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Electrical Properties of Multilayers Based on Zirconium Phosphate/Phosphonate Bonds

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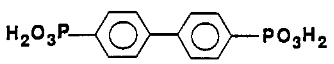
Dielectric constant, resistivity, and dissipation factors at 100 Hz to 1 MHz are reported for three zirconium phosphate/phosphonate-based self-assembled multilayers: Zr biphenylenediphosphonate, a polar azo dye multilayer, and Zr pyrophosphate, all deposited on gold. Experiments with mercury drop top electrodes indicate that these materials are good insulators, with dielectric constants of 3–6 when dry. The magnitudes and frequency dependences of the constants are greatly altered when the layers are hydrated. While the dielectric strength of the materials is sufficient for applications including electrooptics, the porosity of the films to water and evaporated metals needs to be reduced before practical use may be considered.

Introduction

Self-assembly is a technique whereby stable, ordered films may be simply prepared from chemical components containing a wide variety of functional groups.[1] Layers of material are built up by directly applying solutions of the components to suitably primed substrates. One-layer-at-a-time multilayer deposition may be achieved for multicomponent materials by selecting each component so that its terminal functional group, which becomes a surface group on deposition, selectively binds or may be modified to bind the subsequently deposited component. Each component is then deposited alternately and repeatedly from separate solutions.

We are currently investigating multilayers held together by metal phosphate/phosphonate interactions.[2] Many of our envisioned applications of these materials demand that the layers possess specific electrical characteristics. Besides those applications in which the layers might have direct electronic functions such as insulation, other intended uses, such as in electrooptics, indirectly depend on conductivity or dielectric properties. It is therefore important to ascertain the electrical behavior that could be expected from these materials in general. Furthermore, even a cursory electronic characterization of this material class would be expected to provide valuable information as to the composition, morphology, and coherence of the layers.

In this study, we probe the electronic properties of three specific multilayers. The first is composed of the zirconium salt of 4,4′-biphenylenediphosphonic acid (1), a prototypical rigid rod, which is a possible spacer layer for multilayers designed to exhibit long distance electron transfer. The second is the azo dye 2 phosphate/phosphonate multilayer which constitutes our recently disclosed[3] nonlinear optical multilayer. The third is zirconium pyrophosphate, a known layered compound,[4] which represents the first all-inorganic multilayer deposited by self-assembly techniques.



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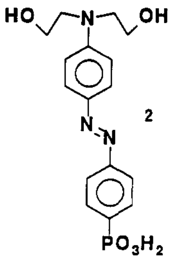

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The three materials were deposited on gold and examined primarily in metal–insulator–metal (MIM) configurations with mercury drops as top contacts. All three are essentially insulating but display changed electronic responses upon thermal aging and dehydration. Cured silver epoxy was demonstrated as an alternative contact in one case. However, attempts to deposit metal directly either by sputtering or by electroless plating led to short circuits, indicating that the multilayers as deposited are not perfectly coherent. Thus, more intensive research will be necessary either to achieve denser packing of the layers in the plane parallel to the substrate or to build metal films more selectively at the top interface of the films.

A preliminary result from this study has been reported.[5] Subsequent to that report, a parallel study of alkylidenediphosphonic acid layers appeared.[6] In that study, dielectric constants similar to ours were reported for related multilayers with long-chain aliphatic components. Langmuir–Blodgett films, which are preassembled at the air–water interface before deposition, have been considered for some of the applications listed above and have also been characterized in MIM structures.[7] These latter films are prepared using much more arduous techniques than those described here and are unstable to solvents and high temperatures. The Zr-based multilayers have been shown

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to maintain their integrity even in the presence of polar solvents at elevated temperature.[2,3]

Sample Preparation

Gold substrates were prepared by evaporation of titanium (ca. 200 Å) and gold (ca. 2000 Å) onto cleaned silicon wafers. After determination of ellipsometric substrate constants, the gold wafers were immediately immersed in a solution of 8-mercaptooctylphosphonic acid[2] (1.5 mM in ethanol) for 3 days, washed with EtOH and spun dry. The phosphonic acid surface was treated overnight with $ZrOCl_2$ (5 mM in H_2O, weighed as the octahydrate), washed with deionized water and spun dry. The zirconated surface was then treated with phosphorus acids as described below. Thicknesses vs layer number are plotted in Figure 1.

