Frequency dependence of dielectric loss in thin aromatic polyimide films

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The dielectric response of thin aromatic polyimide films with thicknesses ranging from 400 to 3×10^4 Å has been measured in the frequency range 10^4–10^9 Hz. The results show the presence of two components of dielectric polarization. One of these components exhibits a frequency dependence of the "universal" type ω^{n-1} with $n = 1.0$ within experimental error, independent of film thickness, and is attributed to hopping electrons generated from excitation of a charge-transfer complex, followed by charge separation. The other component is characterized by a very low dielectric loss and is attributed to the π-electron response of the dielectric lattice. The results indicate that film morphology plays an important role in determining the magnitude of the dielectric loss in the films, but does not affect its frequency dependence.

I. INTRODUCTION

Currently, the morphology of thin aromatic polyimide films is a subject of theoretical and experimental interest. Factor, Russell, and Toney,[1] using grazing-incidence x-ray scattering, have shown that near the surface of films of poly(N,N'-phenoxyphenyl pyromellitimide) (PMDA-ODA), the ordering of the polymer molecules is markedly enhanced, and essentially crystalline order occurs. X-ray-diffraction studies[2] have also shown that in films of poly(p-phenylene biphenyltetracarboximide) (BPDA-PDA) prepared on a substrate, the polymer chains are oriented preferentially parallel to the film plane. Several studies have investigated the effect of film morphology on photoconduction,[3] and on the mechanical[4,5] and optical[6] properties of PMDA-ODA and BPDA-PDA films. These polyimide films were found to exhibit a pronounced anisotropy in these properties, which was related to the polymer-chain orientation. So far, however, very little effort has gone into determining the effect of film morphology on their dielectric properties. Since the orientation of the polymer chains increases with decreasing film thickness,[7] the degree of anisotropy in their dielectric properties is then expected to increase.[6] Understanding the dielectric response of *thin* PMDA-ODA and BPDA-PDA films at high frequencies, up to 10^9 Hz, is therefore of general importance to their applications as insulators in semiconductor devices,[8] since the dielectric constant and dielectric loss influence the signal-carrying capacity and propagation speed of the device.

In this paper we present measurements of the dielectric response of thin films of the aromatic polyimide BPDA-PDA with thicknesses ranging from 400 to 3×10^4 Å at frequencies from 10^4 to 10^9 Hz. We find that the dielectric response of the films departs strongly from the Debye behavior. Our results show the presence of two components of dielectric polarization. One of these, which has a frequency dependence of the "universal" type ω^{n-1}, with $n = 1.0$, independent of film thickness, is attributed to electronic hopping. The other component, which is characterized by a very low dielectric loss and depends on chain orientation, is attributed to the π-electron response of the dielectric lattice. Furthermore, our investigation gives a new insight into the role of film morphology in determining the dielectric response of BPDA-PDA films.

II. EXPERIMENTAL PROCEDURE

Polyimide films were prepared by spin-coating the precursor poly(amic acid) solution in N-methylpyrrolidone onto n-type degenerate Si(100) wafers (phosphorus-doped to $\sim 5 \times 10^{19}$ cm^{-3}). To minimize contamination of the polyimide-silicon interface, a clean hydrogen-terminated surface was formed on the Si wafers immediately before the application of the poly(amic acid) solution. After drying at low temperatures (85 °C for 30 min) to evaporate solvent, thermal imidization was carried out by heating to 400 °C for 1 h in a pure nitrogen atmosphere. Polyimide films prepared under these thermal curing conditions do not exhibit isoimide formation. Polyimide film thicknesses ranging from 400 to 2.4×10^4 Å were obtained by varying the concentration of the polymer solution and the spin speeds. Film thickness was determined using optical ellipsometry measurements to an accuracy of $\pm 5\%$ for films thinner than 100 Å and less than $\pm 1\%$ for thicker films. Metal-polyimide-silicon (M-PI-Si) and metal-silicon (M-Si) structures were then prepared by depositing 5000-Å aluminum, copper, or gold films simultaneously onto the polyimide films and on bare Si wafers through a metal mask defining areas of 2.026×10^{-3}, 5.186×10^{-3}, and 50.645×10^{-3} cm^2. Ohmic contacts to the backside of the Si wafers were accomplished by depositing a 5000-Å-thick Al film. The metal films were deposited using electron-beam evaporation in a pressure of $\sim 1 \times 10^{-7}$ Torr at a rate of 10 Å/s, with the Si wafers kept at room temperature.

