Effect of Molecular Orientation on the Dielectric Properties of Spin-Coated Polyimide Films

LINDA LIN and SUE ANN BIDSTRUP*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30223-0100

SYNOPSIS

The effect of molecular orientation on the dielectric properties of spin-coated polyimide films has been studied in situ for pyromellitic dianhydride with 4,4'-oxydianiline (PMDA/ ODA) and biphenyldianhydride with p-phenylenediamine (BPDA/PPD). The degree of molecular orientation is characterized by the optical anisotropy between the in-plane and the through-plane refractive indices. The through-plane dielectric properties are measured by fabricating parallel-plate capacitors directly onto the silicon substrate. Both the birefringence and the dielectric constant of PMDA/ODA polyimide vary with film thickness; however, these properties are independent of film thickness for BPDA/PPD films. To confirm that the measured dielectric constant obtained from the parallel-plate structures is free from a significant edge effect, finite element modeling of the electrostatic potential within the dielectric is performed. Models for both isotropic and anisotropic dielectric properties indicate that the fringing effects are indeed negligible for the film thicknesses examined. Thus, the changes observed in the measured dielectric constant are attributed to the variations in the molecular orientation. The optical anisotropy observed for the polyimides suggests a corresponding dielectric anisotropy in the films. An estimation using the Maxwell relation indicates that the dielectric anisotropy at 10^5 Hz is 0.31 for PMDA/ ODA and 0.85 for BPDA/PPD. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Due to their thermal stability, chemical resistance, low dielectric constant, and the ability to planarize underlying structures, polyimide films spin-coated from polyamic acid solutions are useful as interlevel dielectrics for integrated circuit devices. As interlevel dielectrics, these thin films (less than 10 μ m in thickness) provide electrical insulation between conduction paths; films with the smaller dielectric constant are desirable for lower line resistance and crosstalk. Upon thermal treatment to transform polyamic acid into polyimide, the spin-coated polyimide films develop a uniform in-plane orientation, such that the in-plane refractive index.¹⁻⁶ The difference between the in-plane and through-plane refractive indices of the film is affected by a variety of factors, including the heating rate,² the film thickness,⁵ and the rigidity of the polymer backbone.^{4,6}

The molecular orientation in polyimide films has been reported to be responsible for material property variations in moisture diffusion⁷ and thermal expansion.⁸⁻¹⁰ The present investigation examines the effect of molecular orientation due to film thickness variations on the electrical insulating properties of the films. The molecular orientation, as characterized by the optical birefringence, has been shown to decrease with film thickness for spin-coated polyimides that include 4,4'-oxydianiline in their backbone.⁶ This effect may be attributed to the presence of a substrate upon which the film is spin-coated and the ability of the flexible polymer chains to become less oriented in the bulk of the film. In this work, an investigation of the effect of film thickness on the dielectric properties of polyimide films with different backbone rigidity was conducted.

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MATERIALS

Two polyimide chemistries with different backbone rigidities are examined: DuPont PI2540 (pyromellitic dianhydride [PMDA] with 4,4'-oxydianiline [ODA]) and DuPont PI2611 (biphenyldianhydride [BPDA] with *p*-phenylenediamine [PPD]). The chemical composition of these two systems is given in Figure 1. Inspection of the diamine component of the two polyimides suggests that the PMDA/ ODA structure is less rigid due to the free rotation available at the ether linkage of the ODA monomer. For a quantitative measure of the polymer backbone rigidity, the Kuhn statistical segment (KSS) for the two polyimides (obtained from theoretical calculations by Birshtein and Goryunov¹¹ is also listed in Figure 1. Based on Gaussian statistics, KSS is the length necessary to describe the polymer chain as a freely joined chain. The larger KSS indicates greater chain rigidity¹²; therefore, BPDA/PPD (KSS = 118Å) has a more rigid backbone structure than that of PMDA/ODA (KSS = 72 Å).