On the basis of optimization studies done on primed silicon wafers, **1** was deposited on a zirconated surface by immersion of the substrate in a 1 mM solution of **1** in 5% H_2O/95% DMSO at 75 °C for 30 min. The sample was washed by immersion in hot (75 °C) DMSO for 15 min, rinsed with EtOH, and spun dry. The phosphonic acid surface was zirconated by immersion in a 5 mM solution of $ZrOCl_2$ in H_2O for 10 min at room temperature, rinsed with H_2O and spun dry. Repetition of these steps resulted in a multilayer assembly that we terminated with a final deposition of **1**. Films of up to 25 layers were prepared in this manner, with a thickness of 16 Å/layer, in good agreement with theoretical expectation.[2]

For deposition of the azo dye, a gold substrate with a primed zirconated surface was immersed in a solution of 4-(4-(*N*,*N*-bis(2-hydroxyethyl)amino)phenylazo)phenylphosphonic acid (**2**, 1.5 mM in 5% H_2O/95% EtOH) at 78 °C for 20 min. After a 10 min wash in hot (78 °C) EtOH and EtOH rinse, the sample was spun dry. The hydroxylated surface was then phosphorylated by immersion in an anhydrous acetonitrile solution of $POCl_3$ (0.2 M)/2,4,6-collidine (0.2 M) for 20 min at room temperature, washed with H_2O and spun dry. (The phosphorylation solution was prepared freshly each day, since a discoloration was noted from either the self-condensation of the solvent or decomposition of the collidine.) Zirconation was accomplished by immersion of the substrate in 5 mM aqueous $ZrOCl_2$ for 5 min at room temperature, rinsing with H_2O and spinning dry. Repetition of these three steps resulted in multilayer formation. A 20-layer sample was prepared, terminating with the dye. The apparent thickness/layer was approximately 24 Å, somewhat higher than the 16 Å/layer obtained in a parallel experiment on Si, where both substrates were treated in identical solutions for identical lengths of time, and which has previously been obtained for this compound on Si.[3] Since the priming procedure for Si probably does not result in as uniform an initial layer of phosphonate as does the thiol on gold, layers on gold may be more densely packed from the start. Alternatively, the discrepancy may reflect ellipsometric uncertainties.[8]

We found that deposition of $ZrOCl_2$/pyrophosphoric acid multilayers could be carried out more quickly than was the case for the above two compounds. A zirconated gold substrate was immersed in a 1 mM solution of **3** for 50 s at room temperature, followed by a 10-s wash. A 50-s immersion in 5 mM $ZrOCl_2$ solution and a 10-s wash completed the layer. Repetition of these steps resulted in multilayer deposition. Either H_2O or MeOH could be used as the solvent, with one of them selected for all the steps

