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Variation of Layer Spacing in Self-Assembled Hafnium–1,10-Decanediylbis(phosphonate) Multilayers As Determined by Ellipsometry and Grazing Angle X-ray Diffraction

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Abstract: Grazing angle X-ray diffraction and ellipsometry have been used to characterize the film thickness, thickness uniformity, density, and index of refraction of multilayer hafnium–1,10-decanediylbis(phosphonate) (Hf–DBP) films grown on silicon wafers. Grazing angle X-ray diffraction is a powerful technique that can be used to assess thickness, density, and thickness uniformity of a wide variety of thin films. Grazing angle diffraction of Hf–DBP multilayer films generally gives a series of peaks (fringes) in the range 0.5–4.0° 2Θ, which arise from interference between X-rays reflected off the front and back of the film. Analysis of the fringes allows an assessment of film thickness which is independent of the physical properties of the films. With less accuracy, these data also permit an assessment of film density and thickness uniformity. Indexes of refraction at optical wavelengths can be determined by comparison of X-ray and ellipsometry data. For a given sample, a plot of film thickness as a function of the number of Hf–DBP layers deposited gives a straight line, indicating that individual layers within a given sample are uniform in thickness. However, large variations in thickness per Hf–DBP layer are observed from sample to sample (ranging from 15 to 21 Å/layer), indicating that substrate effects are important in determining the layer spacing. Estimates of film density indicate that multilayer films are only ~75% as dense as the calculated density of the bulk material. Consistent with this finding, the indexes of refraction of all films studied fall in the 1.485–1.500 range, significantly smaller than the refractive index determined for the bulk compound (1.544). These findings indicate that Hf–DBP multilayers vary substantially in individual layer thicknesses from sample to sample and in general are not as similar to the assumed structure of the bulk compound with respect to the density and mode of metal–phosphonate binding as has been previously suggested for the analogous Zr–DBP films.

Introduction

Monolayer and multilayer thin films self-assembled onto solid substrates have generated considerable interest recently because of the potential for controlling the molecular architecture and chemical and physical properties of layered assemblies on surfaces.[1] The ability to modify surface properties and reactivities is important for controlling corrosion, wetting, catalysis, and selective responses for sensors or membranes.[2] In addition, the possibility of constructing multilayer assemblies allows the preparation of unusual supramolecular structures in which composition, orientation, and thickness can be controlled and varied from layer to layer. These capabilities have been exploited recently for the preparation of thin-film nonlinear optical materials in which the polar orientation of nonlinear optical chromophores has been controlled by the chemistry used to assemble the chromophore monolayers sequentially onto a surface.[3,4]

Although a number of motifs have been developed for multilayer self-assembly,[3,5–8] multilayers formed with zirconium and α,ω-bis(phosphonic acids)[9,10] (or other divalent,[11] trivalent,[12] or tetravalent[13] metals) have attracted wide interest because of their structural order and stability and because of their relative ease of preparation. As first reported by Mallouk and co-workers, zirconium–α,ω-alkanediylbis(phosphonate) multilayers can be prepared by alternately dipping an appropriately functionalized substrate into aqueous solutions of metal ion and bis(phosphonic acid).[9,10]

Several research groups have exploited this simple preparative scheme to make multilayer zirconium–phosphonate materials with unusual structures. Ungashe et al. have prepared materials with alternating layers of bis(phosphonate) electron donors and bis(phosphonate) electron acceptors and have investigated electron transfer between donor and acceptor layers across the zirconium–phosphonate layer.[14] Thompson and co-workers have demonstrated the preparation of zirconium viologen phosphonate thin films with a long-lived photoinduced charge-separated state.[15] By preparing multilayer films with mixtures of 1,10-decanediylbis(phosphonic acid) and phosphoric acid, Rong et al. have made porous "pillared" zirconium–phosphonate films that show selective ion-exchange properties.[16]

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In our research group, we have investigated the preparation of nonlinear optical thin films using polar and polarizable "asymmetric" bis(phosphonate) molecules with π electrons sandwiched between donor (ether) and acceptor (phosphonate) groups.[17] While our work was in progress, Katz and co-workers reported the preparation of nonlinear optical materials comprised of zirconium phosphate–phosphonate multilayers using a polar dye functionalized with a phosphonate moiety,[4] demonstrating the viability of our approach.

Most of the potential applications for such materials require a high degree of order, small numbers of defects, and reproducible layer formation. Evaluation of these properties for zirconium–phosphonate multilayers is difficult because very few analytical tools are readily available for examining nanoscopic thin film materials. While valuable information about alkyl chain ordering and relative density can be obtained by using IR spectroscopy and chemical composition can be assessed by X-ray photoelectron spectroscopy, the only method commonly available for measuring film thickness is ellipsometry. Interpretation of ellipsometry results generally requires knowledge of the index of refraction of the film. This is an unknown quantity and is usually taken to be the same as the value for the bulk material. However, it is quite possible that zirconium–bis(phosphonate) multilayer films deposited layer-by-layer onto a substrate have different densities and indexes of refraction than do the corresponding bulk materials. Indeed, it is possible that these indexes could change from layer to layer. While thicknesses of very thin films (<50 Å) determined by ellipsometry are relatively insensitive to the index of refraction, the thickness of thicker films is more strongly dependent on the assumed index.

Further complicating the issue of accuracy of ellipsometrically-determined film thicknesses are the many examples in the literature where ellipsometrically-measured thicknesses of self-assembled films containing alkyl chains appear to be larger than models of fully extended alkyl chain packing would suggest is possible. These include examples from alkanethiol monolayers self-assembled on gold surfaces[18,19] and multilayers of trichlorosilane derivatives[7] as well as from metal–phosphonate monolayer and multilayer samples.[20] Such discrepancies are usually attributed to "ellipsometric error". An independent thickness measurement is necessary to assess whether such large layer thicknesses are truly representative of the monolayer and multilayer films or whether they are indeed artifacts of ellipsometric error.