Electrical measurements were performed at room temperature in the frequency range 10^4–10^9 Hz with a signal amplitude ranging from 0.1 to 1.25 V. In the frequency range 10^4–10^6 Hz, measurements were made with a Hewlett-Packard (HP) model 4192A impedance analyzer

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and in the range $4 \times 10^5 - 10^8$ Hz with an HP model 4193A vector impedance meter with a modified probe tip accurate to $\pm 3\%$ of magnitude and phase angle readings and with a test fixture designed to minimize residual inductance L, capacitance C, and resistance R (Fig. 1). Good agreement was obtained in the overlapping region. The impedance of the probe and test fixture (shown in Fig. 1 within the dashed lines) was first measured in the frequency range $10^4 - 10^8$ Hz, and the values of L, C, and R were calculated. These values were found to be in close agreement with those for the probe, indicating that the test fixture was not contributing significantly to the residuals. The M-Pl-Si sample was modeled as two resistor-capacitor circuits in series, one being the polyimide film and the other the Si substrate, as shown in Fig. 1. With only the M-Si sample in the circuit, the total impedance was then measured in the frequency range $10^4 - 10^8$ Hz and the impedance of the Si substrate was determined by subtracting the contribution of the probe to the measured value. This was followed by again measuring the total impedance in the same frequency range with now the M-Pl-Si sample in the circuit. The impedance of the polyimide film was then determined by subtracting the contributions of the probe and the Si substrate to the measured value. Finally, the values of the parallel resistance R_p and the parallel capacitance C_p were calculated for the polyimide film using the real and imaginary parts of its impedance.[9]

In order to extend our measurement to 10^9 Hz, a new test fixture was designed which included a microstrip transmission line to maintain a 50-Ω impedance from the SMA connector to the probe tip. Time-domain reflectometry measurements verified that the test fixture would be useable up to frequencies of 1.3×10^9 Hz. As a further verification, this test fixture and an HP model 3577A network analyzer were used to make measurements in the frequency range $10^6 - 2 \times 10^8$ Hz. These measurements were in good agreement with those made with the previous test fixture and the vector impedance meter. Measurements in the frequency range $1.3 \times 10^8 - 10^9$ Hz were then made using an HP 8720B network analyzer and again were in good agreement with those previously made in the overlapping region.

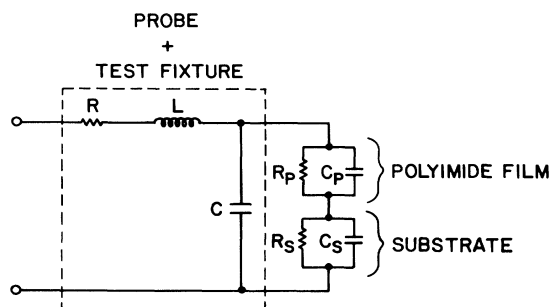We found that a key ingredient in making measure-

ments with a network analyzer is a good broadband 50-Ω load that was designed for calibration purposes. The calibration procedure included using a broadband load, a short, and an open to remove the effects of test-fixture inductance, capacitance, and resistance, so that only the sample parameters were measured. Also, the resolution bandwidth and sweep speed were selected to minimize the effects of noise and relaxation time on the measurements.

III. RESULTS

The data are presented as the real and imaginary parts of the complex dielectric permittivity,

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) ,$$

plotted against the circular frequency $f = \omega / 2\pi$, or alternatively as the frequency-dependent conductivity,

$$\sigma(\omega) = \sigma_0 + \sigma'(\omega) = \sigma_0 + \omega \epsilon''(\omega) ,$$

where σ_0 is the dc conductivity. In Fig. 2 we show the frequency dependence of the ac conductivity $\sigma'(\omega)$ of films with different thicknesses at room temperature. The top electrodes were Al. For samples with top electrodes of Cu or Au, the data are very similar to those shown in Fig. 2. It is evident that in the frequency range $10^4 - 10^8$ Hz, $\sigma'(\omega)$ follows the empirical law[10]