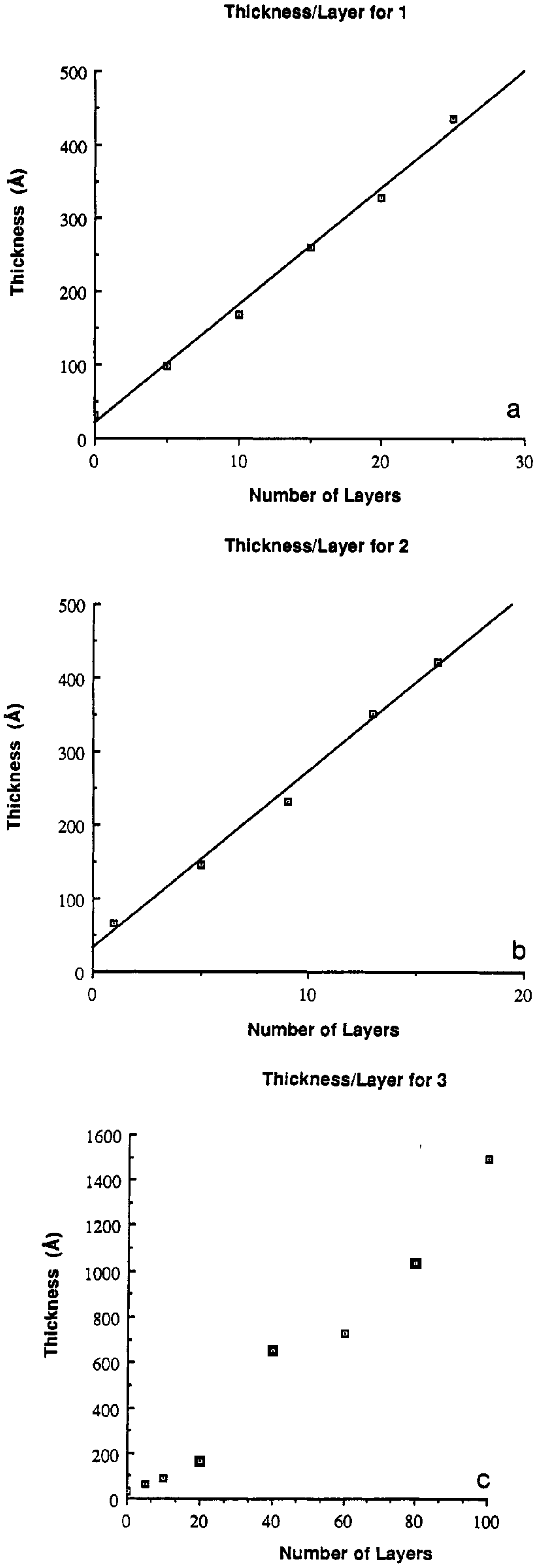

Figure 1. Thickness (Å, ±5%) vs layer number for (a) **1**, (b) **2**, and (c) **3** deposited from aqueous solutions. The lines are best fits to the data. The intercepts represent the apparent ellipsometric thicknesses of the anchor layers plus one layer of Zr.

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in a given sample preparation. Using this procedure, samples of up to 100 layers were prepared. Layer thickness was monitored every 20 layers by ellipsometry. The thickness/layer increased from 7 to 15 Å in going from 20 to 100 layers, suggesting that nucleation occurred with >20 layers. The 100-layer sample was slightly cloudy but not grossly rough. Scanning electron microscope observations of films of this material show 5% of the area of a 20-layer sample covered with an anomalously thick deposit, but much greater fractional coverages as the layer number increased. Zirconium and phosphorus deposition monitored by X-ray fluorescence also increased nonlinearly above this thickness. We do not know the precise morphology or composition of this excess solid, but the X-ray fluorescence data indicate that it contains both Zr and P.

Electrical contacts to the 100-layer sample with Hg were open circuits, perhaps because the Hg drop was resting on the highest points of a rough surface rather than intimately contacting an entire layer. The high surface tension of Hg would prevent it from reaching into "valleys" of the surface topography. This was not the case for the organic layers, on which atomic force microscopy indicates nearly conformal coverage of the gold substrates and <2% of the area taken up by particulates.[9]

Electrical properties under 10 mV rms voltage were measured as a function of frequency, assuming resistance and capacitance in parallel, with a Hewlett-Packard Model 4284A LCR meter using a gold pin pressed onto the underlying gold surface as a contact to the bottom electrode and a gold wire attached to a mercury drop resting on the multilayer as a top electrode. The drop was assumed to make a circular contact with the sample. The contact diameter was measured using a micrometer attached to a goniometer. The thickness was determined by ellipsometry, as previously described.[2] A refractive index of 1.54 was assumed,[2] although variation of the assumed index over ±0.2 changed the calculated thicknesses by <10%, of the same order as the experimental imprecision. Dc experiments were performed with a Keithley Model 617 programmable electrometer and voltage source using the same contacts. The multilayer film was assumed to be the dominant capacitor in the circuit, as discussed previously.[6] Although we have no convenient way to measure the contact resistance or capacitance, the fact that the capacitance decreases as layer thickness increases over 10–25 layers of **1** and that dehydration of the films gave such dramatic changes in electrical properties helps validate the assumption.