EXPERIMENTAL

The parallel-plate capacitor structure was fabricated directly on the polyimide film as illustrated in Figure 2. Thin polyimide films of PMDA/ODA and BPDA/ PPD were obtained by spin-coating the respective polyamic acid solutions (DuPont PI2540 and DuPont PI2611) onto 3 in.-diameter silicon wafers prepared as follows: The silicon wafers were thermally oxidized and then metallized with titanium/

gold/titanium (Ti/Au/Ti) as the bottom electrode. The Ti/Au/Ti metallization (deposited using a dcsputterer) consists of distinct metal layers with a thickness distribution of 75 Å/1400 Å/75 Å. The titanium layers were used to enhance the adhesion of the gold to the silicon substrate and to the polyimide film. The spinning speed was varied to achieve final polyimide film thicknesses ranging between 2 and 10 μ m upon thermal treatment. The thermal imidization schedule employed included a soft bake in air for 15 min at 120°C and a hard bake in nitrogen. The hard-bake step involves ramping the furnace temperature from room temperature to 350°C at 5°C/min and holding the furnace temperature at 350°C for 1 h. The soft bake was performed in a Blue M gravity convection oven with the spin-coated samples placed horizontally on a preheated stainlesssteel block. The remainder of the thermal treatment was performed in a Blue M tube furnace with the samples standing vertically in a quartz boat. The furnace power was turned off at the end of the 1 h hold at 350°C, and the film samples were cooled to approximately 300°C before being removed from the furnace tube. Following the thermal imidization. another 75 Å/1400 Å/75 Å of Ti/Au/Ti was deposited on the polyimide film, and circular top electrodes were defined using standard photolithographic techniques. With wet chemical etching, the excess metal is removed, and top electrodes with 1.16 cm diameter were formed. The ratio of the top electrode diameter to the film thickness is on the order of 10³. According to the empirical fringing capacitance correction equation published in the ASTM D150-87 standard,¹³ the edge effect due to



Figure 1 Polyimide chemistries: PMDA/ODA and BPDA/PPD (KSS values obtained from Ref. 11).



Figure 2 Parallel-plate structure.

fringing fields around the perimeter of the electrode is insignificant for the electrode geometry used. This implies that the electric field between the parallelplate capacitor is perpendicular to the faces of the electrodes. Thus, the electrical properties obtained from these capacitors represent the dielectric properties in the though-plane direction of the film.

Before performing the electrical measurements, the parallel-plate structures were stored at the measurement conditions of 40% relative humidity and 21°C for at least 24 h. A Keithley 590 CV analyzer was used to obtain the ac capacitance and conductance of the parallel-plate structures by modeling the film as a capacitor and a resistor in parallel. The electrical measurements were taken at a single frequency to compare the effect of orientation variation due to film thickness. The dissipation factor $(\varepsilon''/\varepsilon')$ for PMDA/ODA polyimide increases around 10^5 Hz, but the capacitance is constant between 1 and 10⁵ Hz.¹⁴ For a fully cured polyimide, the dielectric constant is dominated by the permittivity, which is proportional to the capacitance. Therefore, the electrical measurements were only taken at 10⁵ Hz.

The relative permittivity ε' and the loss factor ε'' were calculated from eqs. (1) and (2), respectively, using the measured capacitance C and the conductance 1/R:

$$\varepsilon' = \frac{Ct}{\varepsilon_0 A} \tag{1}$$

$$\varepsilon'' = \frac{t}{2\pi f \, \varepsilon_0 R A} \tag{2}$$

A Dektak profilometer was used to determine the film thickness t, and the diameter of the top electrode, to calculate the area of the top electrode A. The permittivity of free space ε_0 used is 8.85×10^{-14} F/cm, and the frequency f is 10^5 Hz. The dielectric constant (ε^*) was then determined from eq. (3):

$$\varepsilon^* = \sqrt{\varepsilon' + \varepsilon''} \tag{3}$$

To characterize the degree of molecular orientation, the birefringence of each film was determined using a Metricon 2010 prism coupler. The prism coupler system uses a He—Ne laser at 633 nm to measure the refractive index in the plane and through the plane of the film. The difference between the in-plane and the through-plane refractive indices is defined as the birefringence. A more detailed description of the prism coupler technique is given elsewhere.⁶ The optical measurements were obtained at approximately 30% relative humidity and 26°C. In addition, the birefringence measurements were taken both before and after the formation of the top electrode. The photolithographic and etching processes used in the electrode fabrication procedure did not affect the birefringence of the polyimide films.