$$\sigma'(\omega) \propto \omega^n , \tag{1}$$

with the exponent $n = 1.0$ within experimental error. This corresponds to the variation of the dielectric loss given by

$$\epsilon''(\omega) \propto \omega^{n-1} . \tag{2}$$

Thus, for $n = 1.0$, this gives a frequency-independent loss, independent of film thickness, as shown in Fig. 3(a). As can also be seen from Fig. 3(b), the capacitance remains constant in the same frequency range for all film thicknesses, giving a frequency-independent ratio of the
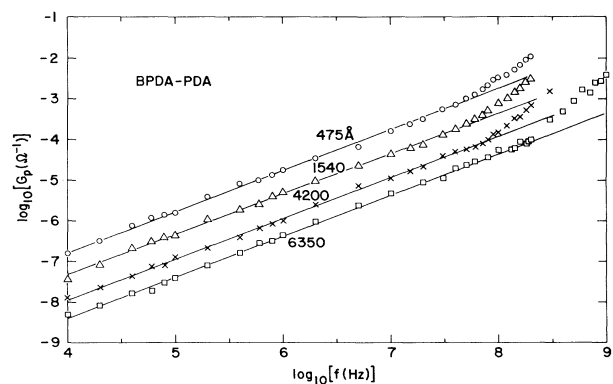

FIG. 1. Equivalent circuit used to calculate the values of the parallel resistance R_p and parallel capacitance C_p of the polyimide film.

FIG. 2. Frequency dependence of ac conductivity G_p of BPDA-PDA films with different thicknesses at 295 K. The solid lines have unit slope. The corresponding dc conductivity σ_0 of the films is several orders of magnitude lower than the ac conductivity. Sample area A is 5.186×10^{-3} cm^2.
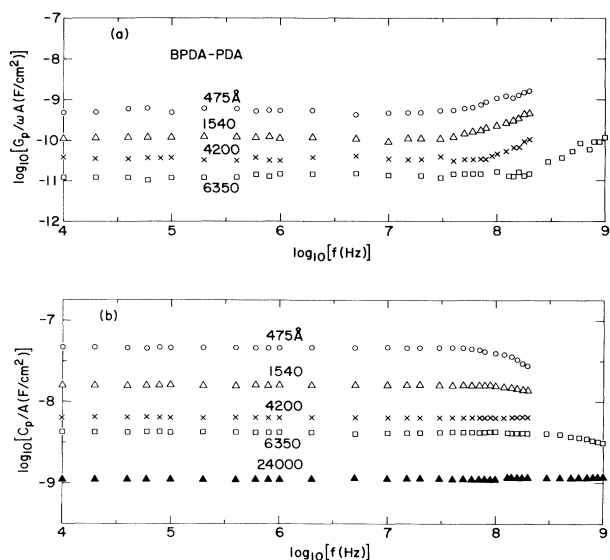
FIG. 3. Frequency dependence of (a) G_p/ω and (b) C_p per unit area for films with different thicknesses. Except for an appropriate change in scale, these correspond to the imaginary and real parts of the complex dielectric permittivity. Sample area A is 5.186×10^{-3} cm^2.

imaginary and real parts of the complex permittivity, which is consistent with Kramers-Kronig relations.[11] This behavior is in complete contrast to the classical Debye response for which this ratio is equal to $\omega\tau$, where τ is the appropriate relaxation time. This also indicates that the behavior observed here is a "true" volume response which does not depend on interfacial processes at the electrodes. This is further supported by the invariance of the measured parameters with respect to changes of the applied signal amplitude. In addition, the measured parameters are not affected by changing the metals used for electrodes—Al, Cu, or Au—which represent a wide range in metal electronegativity. This clearly rules out the presence of a contact barrier layer.[12] Data obtained for structures of the type M-Pl-M were also found to be very similar to those shown in Figs. 2 and 3. We note, however, that the magnitude of the dielectric loss at any given frequency increases with decreasing film thickness.