We report here the use of grazing angle X-ray diffraction in conjunction with ellipsometry as a means of assessing the layer thickness and uniformity of multilayer films of Hf–DBP on silicon substrates. We used hafnium rather than zirconium in order to enhance diffraction from the metal layers in an attempt to detect Bragg reflection from individual metal layers (which we did not generally observe). Hafnium-based films appear to be structurally identical to those prepared with zirconium, based on comparative experiments we have performed. Grazing angle X-ray diffraction provides an independent method for film thickness determination which is not dependent upon knowledge of the optical constants of the material.[21] This technique (also called X-ray reflectivity) can be applied generally to all thin films and also yields information about film density and thickness uniformity. In the case of the Hf–DBP films, we find that the average individual layer thickness varies considerably from sample to sample, from ~15.0 to ~21.0 Å/layer, possibly due to different packing densities, orientation of the alkyl chains, and metal–phosphonate binding in the materials. Estimates of densities from grazing angle X-ray diffraction suggest that the thin films are only ~75% as dense as the theoretical bulk density of the material.

Comparison of both grazing angle diffraction and ellipsometry data allows an assessment of the accuracy of ellipsometry measurements and determination of the effective indexes of refraction of the films. Our data show that the index of refraction for Hf–DBP multilayer thin films is lower than that of the bulk material (1.48–1.50 vs 1.544, respectively), suggesting that use of bulk indexes of refraction in ellipsometric measurements can lead to substantial error in thickness determinations of metal–bis(phosphonate) films by this method.

Experimental Section

Materials. All multilayer films were grown on the native oxide of polished prime (100) single crystal silicon wafers (Silicon Quest) except for sample E, which was grown on silicon with a thick thermal oxide film (~78 Å) from Wacker Siltronic (Portland, OR). Wafers were cleaned prior to use as substrates by rinsing successively in trichloroethylene for 10 min and isopropyl alcohol for 15 min and under flowing ultrapure water for 20 min. The water used in all cleaning procedures and in the preparation of aqueous solutions was purified to a resistivity of 17.0–18.3 MΩ cm with a Barnstead E-Pure water purification system.

Hafnium oxychloride octahydrate was obtained from Teledyne Wah Chang Albany, Inc. 1,10-Decanediylbis(phosphonic acid) (DBPA) was synthesized from 1,10-dibromodecane using the Michaelis–Arbuzov reaction followed by acid hydrolysis.[10]

Substrates. Wafers were functionalized for film growth directly with hafnium using a modified procedure first reported by Hong et al.[22] for the functionalization of Cab-o-Sil silica with zirconium. In our procedure, wafers are heated in a 5.0 mM $HfOCl_2$ aqueous solution to 50 °C for 3 days. Ellipsometric analysis shows an increase in thickness of the silicon oxide film of ~2–10 Å, presumably due to binding of hafnium species to form a thin "hydrous hafnium oxide" film.[23] Control of the temperature during the process is important; if the solution is heated to higher temperature, colloidal hydrous hafnia begins to precipitate from solution, thicker films (>10 Å) are deposited on the surface, and in some cases particles visible by eye can be seen on the surface. When the temperature is maintained at or below 50 °C, reproducibly thin films are deposited on the surface. We use this procedure because, in our experience, films grown on this substrate appear to be more uniform and of higher quality (as judged by grazing angle X-ray diffraction) than those grown on silicon functionalized with 3-(hydroxydimethylsilyl)propanephosphonic acid.[9,10] Our findings that high-quality films can be grown on hafnium-functionalized silicon are consistent with those of Hong et al.,[22] who find that films of zirconium–1,8-octanediylbis(phosphonate) grown on zirconium-functionalized Cab-o-Sil are slightly more crystalline and less defective than are those grown on Cab-o-Sil functionalized with 3-(hydroxydimethylsilyl)propanephosphonic acid.

Preparation of Hafnium–DBP Multilayers. To prepare multilayers, a procedure similar to that of Mallouk and co-workers was used.[9,10] Hafnium-functionalized wafers were placed alternately into aqueous solutions of 1.25 mM DBPA and 5.0 mM $HfOCl_2 \cdot 8H_2O$. Between immersions in the alternating solutions, the wafers were rinsed in flowing ultrapure water for 20 min and dried under flowing N_2. Samples A, D, and E were left in each solution for 4 h. Samples B and C were left in the hafnium solution for 4 hours and the DBPA solution overnight. Table 1 gives a summary of sample preparation parameters (and results) for each of the samples.

Preparation of Bulk Hafnium–DBP. Bulk powder was obtained by mixing stoichiometric amounts of 5 mM $HfOCl_2 \cdot 8H_2O$ solution and 1.25 mM DBPA solution to form a white precipitate. The precipitate was air-dried and refluxed for 15 h in a 1:17 mixture of 48% HF/H_2O to improve crystallinity, following a procedure reported by Dines and DiGiacomo.[24] The refractive index was determined by the immersion method to be very close to 1.544 (an excellent index match was observed when Hf–DBP powder was immersed in benzaldehyde), which is identical to that reported for bulk Zr–DBP.[9] X-ray powder diffraction of the bulk

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Table 1. Sample Parameters and Results

sample	substrate (silicon oxide thickness, Å)^a	Hf anchor layer thickness (Å)^a	time in DBPA solution	time in Hf solution (h)	average layer thickness (Å)^b	index of refraction^c
A	native (~15)^d		4 h	4	16.3	
B	native (11)	4	overnight	4	18.6	1.50
C	native (11)	4	overnight	4	19.9	1.49
D	native (17)	10	4 h	4	20.7	1.50
E	thermal (87)	8	4 h	4	14.8^e	1.50

^{a} Determined by ellipsometry using an index of 1.462 for the film. ^{b} Determined by grazing angle x-ray diffraction. ^{c} Determined by comparison of ellipsometry and x-ray data. ^{d} Estimated, no ellipsometry data available. ^{e} For layers 9–19. For layers 1–6 the average layer thickness is ~19.6 Å. The change in layer thickness may be due to an unusually long rinse following deposition of the eighth layer.

material gives a layer spacing of 16.7 Å. While this is smaller than the 17.3 Å layer spacing reported previously for bulk Zr–DBP powder,[24] it is in close agreement with the 16.9 Å layer spacing of bulk Zr–DBP powder we prepared. While we have not made an extensive study of the reproducibility of the layer spacing in the bulk material, it is possible that some variation in this parameter arises from variability in alkyl chain tilt and packing, as is observed in larger magnitude for the thin films reported in this study (see below).

