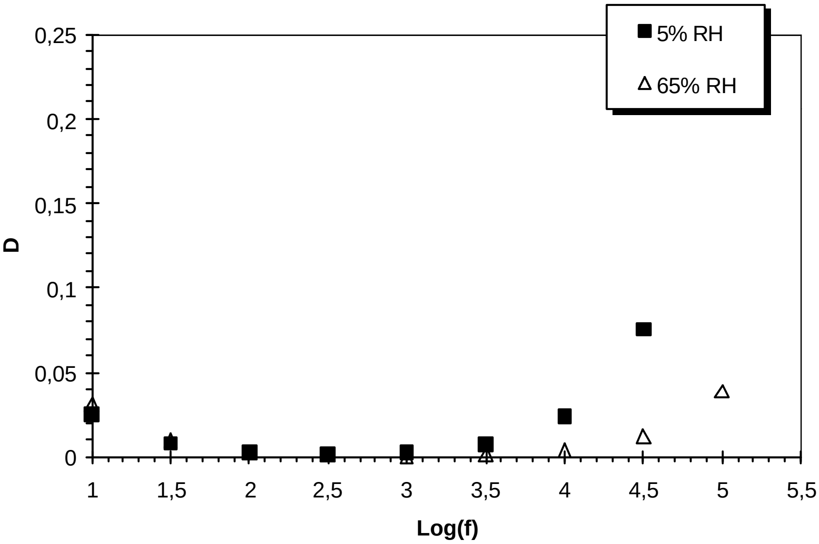

Figure 6: Calculated values of dielectric dissipation factor vs. frequency using Equation (3a) and (3a) for the aged capacitor at humidity values.

4. CONCLUSIONS

In this study, changes observed in the complex permittivity of PI due to high temperature and humidity (RH) aging are modeled using a Debye-type function. A dielectric model required to understand degradation due to various stresses such as high temperature and high humidity so that the implications for long-term reliability is given. The dielectric properties of PI after exposure to high temperature are determined experimentally. The capacitance and the dissipation factor of the PI are calculated for different temperature and frequencies using modified Debye model.

Polyimides are a group of excellent high temperature heat-resistant organic polymers and have good planarization capability, excellent chemical resistance, low relative permitivity and electrical insulating properties. The results obtained in the frame of this work can be used for the reliability of polyimides in microelectronics and sensor applications.

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This work was partially supported by the Research Fund of the University of Istanbul. Project number Ö-479/280998.

Ayten Kuntman received her M.Sc. degree from Istanbul University in 1979 and her Ph.D. degree from Istanbul Technical University in 1989, respectively. In 1980 she joined the Electronics and Communication Engineering Department of Istanbul Technical University. From 1995 to 2001 she was an associate professor of Electrical Power Systems in the Electrical and Electronics Engineering Department of Istanbul University. Since 2001 she is a professor of Electrical Power Systems in the same department. Her research interest include dielectric properties of polymers, semiconductors, aging of cable polymers, microelectronics technologies, thermodinamic properties of polymers and reliability of materials. Dr. Kuntman has authored many publications on polymers, semiconductors and microelectronics technologies.

Hakan Kuntman received his B.Sc., M.Sc. and Ph.D. degrees from Istanbul Technical University in 1974, 1977 and 1982, respectively. In 1974 he joined the Electronics and Communication Engineering Department of Istanbul Technical University. Since 1992 he is a professor of electronics in the same department. His research interest include electronic circuits, modeling of electron devices and electronic systems, active filters, design of analog IC topologies. He has authored many publications on modelling and simulation of electron devices and electronic circuits for computer-aided design, analog VLSI design and active circuit design. Dr. Kuntman is a member of the Chamber of Turkish Electrical Engineers (EMO).