RESULTS AND DISCUSSION

The optical birefringence determined using the Metricon prism coupler and the through-plane dielectric constant obtained from the parallel-plate capacitor structures are shown in Figures 3 and 4, respectively. The data represent an average of three independent sets of duplicate samples. In agreement with previous work,⁶ the birefringence of PMDA/ODA films decreases slightly with film thickness, but the birefringence of BPDA/PPD films is independent of the film thickness. As for the effect of film thickness on the dielectric properties, the dielectric constant of PMDA/ODA films increases with film thickness, but the dielectric constant of BPDA/PPD films is relatively independent of the film thickness. The dielectric constant variation observed for the PMDA/ODA polyimide films is likely due to the molecular orientation effects, as illustrated by the birefringence decrease with film thickness shown in Figure 3. However, before the dielectric constant variation can be conclusively attributed to molecular orientation, the edge effect due to fringing fields in a highly anisotropic material must be determined to be sure that it does not contribute to the experimentally determined dielectric constant.

The edge effect due to fringing fields around the perimeter of the electrodes is influenced by the relative permittivity of the dielectric, the electrode diameter, and the film thickness. With a specific elec-



Figure 3 Birefringence variation with film thickness: (●) PMDA/ODA; (□) BPDA/PPD.

trode diameter for a particular dielectric, the fringing fields become more significant as the film thickness increases. This is due to the fact that the capacitance of the film defined by the top electrode decreases as the film thickness is increased [eq. (1)]. Therefore, the fringing fields contribute to a greater error in the measured capacitance in a thicker film than in a thinner film. As discussed in the Experimental section, the edge effect in the parallel-plate capacitor geometry under consideration is negligible, according to the empirical relation in the ASTM D150-87 standard. The empirical relation is based on a variety of materials that may or may not possess anisotropic electrical properties.¹⁵ For spin-coated polyimide films whose in-plane refractive index is greater than the through-plane refractive index, the in-plane dielectric constant is anticipated to be larger than the through-plane dielectric constant. This dielectric anisotropy may result in a greater edge effect contribution to the total capacitance than that in isotropic materials. To determine whether the dielectric variation with film thickness is due to excessive edge effect as a result of the anisotropic nature of the polyimide, the extent of fringing fields for parallelplate capacitors is examined by theoretical calculation of the electrostatic potential.

The electrostatic potential between the electrodes of the parallel-plate capacitor is calculated using ANSYS, a finite element analysis package from Swanson Analysis Systems, Inc.¹⁶ A direct analogy exists between heat conduction and electrostatic field equations¹⁷; therefore, the heat-transfer module of ANSYS is utilized to evaluate the electrostatic potential within the polymer dielectric. As the polyamic acids used to form the polyimide films are of electronic grade with very low levels of ionic impurities, it is assumed that there is no free charge within the dielectric. Therefore, the electrical potential distribution, Φ , between a pair of electrodes is governed by the Laplace eq. (4):

$$\varepsilon'_{x} \frac{\partial^{2} \Phi}{\partial x} + \varepsilon'_{y} \frac{\partial^{2} \Phi}{\partial y^{2}} + \varepsilon'_{z} \frac{\partial^{2} \Phi}{\partial z^{2}} = 0 \qquad (4)$$

The ε'_x and ε'_y represent the relative permittivity in the planar direction of the dielectric, and ε'_z is the relative permittivity in the thickness direction of the dielectric. Independent values of ε'_x , ε'_y , and ε'_z may be specified in ANSYS to examine the effect of dielectric anisotropy on the electrical potential distribution.

The solution of the electrical potential enables the determination of the electric field intensity \mathbf{E} , the electric displacement \mathbf{D} , and the amount of electrical potential energy U_e stored in the system as described in eqs. (5), (6), and (7), respectively:

$$\mathbf{E} = -\left(\frac{\partial\Phi}{\partial x}\,\hat{x} + \frac{\partial\Phi}{\partial y}\,\hat{y} + \frac{\partial\Phi}{\partial z}\,\hat{z}\right) \tag{5}$$

$$\mathbf{D} = -\left(\varepsilon'_{x}\frac{\partial\Phi}{\partial x}\hat{x} + \varepsilon'_{y}\frac{\partial\Phi}{\partial y}\hat{y} + \varepsilon'_{z}\frac{\partial\Phi}{\partial z}\hat{z}\right) \quad (6)$$

$$U_e = \frac{1}{2} \int_v \mathbf{E} \cdot \mathbf{D} dV \tag{7}$$

The energy stored, U_e , in the capacitor is also related to the capacitance, C, and the potential ΔV applied across the parallel plates as given in eq. (8):

$$C = \frac{(2 \times U_e)}{\Delta V^2} \tag{8}$$

The calculated capacitance from eq. (8) can then be used to compute the relative permittivity of the dielectric from eq. (1). If the edge effect is insignificant, the computed relative permittivity will be