Methods. Grazing angle X-ray diffraction was obtained on a Scintag XDS-2000 θ-θ powder diffractometer using Cu Kα radiation (λ = 1.54 Å). Alignment of the diffractometer source, sample, and detector is critical for grazing angle experiments. Reproducible alignment was achieved using a custom sample holder.[25]

Ellipsometry measurements were performed on a Rudolph Thin Film Ellipsometer 43702–200E using 632.8 nm radiation from a tungsten-halogen lamp. Thicknesses of silicon oxide and hafnium-DBP films were calculated using the DafIBM program provided by Rudolph. Refractive indexes of 1.462 for SiO_2 and 3.858 – 0.01*i* for Si were used.

X-ray diffraction and ellipsometry data were always taken after hafnium deposition, i.e. a "one-layer sample" consisted of a hafnium-functionalized silicon wafer onto which one DBP layer was deposited and capped with a hafnium layer.

Results and Discussion

Grazing Angle X-ray Diffraction. Grazing angle X-ray diffraction data of multilayer hafnium–DBP films thicker than ~40 Å generally show peaks, or "fringes", at low angles (0.5–5.0° 2θ). Representative data for 10- and 25-layer films (of the same sample, A) are shown in Figure 1. In general, as the thickness of the film is increased, the number of observed fringes increases and they move to lower angle. Such fringes can be attributed to interference between reflection of X-rays from the front and the back of a film and were first reported by Kiessig in 1931 for nickel films on glass.[26] The simplest analysis involves use of the Bragg equation:

$$n\lambda = 2d \sin\theta \qquad (1)$$

where in this case d is the total thickness of the film, n is the order of reflection interference, λ is the X-ray wavelength, and θ is in degrees. The film thickness is simply $n\lambda/2 \sin\theta$, which can be determined for each observed peak by properly assigning n. The thickness of the film determined in this way should asymptotically approach a constant value for higher order peaks. Lowest angle peaks often give values of thickness which are too low because absorption and index of refraction corrections (which are neglected in this simple analysis) become important at very low angles (<1° 2θ).

A more sophisticated analysis[21,27] takes into account the index of refraction of the film at X-ray wavelengths which can be written as

$$n = 1 - \delta - i\beta \qquad (2)$$

where δ and β are the dispersive and absorption corrections to the index of refraction, respectively, and are both positive numbers on the order of 10^{-5}–10^{-6}. If the absorption correction can be neglected, δ is related to the critical angle (θ_c) for total reflection of X-rays and to the density of the material by the following relationships:

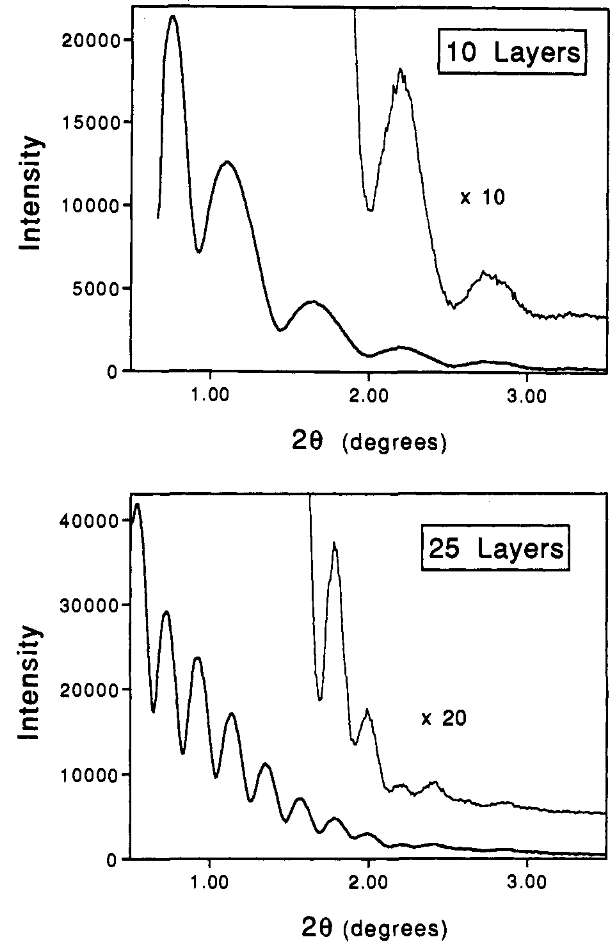

Figure 1. Grazing angle X-ray diffraction from a Hf–DBP multilayer film (sample A) after (top) 10 layers and (bottom) 25 layers.

$$\theta_c = (2\delta)^{1/2} = \left(\frac{N_a r_0 \rho f_1}{\pi A}\right)^{1/2} \lambda \qquad (3)$$

where N_a is Avogadro's number, r_0 is the classical electron radius (= 2.818 × 10^{-13} cm), ρ is the density, f_1 is the real part of the atomic form factor (~atomic number Z), λ is the wavelength, and A is the atomic mass.

If the index of refraction of the film is greater than that of the substrate (which occurs when the film has a lower electron density and is the case for our samples), then the following modification of the Bragg equation applies:

$$n\lambda = 2d(\theta_n^2 - \theta_c^2)^{1/2} \qquad (4)$$

Here d is again the total film thickness, θ_n is the position of the fringe maximum corresponding to nth order interference, and θ_n and θ_c are in radians. Using this relationship, a plot of θ_n^2 vs n^2 should give a straight line of slope $\lambda^2/4d^2$ and intercept θ_c^2.

The film thicknesses reported here are the result of this more sophisticated analysis, but it is worth noting that essentially identical thicknesses are obtained with the simpler analysis described above. The 10- and 25-layer X-ray data for sample A

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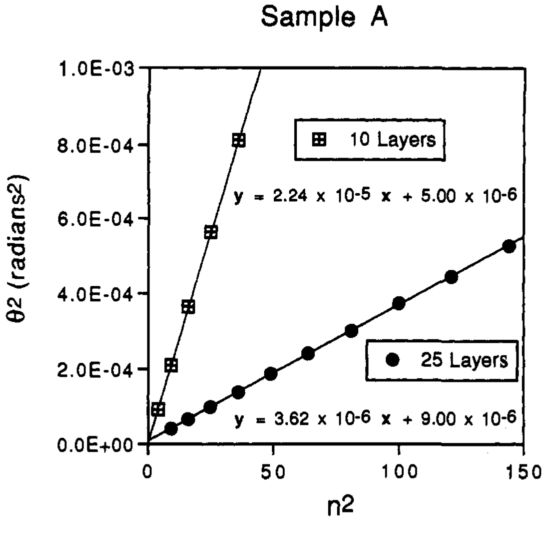

Figure 2. Plot of θ^2 vs n^2 for the diffraction data shown in Figure 1. Slopes of the lines are $\lambda^2/4d^2$, where d is the film thickness.