Results and Discussion

Table I lists key resistivities ρ, dielectric constants ϵ, and dissipation factors D obtained for the three materials. All samples listed in the table were 20–25 layers thick. At least four determinations of capacitance and D were used for each data point, giving uncertainties of 10% and 20%, respectively. Low-frequency resistivity was chosen for listing to indicate an approach to the dc value, and thus represents a lower dc limit.[10] High-frequency capacitance, on the other hand, indicates the upper limit of ϵ without contributions from polarization involving molecular migration.

Table I. Electrical Properties of Zr Multilayers

core material	ρ (100 Hz)^a	ϵ (1 MHz)	D (1 MHz)	conditions
1	2×10^9	12	0.14	air dried
1	8×10^9	4.9	0.14	50 °C vacuum 1.5 h
1	1×10^9	5.2	0.07	100 °C vacuum 1.5 h
1	4×10^{10}	6.3	0.05	100 °C vacuum 16 h
2	6×10^8	12	0.14	air dried
2	2×10^9	5.7	0.06	75 °C vacuum 3 h
2	9×10^9	6.2	0.05	75 °C vacuum 16 h
3^b	$[>10^9]^d$	3.4	0.16	air dried
3^c	9×10^9	11	0.25	immediately after deposition
3^c	5×10^9	2.7	0.04	100 °C vacuum 30 min
3^c	4×10^9	6.3	0.08	40 °C, 100% rel humidity, 3 h^e
3^c	2×10^{10}	8.4	0.08	immediately after deposition of 1 additional layer^e

^{a} Ω cm. ^{b} Deposited from H_2O. ^{c} Deposited from MeOH. ^{d} Too resistive to measure at 100 Hz, limit based on 1-kHz value. ^{e} Dried sample rehydrated.

For **1**, samples of <15 layers were marginally insulating, with mercury drops frequently sticking to the samples and leading to short circuits. Above 15 layers, insulating behavior was more reliable, but there was a large dispersion in ϵ and D, as illustrated in Figure 2. An apparent maximum is observed in D in the kilohertz range. The ac resistance varied strongly with frequency, as illustrated in Figure 3, where the log–log treatment is valid for systems with high dc resistance.[10] Most of the samples examined showed similar ρ vs f behavior, indicating that the ac resistance is dominated by the capacitive, rather than the resistive equivalent parallel circuit element at the frequencies monitored, and consistent with the qualitatively similar variation in C and D with frequency observed among the samples. Ideal capacitative behavior would have led to low, constant values for ϵ and D as functions of frequency.

The apparent ϵ for **1** increased from 3.3 to 5 as thickness increased form 10 to 25 layers. Two factors could have been responsible. The surface roughness of the gold substrate was on the order of 50 Å as determined by atomic force microscopy, so close lateral or diagonal contacts between the two electrodes could artificially increase the capacitance of very thin layers. Trapped water could have increased the minimum attainable ϵ in dried thick layers.

The onset of dielectric breakdown (nonohmic behavior) in this material (10-layer sample, 130 °C vacuum oven 0.5 h) was 750 kV/cm, and the measured dc ρ was 10^{13} Ω cm, in reasonable agreement with the value obtained by extrapolating a plot of $1/\rho$ vs frequency to zero frequency. After brief heating under vacuum, ϵ and D were lower and the dispersion was less, as shown in Figure 2. After prolonged heating, the high-frequency ϵ increased slightly. This is consistent with less ionic conductivity from trapped aqueous ions as water is removed but also may reflect

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[9] Details will appear in a separate paper. Schilling, M. L.; Katz, H. E.; Stein, S. M.; Shane, S. F.; Wilson, W. L.; Ungashe, S. B.; Buratto, S.; Taylor, G. N.; Putvinski, T. M. *Langmuir*, accepted for publication.

[10] The value of $1/R$ for a capacitive circuit is $(2\pi fCD) + 1/R_{dc}$. If R_{dc} is very high, then $-\log R$ is the sum of the logs of several terms and $\log f$. See: Bartnikas, R., Eichhorn, R. M., Eds.; *Engineering Dielectics*; ASTM: Philadelphia, 1983; Vol. IIa, pp 57–58. The slope of the log–log plot would be −1 if C and D were frequency independent. Because this is not the case here, the slope deviates from ideality. At some frequency below 100 Hz, in a range not covered by these experiments, the $1/R_{dc}$ term becomes dominant. This would be manifest as a flattening of the log–log plot near zero frequency, and $1/R_{dc}$ would be the intercept of a conventional plot of $1/R$ vs f.