Above 10^8 Hz, the experimental data show a departure from the frequency-independent response, which becomes more pronounced as the film thickness is decreased (Fig. 3). Since a small amount of circuit inductance was always present, the effect of sample capacitance on the measurements had to be considered in order to determine whether this departure was due to circuit effects. By decreasing the sample capacitance as the film thickness is decreased, the resonance frequency of the circuit could be increased to well above 10^9 Hz, thus greatly improving the accuracy of the measurements. It should be emphasized here that measurements at frequencies close to or above resonance are not meaningful. The effect of sample capacitance is clearly demonstrated by the data in Fig. 4, which show the frequency dependence of the ac

conductivity, the dielectric loss, and the capacitance for a film thickness of 6350 Å in the frequency range 10^8–10^9 Hz. Based on these results, we therefore conclude that the observed departure is indeed due to circuit effects and that the frequency-independent behavior holds up to 10^9 Hz. This is consistent with the results previously report-
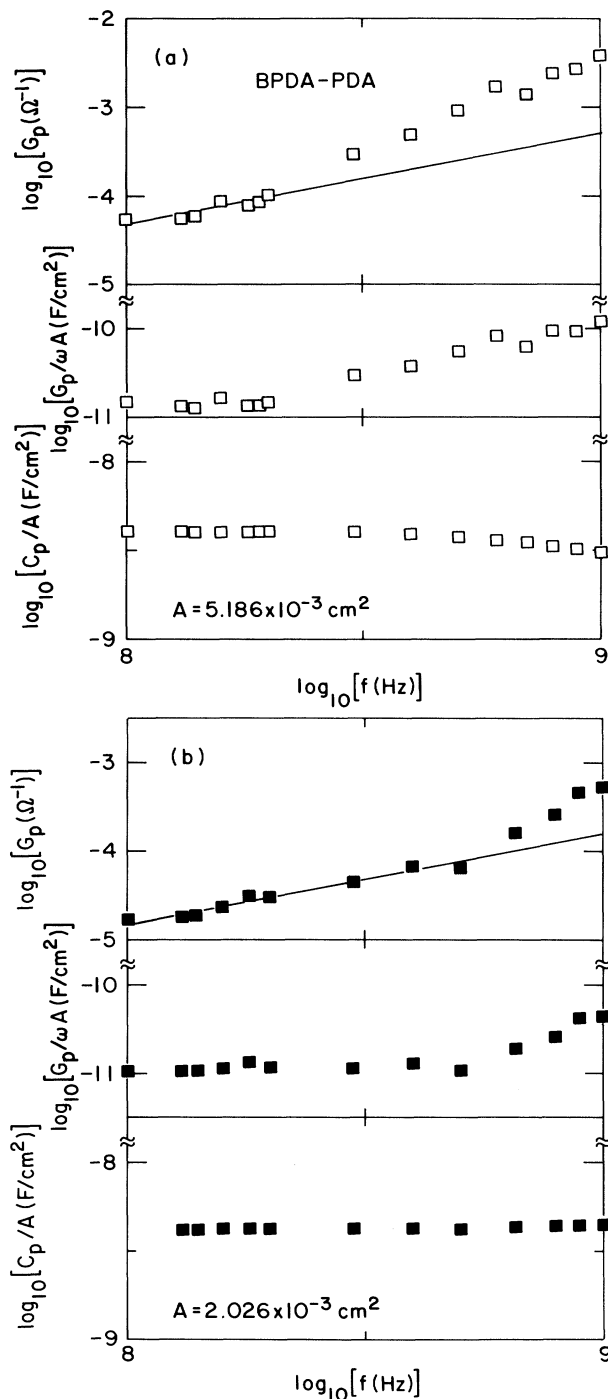

FIG. 4. Effect of sample capacitance on the frequency dependence of G_p, G_p/ω, and C_p per unit area for a film thickness of 6350 Å. Sample area A is (a) 5.186×10^{-3} and (b) 2.026×10^{-3} cm^2.

ed for a wide range of dielectric materials regardless of their physical, chemical, and geometrical properties and also regardless of the nature of the electrically active species responsible for polarization, whether electrons, ions, or dipoles.[10,11]

IV. DISCUSSION

The frequency dependence of the ac conductivity observed here suggests the dominance of a hopping mechanism[10,11] in which charge carriers move by hopping between localized states in BPDA-PDA polyimide. The frequency-independent behavior (2) cannot be explained on the basis of a distribution of relaxation times, since, as argued by Jonscher,[13] it is difficult to see how the required range of τ, extending over many decades of time, can be justified in any particular system, and also to understand how the same power law should result, even though with different values of the exponent n, for a large number of essentially dissimilar materials. To obtain some insight into the nature of the localized states responsible for the hopping mechanism, we begin by assuming that conjugation between dianhydride fragments and diamine fragments along the polymer chain is negligible. This has been shown to hold for PMDA-ODA (Ref. 14) and is assumed to be true also for BPDA-PDA. The high degree of localization of states is attributed to the torsional angles between the aromatic planes along the polymer chain so that the π orbitals overlap only insignificantly.[15] This view is supported by the results of experimental studies,[14,16] using ultraviolet and x-ray photoemission, and inverse photoelectron spectroscopies.