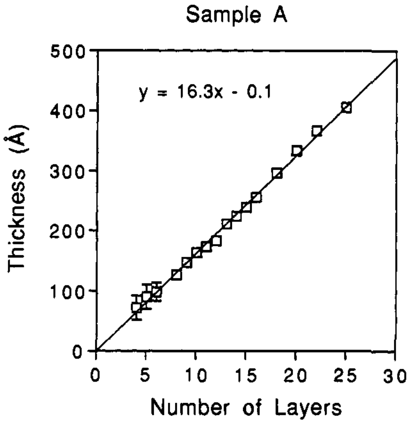

Figure 3. Sample A film thickness determined by grazing angle X-ray diffraction as a function of the number of Hf–DBP layers deposited.

(Figure 1) will be used to illustrate the application of this analysis to our data. Plots of θ_n^2 vs n^2 for both diffraction patterns are given in Figure 2, which indicate the linear equations determined by a linear least squares regression for each set of data. From the slope of the lines, the thicknesses of the 10- and 25-layer films are determined to be 163 and 405 Å, respectively. From the intercepts, the critical angle θ_c is determined to be 0.13° for the 10-layer film and 0.17° for the 25-layer film. The thicknesses determined by this method have a relatively small error (±5 Å), except when there are only one or two fringes observed, as in the case of the thinnest multilayers with only 3–5 layers. In these cases, the plots of θ_n^2 vs n^2 would contain only one or two points and the simpler analysis outlined above is applied; the error is estimated to be ±10 Å (these less accurate thicknesses are marked with error bars in Figures 3 and 5–7).

Thickness as a function of the number of layers is plotted for sample A in Figure 3. Each point in this plot is derived from a diffraction pattern taken using the same substrate after deposition of the indicated number of Hf–DBP layers. The slope of the line gives the average thickness per layer for this sample, which is 16.3 Å/layer. This is close to the layer spacing for bulk Hf–DBP, which we determined to be 16.7 Å.

Film Density. In principle, the film density can be determined from the intercepts of the linear θ_n^2 vs n^2 plots by the relationship given in eq 3. The intercepts (and hence the critical angles and densities determined from the intercepts) for data taken at different stages of multilayer growth of a given sample should be identical (assuming the density of the film does not change with the number of layers). However, determination of the critical angle by this method is much more strongly dependent upon accurate alignment of the diffractometer than are thickness determinations. Indeed, a 0.01° offset in 2θ from the true zero ($\theta = 2\theta = 0$) influences the thickness determination by less than 0.05% but changes θ_c by ~13% and the density calculated using eq 3 by ~30%. Further, error in peak position determination could give a slight variation in one or more of the points in the θ_n^2 vs n^2 plot; this would have a negligible effect on the slope but could change the intercept markedly, especially since the intercept is so close to zero. Data for thicker samples with smaller slopes of θ_n^2 vs n^2 will be most reliable for θ_c determinations, both because there are more data points (fringes) and because the smaller slopes make the intercept less susceptible to large errors.

The θ_n^2 vs n^2 data for sample A obtained at 16 different stages in multilayer growth (i.e., different numbers of layers) yielded varying intercepts, although all were very close to zero (in the 10^{-5}–10^{-6} range). A few of the intercepts were slightly negative (i.e. $\sim -1 \times 10^{-6}$). These are clearly not physically meaningful and again indicate that the intercept values are more sensitive to alignment or peak assignment errors than are the values of the slopes. Averaging all of the intercept values gives an average critical angle of 0.13 ± 0.06° for sample A. Using only the most reliable data from the later stages of multilayer growth (i.e., from the 20-, 22-, and 25-layer data) would give an average critical angle of 0.18 ± 0.01°.

The critical angle can be used to estimate the film density using the relationship given in eq 3, assuming an average atomic number (5.6) for f_1 and an average atomic mass (12.2 g/mol) based on the ideal formula unit [$Hf(O_3P\text{–}(CH_2)_{10}\text{–}PO_3)$]. Using these values, the calculated density is 0.90 ± 0.74 or 1.73 ± 0.18 g/cm^3 using all data ($\theta_c = 0.13°$) and the data from 20, 22, and 25 layers ($\theta_c = 0.18°$), respectively. Both values are significantly smaller than the 2.0 g/cm^3 expected for the bulk material (calculated using 24 Å^2 × 16.7 Å unit cell per formula unit[24]). For this bulk density, a critical angle of ~0.20° is expected.

The range of critical angles determined from the other film data (samples B-E below) is consistent with what is observed for sample A, i.e. that the film densities are on the order of 0.9–1.7 g/cm^3 and that they are consistently less than the calculated bulk density. A film density lower than that expected for bulk material is corroborated by independent X-ray reflectometry experiments performed on several of our 10- and 25-layer Hf–DBP samples at Siemens AG in Munich,[28] which determined the density of these Hf–DBP films to be 1.48–1.50 g/cm^3 (corresponding to a critical angle of 0.17°). In these cases, X-ray reflection was measured from 0.0° to 10.0° 2θ over 8 orders of magnitude of reflected X-ray intensity. Since the critical angle is measured directly in these experiments, these density values are much more reliable. (We are unable to measure the critical angle directly with our diffractometer because the through-beam saturates our detector up to ~0.5° 2θ.) On the basis of the more precise measurements made at Siemens AG of different samples and on the range of critical angle data determined for samples A-E presented here, it is reasonable to conclude that Hf–DBP films prepared by the methods outlined above have densities which are on the order of ~75% of the theoretical bulk density.