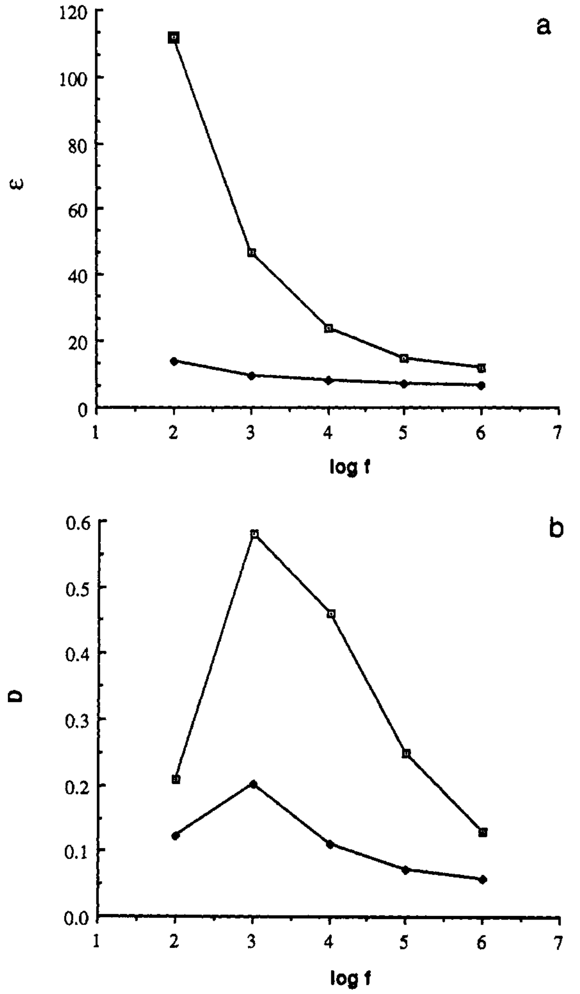

Figure 2. Plots of (a) ϵ, ±10% and (b) D ±20% vs log frequency [f] for 25 layers of 1, air-dried (open squares) and heated under vacuum (filled diamonds).

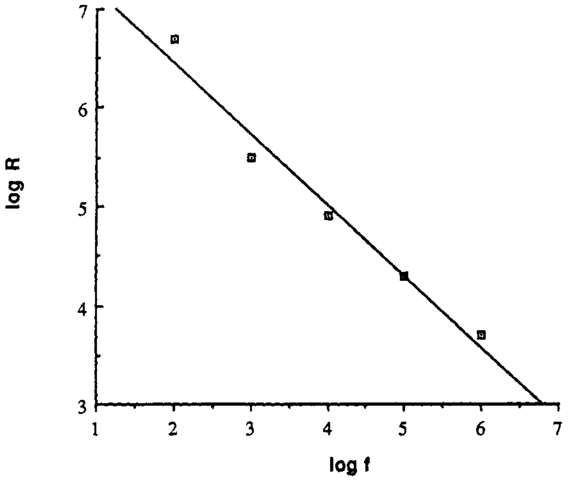

Figure 3. log–log plot of resistance vs f for 25 layers of 1, air dried.

increased penetration of mercury into pores vacated by evaporated water. The effects of hydration and dehydration are primarily observed at lower frequencies and were not considered in a contemporaneous electrical study of aliphatic multilayers.[6]

The azo dye **2** behaved in a manner consistent with what was found for **1**, despite the greater polarity and numerous basic sites of **2**. The limiting ϵ and ρ approached constant and reasonable values as drying occurred, first in air and then under vacuum at elevated temperature. The dc ρ was 10^{12} ohm cm. The onset of dielectric breakdown was 1–2 V on a 20-layer sample, with catastrophic breakdown at 10 V, corresponding to 2.5 MV/cm applied field, suitable for electrooptic applications.