Many aromatic polyimides are known to absorb at about 600–700 nm. This absorption has been attributed to a charge-transfer complex[17] (CTC), originating from the interaction between diamine fragments (acting as donors) and dianhydride fragments (acting as acceptors). This charge transfer can be described as an overlap of the highest occupied molecular orbital of the diamine-fragment donor (HOMO) with the lowest unoccupied molecular orbital of the dianhydride-fragment acceptor (LUMO), as shown schematically in Fig. 5. This orbital overlap, however, will occur only if the involved orbitals are in appropriate sterical configuration to each other. It can be seen from Fig. 5 that the charge-transfer orbital overlap requires chain crossing, which is possible only in the amorphous phase of the polyimide. That the CTC formation is restricted to the amorphous region has previously been pointed out by Freilich and Gardner.[17] In the crystalline phase CTC formation cannot occur because the chains are arranged parallel to one another, and donors are lined up with donors and acceptors with acceptors. This model of the CTC is consistent with measurements of the pressure dependence of photoconduction in semicrystalline polyimides.[18]

Excitation of a charge-transfer complex and subsequent charge separation, i.e., complete transfer of an electron from the donor HOMO into the acceptor LUMO can occur under the influence of the applied electric field, and if the CTC is located adjacent to a crystal, the separated electron can be injected into the crystal
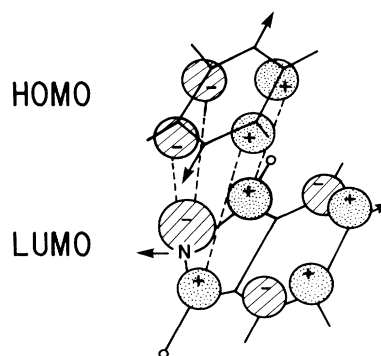

FIG. 5. Schematic of the charge-transfer complex between the BPDA imide ring LUMO (on the bottom) and the PDA HOMO (on the top). The arrows indicate continuation of the chains. Note that the chains must cross to allow the formulation of CTC.

LUMO's. In the amorphous region the dianhydride-fragment LUMO's are variously spaced and in varying energetic positions making the hopping process much less effective. Thus we are dealing here with a situation where charge carriers are generated in the amorphous regions of the films and move in the crystalline regions by hopping between aligned acceptor LUMO's which are spaced at equal distances and have the same energies. It is important to point out that the acceptor LUMO's are localized states and do not overlap with LUMO's of adjacent chains.[15] When an acceptor LUMO is occupied by an electron, its energy level is lowered relative to its value when unoccupied due to the relaxation of the surrounding lattice. (The acceptor now becomes ionized,[19] giving rise to a modification in the lattice vibrational frequencies.) The hopping between crystal acceptor LUMO's having the same energies can then be considered to occur in three stages: (1) excitation of the electron into a virtual state corresponding to the unrelaxed energy of the empty state, (2) tunneling transition, and (3) relaxation of the electron at the newly occupied site. Here the polarization relaxes relatively slowly in comparison with the time taken by the tunneling process (2), as evidenced by the strong dispersion of ac conductivity with frequency (Fig. 2). The energy lowered due to the relatively slow relaxation process (3) thus constitutes an irreversible loss associated with every electron transition. Our results show that in the frequency range studied, this loss of energy is independent of frequency regardless of the degree of crystallinity in the films. This is consistent with the hopping model proposed by Jonscher[10,11] and should be contrasted with the frequency-dependent loss normally associated with hopping conduction in nonpolarizable media, which gives rise to characteristic loss peaks as a function of frequency. It has recently been shown[7] that the degree of crystallinity in BPDA-PDA films increases markedly as the film thickness is decreased below ~1000 Å. The increase in the magnitude of the dielectric loss with decreasing film thickness can then be understood in terms of additional hopping sites becoming available with increasing degree of crystallinity in the films.
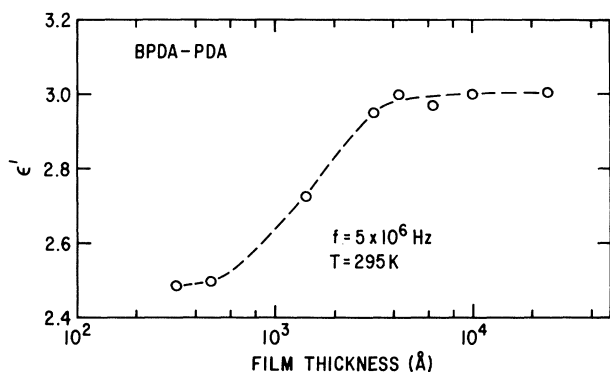
FIG. 6. Thickness dependence of the dielectric constant measured perpendicular to the film plane.