While it is generally accepted that zirconium–bis(phosphonate) multilayer films are comprised of compact layers which are structurally similar to the corresponding bulk materials,[29] our density results are in accord with recent studies which indicate that alkyl chains in zirconium–1,16-hexadecanediylbis(phosphonate) multilayers are only approximately one-half as densely packed as are alkyl chains in self-assembled alkylsiloxane monolayers.[30]

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Thickness Uniformity. It is also possible to use the grazing angle X-ray data to estimate the thickness uniformity of the films. Variation in the thickness of a film will serve to decrease the coherence of X-rays reflected from the front and back of the films at the various interference maxima (fringes). Higher angle fringes are more strongly affected by variations in film thickness and so are more broadened by this type of variation than are low-angle fringes. This effect was first described by Wainfan and Parratt,[31] who suggested that the presence of strong interference maxima is indicative of film "smoothness". They proposed that the variation in thickness, Δt, that would broaden the nth fringe maximum at θ_n so that it could no longer be observed would be given by

$$\Delta t = \lambda/[4(\theta_n^2 - \theta_c^2)^{1/2}] \qquad (5)$$

Using this relationship, we can estimate the thickness uniformity of the Hf–DBP films. For sample A, fringes are not observed above ~4.0° 2θ, corresponding to a Δt of 11 Å. In general, the highest angle fringes observed fall below ~2.5–4.0° 2θ (depending on the sample and the number of layers). Using eq 5, these values correspond to a Δt of 18 and 11 Å, respectively. While this range of thickness variation is respectable for films of this nature, these values suggest an explanation for the inability to detect Bragg reflection from individual hafnium layers.

We used hafnium in our studies rather than zirconium in an attempt to observe Bragg diffraction from the individual layers, from which we would expect a diffraction peak at ~4.5° 2θ (corresponding to a d-spacing of ~20 Å). In general, we do not observe a peak in this region; in a few cases, a very broad peak is observed for samples with more than 10 layers. The estimated thickness variation in these samples is relatively small compared to the total thickness of a 5–20-layer film, but is large compared with the individual layer spacing, and probably is responsible for broadening the Bragg peak to the extent that it can no longer be observed in most cases. This would correspond to a situation where thickness of individual layers varies enough to give incoherent scattering at the Bragg angle (i.e., a variation of layer thickness large enough to broaden the Bragg peak so that it is no longer observable).

An alternative explanation for lack of a well-defined Bragg peak could be that individual layers are very uniform in thickness but that the thickness of each layer varies so as to broaden the collective Bragg peak. If this were the case, however, the overall film would be expected to be very uniform in thickness, much more uniform than is indicated by the analysis above. While we cannot exclude either possibility without extensive modeling (which is underway), the estimated thickness variations for the overall films favor the first explanation involving thickness variations within individual layers. One plausible model we are exploring involves "domains" within each layer that correspond to regions of a particular alkyl chain density, tilt angle, and orientation. This model is described in a later section.

While estimation of thickness uniformity using eq 5 is used only qualitatively here, it provides a useful parameter for evaluating the overall order and uniformity of individual samples. Samples which show X-ray interference fringes to higher angles are more uniform in thickness. In the case of sample E (discussed below), which was grown on a thick SiO_2 layer, fringes from both the SiO_2 layer and the multilayer film were observed. However, the fringes of the SiO_2 layer were observable to much higher angles (7.5–8.0° 2θ) than were the fringes from the Hf–DBP film (~2.5–3.0° 2θ), indicating that the variation in thickness of the SiO_2 layer (Δt ~ 5.5 Å) was much less than that in the Hf–DBP film (Δt ~ 16 Å).

Ellipsometry Results. Ellipsometry data is not available for sample A. However, in all of the following samples for which data are presented, both ellipsometry and X-ray diffraction data are available for comparison. When comparing the two different types of data, it is important to differentiate which parts of the multilayer films are probed by each technique. In the case of ellipsometry results, we assumed a two-layer model, whereby the Hf–DBP film was grown on an SiO_2 layer of known (ellipsometrically measured) thickness on a silicon (100) substrate. Additional increments of thickness during layer growth are attributed directly to a film of some index n. The film thickness thus includes the hafnium "anchor" layer. While the assumption that the initial hafnium layer has the same index of refraction as the subsequent multilayer film might not be physically valid, in the cases of such thin films (2–10 Å), the ellipsometrically-determined thickness is nearly independent of the index of refraction and this will not be a significant source of error. Further, any error associated with the substrate–hafnium anchor thickness determination will be a constant error and subsequent growth will still be accurately determined.

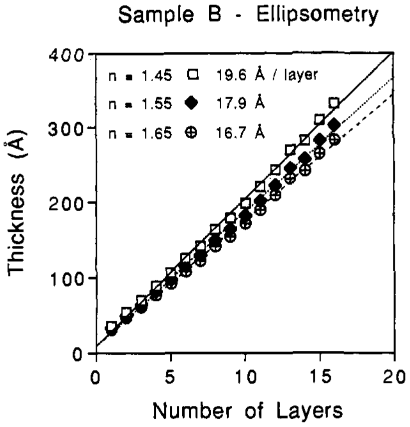

Figure 4. Thickness of sample B as a function of the number of Hf–DBP layers calculated from ellipsometry data using three different indexes of refraction for the Hf–DBP film (n = 1.45, 1.55, 1.65).

In the case of the grazing angle X-ray data, the absolute source of the observed "front-back" interference is not known with certainty. The "front" and "back" of the observed interference pattern will be interfaces of relatively abrupt changes in electron density. The "front" is unambiguously assigned to the air–film interface. The "back" may be the multilayer film–hafnium anchor interface or possibly the hafnium anchor–SiO_2 interface. However, while we are not certain how much of the film/anchor/substrate composite the grazing angle experiment probes, incremental changes in thickness can be directly attributed to increase in film thickness. Thus, the "slope" of a thickness vs number of layers plot such as that shown in Figure 3 derived from X-ray data is a reliable average layer thickness. Likewise, the slope of the thickness vs number of layers determined by ellipsometry should give a reliable average layer thickness, which should be the same as that determined by X-ray diffraction. Because the X-ray thickness determination is independent of optical constants, we match the ellipsometry data by adjusting the index of refraction to duplicate the slope of thickness vs number of layers given by X-ray data. Figure 4 shows ellipsometry data for sample B, for which thickness as a function of the number of layers is plotted for three different assumed indexes of refraction for the multilayer Hf–DBP film (n = 1.45, 1.55, and 1.65). It can be seen that the influence of the assumed index has relatively little effect on the thicknesses of thin films (<50 Å) but has a progessively larger effect on the determined thickness of thicker films and thus affects the slope (i.e., the average layer thickness) significantly.