Figure 4 Dielectric constant variation with film thickness: (\bullet) PMDA/ODA; (\Box) BPDA/PPD.

equal to the value of ε'_z specified; otherwise, the computed relative permittivity will be greater than the specified ε'_z . Since the measured loss factor ε'' obtained from eq. (2) is small compared to the measured relative permittivity ε' , ε^* is effectively equal to ε' . Therefore, the edge effect determined from the theoretical calculations of the energy stored in the dielectric is the same as the edge effect on the measured dielectric constant.

The significance of the edge effect has been obtained using ANSYS to model real capacitors with fringing and ideal capacitors without fringing. Parallel-plate capacitors with a top electrode diameter of 1.0 cm are modeled for film thicknesses ranging from 500 to 2 μ m. A two-dimensional, rather than a three-dimensional, model is used since the molecular orientation of spin-coated polyimide is uniform in the plane of the film,⁶ and, therefore, ε'_x can be assumed to be equal to ε'_{y} . The geometries of the parallel-plate models are shown in Figure 5. Equal electrodes are used to model an ideal parallel-plate capacitor in which fringing is totally eliminated by specifying adiabatic boundary conditions at the edge of the polymer dielectric. To capture the fringing fields that exist at the edge of a real capacitor, a finite element model consisting of unequal electrodes is used. The polymer dielectric between the unequal electrodes extends twice the length of the top electrode diameter on both ends of the electrode. Due to the vertical symmetry of the capacitor, symmetry boundary conditions can be used along the vertical centerline for both capacitor models; therefore, only half of the capacitor geometry is actually defined in the ANSYS code. The length/width ratio specified for the finite element mesh is between 0.1 to 1. Dielectrics with both isotropic and anisotropic permittivities have been modeled by specifying the appropriate in-plane (ε'_x) and through-plane (ε'_z) permittivities. The fringing effect is analyzed by



Figure 5 Finite element models: (A) equal electrodes without edge effect; (B) unequal electrodes with edge effect.

Film Thickness (Microns)	Relative Permittivity (Without Fringing)	Relative Permittivity (with Fringing)	
500	3.00	3.15	
50	3.00	3.02	
8	3.00	3.00	
5	3.00	3.00	
2	3.00	3.00	

Table	I	Finite	Element	Analysis	Results
from .	AN	SYS			

comparing the relative permittivity, calculated using the capacitance obtained from the ANSYS analysis for capacitors with equal and unequal electrodes.

The ANSYS model is first tested for a dielectric with isotropic permittivities, ($\varepsilon'_x = \varepsilon''_z = 3.0$). To examine the effect of film thickness on the amount of fringing, ANSYS is used to model films with thicknesses ranging from 500 to 2 μ m, as shown in Table I. For the ideal model with equal electrodes in which fringing is nonexistent, the calculated dielectric constant does not change with film thickness. The real model with unequal electrodes that can capture the fringing effect shows that as the film thickness increases the calculated dielectric constant also increases. However, for films between 2 and 8 μ m, the capacitor geometry does not affect the calculated dielectric constant, indicating that the effect of fringing is negligible for an isotropic film less than 10 μ m. This observation is in agreement with the empirical fringing capacitance correction relation found in the ASTM D150-87 standard. A comparison of the fringing effect on the measured dielectric constant from the ASTM empirical relation and the ANSYS solution is presented in Table II for an isotropic material with a relative permittivity of 3.