This model of localized electron hopping in the crystalline domains is also consistent with the following experiment: In order to generate excess hopping charge carriers, measurements were made under the combined influence of the applied electric field and ultraviolet light. Light was found to increase the dielectric loss, with the increase becoming more pronounced with decreasing film thickness regardless of the nature of the top electrode.[20] The loss in the presence of light, however, still showed the same frequency-independent behavior. Clearly, the light leads to increased charge separation,[17] thus producing excess electrons which can be injected into crystal acceptor LUMO's. The fact that the frequency dependence of conductivity is not influenced by light indicates that the dark carriers originate from charge-transfer complexes.

Let us now consider the contribution to the overall dielectric polarization arising from the π electrons. Here the contributions of π electrons and hopping electrons are additive. In the amorphous phase the dielectric parameters ϵ' and ϵ'' are determined by the π-electron polarization of the aromatic planes, which depends on the chain orientation; the contribution arising from the hopping electrons is negligible. In the frequency range studied here, the dielectric loss associated with the π-electron polarization is extremely low since their relaxation frequency is on the order of 10^{15} Hz, as can be seen from the data in Figs. 3 and 4 for the thicker films in which the degree of crystallinity is substantially lower.[7] Since the polarization perpendicular to the π-electron clouds has been shown[21] to be smaller than in the plane and because films of BPDA-PDA prepared on a substrate exhibit a pronounced orientation of chain axes parallel to the film plane,[2,22] the polarization perpendicular to the film plane

is smaller than the in-plane polarization. Because chain orientation also increases with decreasing film thickness,[7] the dielectric constant perpendicular to the film plane is therefore expected to decrease with film thickness, assuming that the in-phase part of the polarization caused by the hopping electrons makes a relatively small contribution to the overall dielectric constant. This is indeed the case here, as shown in Fig. 6. The in-plane dielectric constant is then expected to increase with decreasing film thickness, resulting in anisotropic dielectric properties, consistent with recent experiments.[6]

As mentioned earlier, the degree of crystallinity in the BPDA-PDA films also increases markedly with decreasing film thickness. This leads to an increase in the overall dielectric loss perpendicular to the film plane with decreasing film thickness due to the increasing contribution of the hopping electrons. On the other hand, the in-plane hopping loss is very low[20] since in a crystal the distance between dianhydride-fragment LUMO's is considerably larger along the chain than in the interchain direction, thus resulting in a very low overall in-plane dielectric loss. It is therefore evident that while film morphology plays an important role in determining the magnitudes of ϵ' and ϵ'', it does not affect their frequency dependence.

V. CONCLUSION

We have presented measurements of the dielectric response of thin BPDA-PDA films which show the presence of two components of dielectric polarization. One of these components has a frequency dependence of the "universal" type ω^{n-1}, with $n = 1.0$ within experimental error, independent of film thickness, and is attributed to hopping electrons generated from charge-transfer complexes. The other component is characterized by a very low dielectric loss and is attributed to the π-electron response of the dielectric lattice. The observed dependence of the magnitudes of ϵ' and ϵ'' on film thickness is related to increased chain orientation and degree of crystallinity with decreasing film thickness. However, the frequency dependence of ϵ' and ϵ'' is independent of film morphology.

ACKNOWLEDGMENTS

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