Layers prepared from **3** in water or MeOH were initially more resistive than the organic multilayers and had low limiting ϵ but very high ϵ at low frequency and fairly high D. The onset of high D and the maximum in D move to lower frequency as samples are dried under vacuum, and back to high frequency as samples are rehydrated. The data points for the sample on which an additional layer was grown from MeOH indicates that this process increases the hydration of the sample to a greater degree than does exposure to humid air. The effect of thickening the sample by one layer should have been negligible. This reversibility, evident from the graphs in Figure 4, supports the hypothesis presented above for **1** concerning the influence of included water on the low-frequency behavior. Drying causes the hydrated domains to become smaller and less connected. Ionic mobility is lessened, and ionic polarization requires longer time scales. Thus, the transition in D moves to lower frequency on drying. The reverse occurs on rehydration; mobility increases, and polarization occurs at higher frequency.

The pyrophosphate layers were amenable to examination using silver epoxy electrodes. While these electrodes formed contacts without short circuiting, the measured capacitances were only half of those obtained from Hg contacts of the same size. Thus, only half of the epoxy–multilayer interface could be considered to be an intimate conductor–insulator contact. On the other hand, attempts to deposit metal electrodes on any of the three materials either by evaporation of gold or by electroless plating of nickel invariably gave short circuits. There are apparently pores of molecular dimensions through which energetic metal atoms or growing filaments of electroless metal can penetrate but that are not wet by silver epoxy. Furthermore, the interfacial capacitance of the mercaptooctylphosphate anchor layer on gold was unaffected by 20 layers of **2** or **3** when examined by cyclic voltammetry through a pool of 1 M aqueous KCl.[9] Thus, the morphology of these layers is extremely porous, allowing contact from the outer solution to a nearly continuous conducting region near the anchor layer. The layers are a poor barrier to aqueous electrolyte penetration as presently constituted, despite their apparently excellent inherent resistivity. This is in contrast to the behavior of Hg drops, whose high surface tension precludes penetration into the material and the establishment of conductive paths.

Conclusions

Three layered Zr phosphate–phosphonate materials have been electrically characterized as functions of frequency and state of hydration. All three materials were similarly insulating. The two organic-based multilayers displayed similar ϵ and breakdown fields, both of which would be appropriate for use in electrooptics. The pyrophosphate-based material, the first all-inorganic self-assembled multilayer, had a significantly lower ϵ than did the organics. All of the electrical properties were dominated by hydration effects, suggesting that ionic mobility, rather than electronic conduction or polarization, determines the dielectric behavior of these materials. The difference in ϵ between the organic and inorganic materials