Figures 5–8 show thickness as a function of the number of layers determined by both X-ray diffraction and ellipsometry for four different samples (B-E). In each case, an index of refraction

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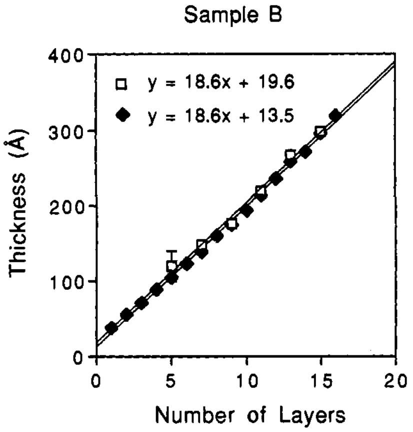

Figure 5. Sample B film thickness determined by grazing angle X-ray diffraction (open squares) and ellipsometry ($n = 1.500$) as a function of the number of Hf–DBP layers deposited.

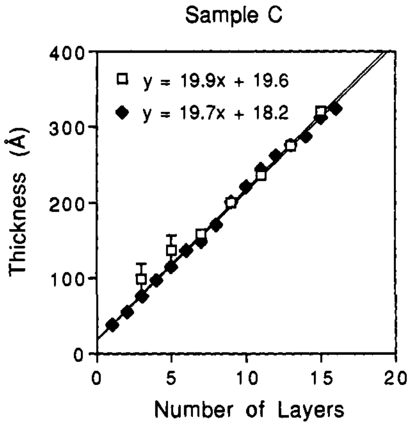

Figure 6. Sample C film thickness determined by grazing angle X-ray diffraction (open squares) and ellipsometry ($n = 1.485$) as a function of the number of Hf–DBP layers deposited.

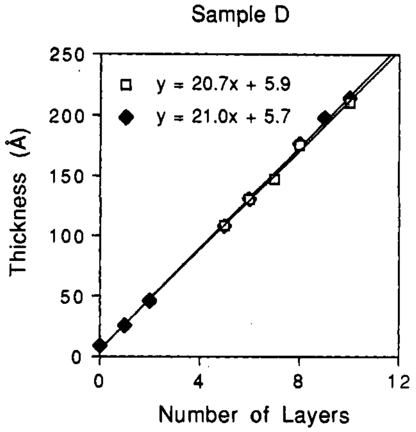

Figure 7. Sample D film thickness determined by grazing angle X-ray diffraction (open squares) and ellipsometry ($n = 1.500$) as a function of the number of Hf–DBP layers deposited.

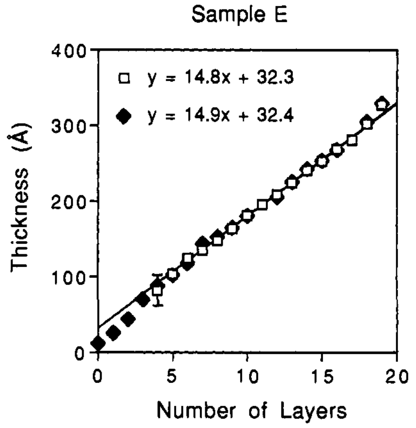

Figure 8. Sample E film thickness determined by grazing angle X-ray diffraction (open squares) and ellipsometry ($n = 1.500$) as a function of the number of Hf–DBP layers deposited.

was determined independently to make the slope of the ellipsometry data match the slope of the X-ray thickness determinations (in the case of sample E, the slopes were matched for the intermediate data corresponding to 6-18 layers). Surprisingly, the indexes of refraction determined this way are all nearly identical as shown in Table 1 ($n = 1.500$ for samples B, D, and E and $n = 1.485$ for sample C). These indexes of refraction are lower than that of the bulk material ($n = 1.544$), which is consistent with the observation above that film densities appear to be significantly lower than would be expected for the bulk material.

Variation of Average Layer Thickness. The straight-line behavior of the thickness vs number of layers plots (Figures 3 and 5–8) indicates that, for a particular sample, individual layers are fairly uniform in average thickness. However, a comparison of the average thickness per layer for samples A-E (Table 1) shows that this parameter varies markedly from sample to sample, ranging from 14.8 to 21.0 Å/layer. These values fall above and below the layer spacing of 16.7 Å determined for bulk Hf–DBP. This range of variation is remarkable and indicates that the average layer thickness depends upon more than the solutions used for layer deposition and the bare silicon substrates. We hypothesize that this variation in average layer thicknesses is a result of variation in the binding site density of the hafnium-functionalized substrate surfaces, which in turn influences the tilt angle (and lateral density) of the bis(phosphonate) alkyl chains. The lateral density of hafnium ions present in the initial hafnium layer is then retained and perpetuated with multilayer growth.

While the structure of bulk Zr–DBP or Hf–DBP has not been determined directly, it is generally assumed[24,32] to have the same metal–phosphonate binding as that observed for α–zirconium phosphate monohydrate (α-ZrP).[33] In this structure, each metal ion is octahedrally coordinated by six oxygens from six different phosphonate moieties and each of the three oxygens of a phosphonate group are bound to three different metals to give a highly cross-linked inorganic layer. The fourth oxygen of each phosphonate group bears a proton and is directed into the interlamellar region nearly perpendicular to the metal–phosphonate layer. If the inorganic layer structure is maintained in the Zr–DBP and Hf–DBP structures (as is the case for the related zirconium phenylphosphonate[34]), then the phosphorus–carbon bonds of the bis(phosphonates) are also oriented perpendicular to the inorganic layers. Using the layer spacing of isostructural zirconium phosphite ($Zr(O_3PH)_2$) (5.61 Å)[24] and typical P–C and P–H bond lengths (1.87 and 1.42 Å, respectively), the distance across the inorganic layer from the center of the first carbon below to the first carbon above the layer should be 6.5 Å. The projection of an all-trans alkyl chain on the chain axis is ~ 1.27 Å/CH_2 unit,[19] and in the case of DBP, the remaining nine alkyl bonds would add to give a maximum of 17.9 Å/layer of Zr–DBP or Hf–DBP. If the alkyl chain axis is oriented ~31° from the normal (as would be the case for a P–C bond normal to the metal–phosphonate plane[35]), then the expected layer thickness would be 16.3 Å. This is exactly the average layer thickness observed for sample A. In the case of sample E, the observed average layer thickness of 14.8 Å would correspond to an alkyl

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chain tilt angle of 43° from the inorganic layer normal using this structural model.