To examine the effect of dielectric anisotropy on the fringing effect, the in-plane permittivity is assumed 25% greater than the through-plane permittivity; $\varepsilon'_x = 3.75$ and $\varepsilon'_z = 3.00$. This assumption is based on a previously predicted dielectric anisotropy in BPDA/PPD polyimide film.¹⁸ The calculated dielectric constant for 2–8 μ m dielectric films with anisotropic permittivities is also 3.00. Thus, a 25% dielectric anisotropy in films less than 10 μ m does not increase the edge effect due to fringing fields, and the dielectric constant experimentally obtained from the parallel-plate capacitors represents a true through-plane dielectric constant. Therefore, the observed increase in the dielectric constant with film

Film Thickness (Microns)	Electrode Diameter-to-Film Thickness Ratio	Relative Permittivity (ASTM D150-87)	Relative Permittivity (ANSYS) 3.15	
500	20	3.06		
50	200	3.01	3.02	
8	1250	3.00	3.00	
5	2000	3.00	3.00	
2	5000	3.00	3.00	

Table IIComparison of Edge Effect Based on the ASTM and ANSYS Methods for an Isotropic Materialwith a Relative Permittivity of 3

thickness (Fig. 4) is not due to fringing effects and may be attributed entirely to structural variation within films of varying thicknesses.

As changes in the birefringence indicate variations in the molecular orientation of the film, the increase in the dielectric constant (Fig. 3) can be attributed to orientation variation of the polyimide with film thickness. Previous works^{2,5,6} showed that the birefringence of spin-coated PMDA/ODA polyimide film decreases with film thickness. This effect has been attributed to the formation of a skin layer due to a stress gradient and the presence of the air/ polymer/substrate interfaces. The contribution from the bulk film increases with film thickness, causing the birefringence to decrease with increasing film thickness. With the edge effect being negligible, the dielectric constant obtained from the parallelplate capacitors is purely a through-plane property and should be correlated with the through-plane refractive index.

The through-plane refractive index for both PMDA/ODA and BPDA/PPD polyimide films are plotted in Figure 6. For the PMDA/ODA films, the through-plane refractive index increases with film thickness, but the through-plane refractive index of BPDA/PPD does not change with film thickness.



Figure 6 Through-plane refractive index vs. film thickness (\bullet) PMDA/ODA; (\Box) BPDA/PPD.

These trends are consistent with the trends shown in Figure 4, in which the dielectric constant of PMDA/ODA varies with film thickness, but the dielectric constant of BPDA/PPD is relatively independent of film thickness. The optical refractive index and the relative permittivity are theoretically related by the Maxwell relation¹⁹;

$$\varepsilon' = n^2 \tag{9}$$

Application of the Maxwell relation to examine the through-plane optical and electrical properties of PMDA/ODA films is shown in Table III. The through-plane refractive index of the PMDA/ODA films is listed along with the relative permittivity calculated from eq. (9) and the relative permittivity obtained from the parallel-plate capacitor structures at 10⁵ Hz. Although both the measured and the calculated permittivities increase with film thickness, the magnitudes of the permittivities are different. The relative permittivity is a function of the total polarizability of the material due to electronic, atomic, and dipole response under an applied electric field. The laser wavelength output at 633 nm used to measure the refractive index corresponds to a frequency on the order of 10¹⁴ Hz, much higher than that used for the electrical measurements (10^5 Hz) . At the higher frequency, the dipole polarization does not have enough time to reach equilibrium. Therefore, the relative permittivity predicted from eq. (6) using the optical refractive index at 633 nm constitutes contributions of electronic and atomic polarizations but does not include the complete contribution of dipole polarization. As a result, the magnitude of the relative permittivity calculated from the optical refractive index using the Maxwell equation is smaller than is the measured relative permittivity. The difference between the predicted and the measured through-plane relative permittivity may be regarded as the dipole contribution to the total polarizability.

The results shown in Figures 4 and 6 indicate that even a slight variation in the molecular orien-

Film Thickness (Microns)	Through-plane Refractive Index	Relative Permittivity [from Eq. (6)]	Relative Permittivity (Measured at 10 ⁵ Hz)	
2.14	1.6346	2.6719	3.06	
3.71	1.6354	2.6745	3.07	
5.42	1.6361	2.6768	3.08	
7.91	1.6370	2.6798	3.09	

Table III Through-plane Properties of PMDA/ODA Films

tation with film thickness results in a detectable, although small, influence on the through-plane dielectric property of thin polyimide films. For PMDA/ODA polyimide between 2 and 8 μ m, the birefringence variation from 0.0935 to 0.0915 (Fig. 3) is accompanied by an increase in the dielectric constant from 3.06 to 3.09. The in-plane molecular orientation has also been responsible for the large difference between the in-plane and through-plane coefficient of thermal expansion found in spincoated PMDA/ODA films (33 µm/m °C in-plane vs. 129 μ m/m °C through-plane).¹⁰ Considering the optical anisotropy observed for the polyimides (0.09 for PMDA/ODA and 0.22 for BPDA/PPD), a significant dielectric anisotropy between the in-plane and the through-plane directions is expected from the Maxwell relation.