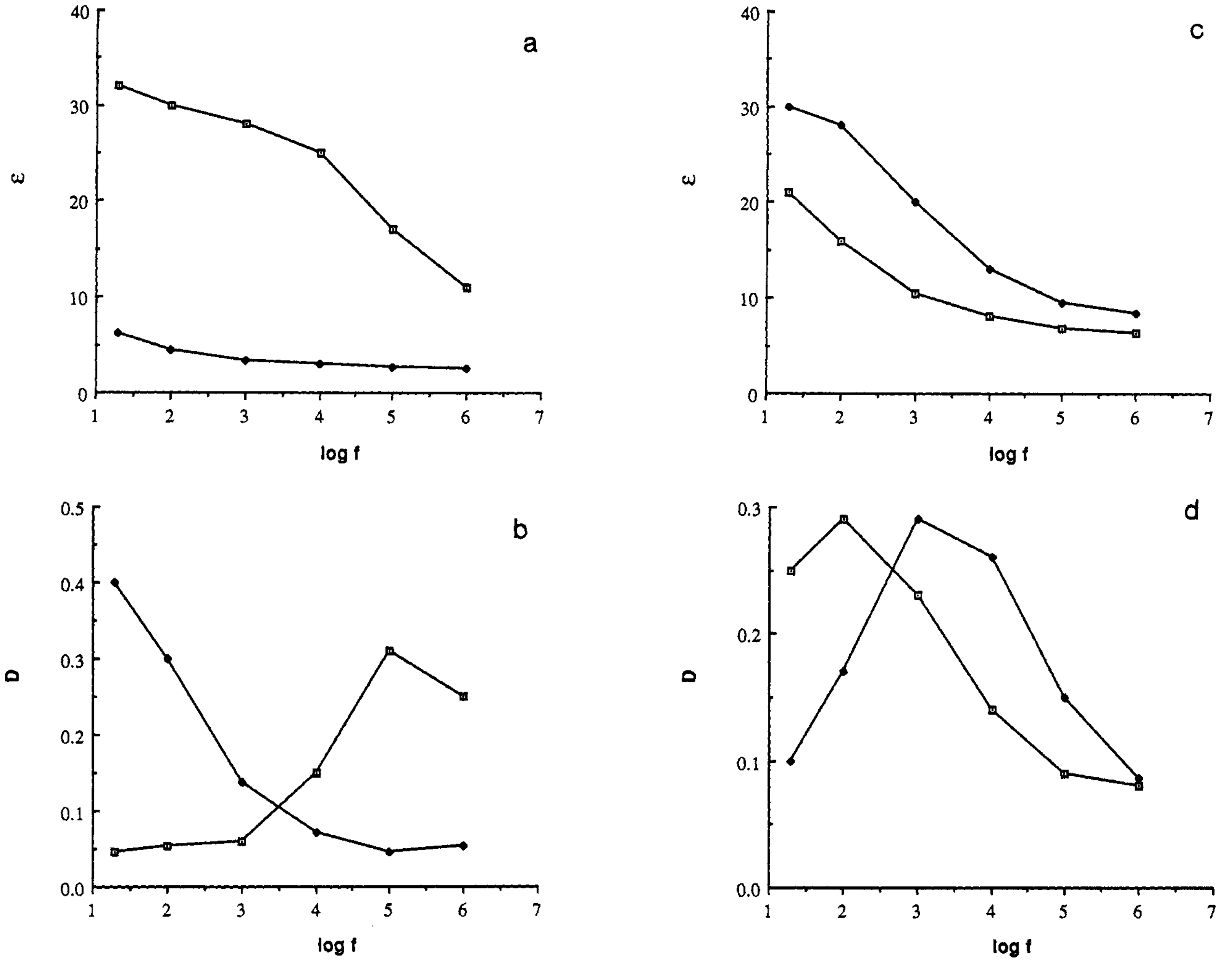

Figure 4. Plots of (a, c) ε and (b, d) *D* vs log *f* for 15 layers of **3** deposited from MeOH, showing effects of dehydration and rehydration. For (a, b): open squares, as deposited; filled diamonds, dried at 80 °C for 16 h. For (c, d): open squares, dried sample rehydrated at 40 °C in humid air for 3 h; filled diamonds, immediately after one additional layer was deposited onto the rehydrated sample from MeOH, with the Zr solution 40 mM in H_2O.

may simply reflect differences in pore sizes and shapes, and the tenacity with which they hold water and ions during "drying" procedures. Another factor which could contribute to the difference is the density and polydenticity of PO bonding in the multilayers; the pyrophosphate may form a more rigid bonding network than do the organics.

The dielectric constants (3–6) and dissipation factors ≈0.05 of the films described here are in the same range as observed in moderately polar polymers and are in agreement with those found in a simultaneous study.[6] The closest analogies to these films that have been electrically characterized are Langmuir–Blodgett films. In the most ideal cases, Langmuir–Blodgett films of fatty acids or polymerized diacetylenic acids have dielectric constants of 3 and kilohertz dissipation factors of 0.01–0.1.[11] Similar magnitudes and dehydration effects to those discussed here have been observed in the dielectric constants of powdered samples of layered zirconium phosphates.[12]

Because of their excellent resistance to electronic conduction, these materials show promise for dielectric and electrooptic applications. However, the extreme porosity and otherwise high defect concentration of our multilayers, evidenced by the ease of water penetration, would have to be reduced or eliminated before introducing these materials into practical systems. Means of densifying and smoothing these multilayers are currently under investigation.

Acknowledgment. We are indebted to G. E. Johnson, C. E. D. Chidsey, and E. A. Chandross for many enlightening discussions. We additionally thank Dr. Chidsey for assistance with the cyclic voltammetry experiment and T. M. Putvinski for assistance with the gold evaporation.

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