The observed average layer spacings of the other Hf–DBP samples (B, C, and D) are larger than the maximum 17.9 Å predicted by this α-ZrP model. Note also that this maximum requires very unnatural bond angles (i.e., the alkyl chain must be oriented perpendicular to the inorganic layer, requiring nontetrahedral bonding of *C1* and *C10* of the alkyl chain) or, more likely, a different type of metal–phosphonate binding. One possible explanation for the observation of such large average layer thicknesses has been suggested by Talham and co-workers.[35] In their studies of multilayer zirconium octadecanephosphonate films prepared by Langmuir–Blodgett techniques, they observe layer spacings of 52 Å, substantially larger than the 43 Å predicted for the expected hydrocarbon chain tilt angle of 31°. They suggest that the alkyl chains are oriented normal to the inorganic layer and that this arrangement is made possible by a tilting of the PO_3 groups such that the three phosphonate oxygens no longer have equivalent orientations to the plane of metal ions in an arrangement similar to that observed for γ-ZrP.[36] Taking this argument one step further, if only two of the phosphonate oxygens bind to the metal ions, then the maximum layer spacing is somewhat larger than the maximum predicted for the α-ZrP model. With this type of arrangement, a layer thickness of ~19 Å for the DBP system can be rationalized, which is close to the layer spacing observed for sample B.

However, the average layer thicknesses of samples C and D (19.8 and 21.0 Å, respectively) are significantly larger than 19 Å. We cannot dismiss the average layer thicknesses of these samples as anomalous because layer spacings on the order of 19–21 Å are representative of approximately one-half of the ~20 different Hf–DBP and Zr–DBP multilayer samples that we have prepared and studied by diffraction. While we have no explanation for this observation at present, it is clear that a more extreme variation of metal–phosphonate binding from that of α-ZrP than suggested above is necessary to account for these larger layer thicknesses.

One possibility is that coordinated water increases the layer thickness. Indeed, "hydration" has been shown to occur in zirconium–phosphonate multilayer films and appears to be important in the electrical properties of these materials.[37] Although we have never observed any changes in film thickness when films are exposed to ambient conditions (suggesting that dehydration does not occur significantly under these conditions), it is certainly likely that there is some water in the films. If water (or some other ligand) directly coordinates to metal ions in these films, then it is possible that the coordinated metal octahedron could orient such that a 4-fold axis is normal to the metal ion plane (instead of in a canted orientation, as in α-ZrP), with axial binding to oxygens from a phosphonate above and below. This would increase the maximum layer spacing to ~21 Å. However, this reduces metal–phosphonate binding considerably and requires other ligands (e.g., water, hydroxide, oxide, or chloride) to coordinate the metal equatorial octahedral sites. Further studies are necessary for elucidation of the nature of metal–phosphonate bonding in these systems.

A Domain Model for Metal-Bis(phosphonate) Multilayers. One model we are investigating involves "domains" within each layer that correspond to regions of a particular alkyl chain density, tilt angle and orientation, and metal–phosphonate binding motif, all of which are presumably dictated by lateral hafnium density on the functionalized substrate surface. As shown in Figure 9, such domains would have different thicknesses and could account for the variations in total film thickness as well as the lack of a well-defined Bragg reflection corresponding to the individual layer spacing. In addition, domain boundaries would inevitably be disordered and could easily trap void space or solvent to contribute to the relatively low density estimated from critical angle data. Quite possibly, as more layers are self-assembled, some domains may "grow" at the expense of others, changing the average layer thickness as films are grown. Preliminary modeling of X-ray reflectivity from a multilayer film with a domain structure has been performed using a recursive calculation based on a dynamical model of X-ray reflection.[38-40] The model used for this calculation assumed a 10-layer sample averaged over 20 domains, with a two-layer repeat unit consisting of an inorganic layer (approximated by Sc, which has the average atomic number of the Hf–$(PO_3)_2$ unit), and an organic layer which was approximated by a single light element (atomic number 2.67, atomic mass 4.67 amu, and density ~0.6 g/cm^3). Domains are assumed to be large compared with the X-ray coherence length (i.e., domains are on the order of 2000 Å in length). In preliminary calculations, we assumed a constant thickness for the inorganic layer (6.0 Å) but used a randomly-generated variable thickness of the organic layer (12 Å ± Δ) in each layer of each domain. The range of Δ was selected to be between 0 and 1 Å, or 0 and 2 Å, etc. These calculations suggest that a variation in the organic layer corresponding to $0 \leq \Delta \leq 4$ Å is necessary to "smear out" the Bragg reflection from a 10-layer sample with 20 domains (under these conditions, the front–back interference at lower angles is still observed in the calculated diffraction pattern). These calculations are very crude because they assume sharp boundaries between organic and inorganic layers; they do not correctly model the electron density distribution of the inorganic layer, and the thickness of the inorganic layer has been held constant. Nonetheless, they are consistent with our observations that self-assembled metal–bisphosphonate multilayers have a higher degree of variability and disorder than has previously been assumed. More sophisticated modeling studies are underway.

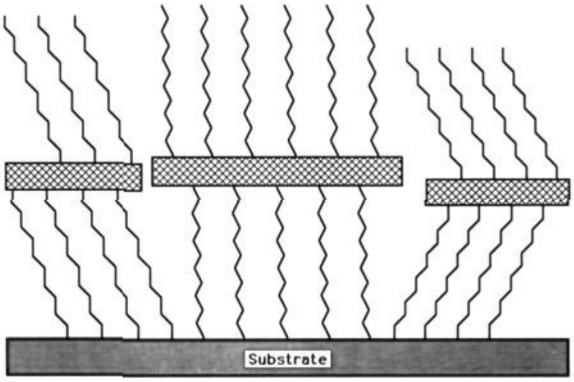

Figure 9. Schematic of the proposed domain structure. Lines represent the bis(phosphonate) alkyl chains; cross-hatched areas represent the inorganic hafnium–phosphonate layers. Lateral density of bis(phosphonate) chains, chain tilt angle, and layer thickness vary from one domain to the next.