In using polyimides as interlevel dielectrics for multilevel devices, both the in-plane and the through-plane dielectric properties are critical parameters. The parallel-plate capacitor structures can be used to determine the through-plane dielectric constant, but a technique to measure directly the in-plane dielectric property of thin films is lacking.¹⁸ An estimate of the in-plane dielectric constant, however, may be obtained by applying the Maxwell relation and assuming that the dipole contribution to the in-plane property is the same as that to the through-plane property. Using the Lorentz-Lorentz method to determine the UV-VIS absorption and applying the Spitzer-Kleinmann dispersion analysis to determine the IR absorption, Boese and coworkers¹⁸ predicted the dielectric anisotropy of BPDA/PPD to be 0.7 for 10^6 Hz. In the present work, a direct application of the Maxwell relation is used to predict the in-plane dielectric constant of PMDA/ODA and BPDA/PPD from the in-plane refractive index obtained at 633 nm (Table IV). The difference between the measured through-plane dielectric constant and that calculated from eq. (6) is assumed to apply to the frequency dependence of the in-plane dielectric constant. Both polyimides exhibit significant dielectric anisotropy; the dielectric anisotropy is 0.31 for PMDA/ODA and 0.85 for BPDA/PPD. The effect of backbone rigidity on the optical and electrical properties is evident in Table IV. The anisotropy between the in-plane and through-plane properties is greater for the more rigid BPDA/PPD polyimide. The expected dielectric anisotropy should be taken into the design considerations of integrated circuit devices; the spacing between adjacent metal lines in the same plane needs to be greater than the spacing between lines directly above each other to achieve equal electrical insulation. In addition, an *in situ* technique to measure in-plane dielectric constant of thin films is still needed to determine the actual dielectric anisotropy.

CONCLUSIONS

Depending on the rigidity of the polyimide backbone, the dielectric constant can vary with film thickness.

Table IV Effect of Polyimide Backbone Rigidity on the Optical and Electrical Anisotropy of 5 μ m-thick Film

Polyimide	Kuhn Statistical Segment ^a (KSS in A)	Measured Refractive Index (Through-plane)	Measured Refractive Index (In- plane)	Measured Dielectric Constant (Through-plane)	Predicted Dielectric Constant (In-plane)
PMDA/ODA	72	1.6361	1.7283	3.08	3.39
BPDA/PPD	118	1.6110	1.8582	3.03	3.88

^a Ref. 11.

The contributing factor of this variation has been investigated by finite element analysis of the electrostatic potential within the parallel-plate capacitor structure used for the electrical measurements. The edge effect has been determined to be insignificant for the film thicknesses examined in this work. Therefore, the increase in the dielectric constant of PMDA/ODA with film thickness is attributed to molecular orientation variation in the thin films. The through-plane refractive index and the throughplane dielectric constant both increase with film thickness for PMDA/ODA polyimide, but these properties are independent of film thickness for BPDA/PPD. The through-plane dielectric constant predicted from the Maxwell equation is lower than that measured from the parallel-plate capacitors. The difference between the theoretical prediction and the experimental measurement arises due to incomplete dipole polarization at the wavelength used for the refractive index measurement.

Both polyimides examined possess significant optical anisotropy that should result in dielectric anisotropy. The through-plane dielectric constant has been measured using a parallel-plate capacitor; however, direct measurement of the in-plane dielectric constant of thin film cannot be obtained. As an approximation, the in-plane dielectric constant is estimated from the Maxwell relation by assuming that the frequency dependence of the in-plane property is equal to that of the through-plane property. Greater dielectric anisotropy is predicted for the polyimide with a stiffer backbone structure. At 10^5 Hz, the dielectric anisotropy in PMDA/ODA film is estimated to be 0.31. Having a more rigid backbone than that of PMDA/ODA, BPDA/PPD film is expected to have a dielectric anisotropy of 0.85.

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