A Closer Look at Ellipsometry and Grazing Angle X-ray Data. Because the "back" of the film measured by ellipsometry and grazing angle X-ray diffraction may be different, it is not necessarily expected that matching slopes of thickness vs number of layers plots will give identical intercepts in plots of thickness vs number of layers. However, as is seen in Figures 5–8, in general, the ellipsometry and X-ray data match very well, suggesting that the X-ray diffraction and ellipsometry experiments probe essentially the same portion of the film (i.e., the "back" is actually the hafnium–SiO_2 interface).

However, if this is the case, then the intercepts for both the ellipsometry and X-ray thicknesses (corresponding to zero layers)

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should give the thickness of the hafnium "anchor" layer, which should be in the range ~2–10 Å. For all but samples A and D, the intercepts are much larger than this; another explanation is necessary to account for the unexpectedly high intercepts. The most plausible explanation may lie in the irregularity of the first several layers which are deposited. Because grazing angle diffraction is not observed until films are ~40 Å thick, we have only ellipsometry data for the very early stages of growth. What this data indicates, however, is that in the cases of samples B and C, the first layer is much thicker than are subsequent layers (~30 Å in each case). We have no reasonable explanation for this observation. Whatever the cause, we note that a similar observation regarding an unusually large (or dense) first layer has been made in the case of Zr–DBP layers grown on an LB template, for which multilayer growth was monitored by the integrated area of the asymmetric CH_2 band in the IR spectrum.[41]

In the case of sample E, the first several layers, while not unreasonably large, are thicker on average than are subsequent layers (the initial slope is ~19.6 Å/layer for the first 5–6 layers). For this latter sample, a change in the slope at ~6–8 layers to the smaller average layer thickness may be due to an unusually long rinse (1.5 h) in ultrapure water following the deposition of the eighth DBP–Hf layer. This long rinse may have removed more hafnium from the sample surface than the usual (20 min) rinse, leaving a different (lower) density of surface hafnium atoms for subsequent DBP layer binding. The different density of the ninth hafnium–DBP layer subsequent to this rinse could lead to a different (thinner) layer thickness (and a larger alkyl chain tilt from the inorganic layer normal) which is then perpetuated with further multilayer growth. Indeed, the X-ray critical angle determinations corroborate this interpretation, suggesting that the density for this sample with fewer than eight layers is significantly greater than the density for the same sample with more than eight layers.

Sample E is notable for another reason: it was the one sample in the group which was grown on a thick thermal oxide, and because an X-ray diffraction fringe pattern from the oxide was observed independently from the fringe pattern of the multilayer film, some insights regarding the hafnium functionalization of the oxide layer are more easily extracted from analysis of X-ray and ellipsometry data. Before functionalization, the thickness of the oxide layer was determined to be 78 Å by grazing angle diffraction. Ellipsometry gave a much larger thickness for this oxide layer (87 Å, assuming a refractive index of 1.462). In order to match the thicknesses determined by ellipsometry and X-ray diffraction, an unreasonably high index of refraction (1.60) would be necessary. Since the refractive index of the silicon oxide is not likely to be much different from 1.462, the only explanation for this discrepancy is that the two techniques measure different portions of the oxide film. This would be the case if, for example, a layer of surface water is not detected by the X-ray diffraction experiment but is detected by the ellipsometry measurement. In any case, the discrepancy appears to be real.

Interestingly, after functionalization with hafnium, the film thickness from X-ray diffraction appears to decrease from 78 to 75 Å, while ellipsometry also shows the film thickness to be decreasing from 87 to 84 Å (assuming the hafnium oxide and silicon oxide layers combined have an index of 1.462). This indicates that, at least in this case, some of the oxide is actually etched away by the hafnium oxychloride solution. While the hafnium oxychloride solutions used are quite acidic (pH 2–3), a decrease in film thickness is not generally observed in the ellipsometry of the native oxide films upon hafnium functionalization: these generally show a 2–10 Å increase in the oxide layer thickness. Perhaps the thermal oxide surface is more susceptible to etching than is the native oxide surface. However, it is possible that some etching takes place in the case of the native oxide as well and the thickness of the adsorbed hafnium layer is actually thicker than the observed increase of 2–10 Å.

Conclusions. The data presented here show that ellipsometry cannot be used with accuracy to determine film thicknesses of metal–bis(phosphonate) multilayers because the index of refraction is not known a priori and, in general, is not the same as that of the bulk material. Grazing angle X-ray diffraction has been used in this study as an independent method for thickness determination of Hf–DBP multilayers grown on hafnium-functionalized silicon and reveals some new structural information about these types of films.

For a given Hf–DBP sample, multilayer growth is generally uniform from one layer to the next, but a wide range of variation in the average layer thickness from sample to sample has been observed (from ~15 to 21 Å/layer in multilayer films, *cf.* 16.7 Å for bulk Hf–DBP). This variation is presumably dependent upon the lateral density of surface binding sites produced in the original surface functionalization, since once multilayer growth begins, the layer thicknesses are fairly uniform.

To address the issue of the relationship between the observed variation of layer spacing and surface functional density, studies of films grown on a variety of different substrates have been undertaken in our laboratory. These studies will be reported in a subsequent paper, but they suggest that Hf–DBP multilayers grown on gold are similar to those reported here, and therefore the data presented here are not peculiar to the particular substrate or surface functionalization technique employed.

Average thicknesses smaller than or similar to the bulk layer spacing can be accounted for by assuming metal–phosphonate binding similar to that observed in α-ZrP, assuming different alkyl chain tilt angles relative to the metal–phosphonate layer normal. Larger thicknesses, however, require a departure from this structural model to account for the observed layer thicknesses.

Grazing angle X-ray diffraction suggests that, on average, films appear to have densities only ~75% of those expected for a bulk material with the α-ZrP structure. This observation is consistent with the lower index of refraction necessary to match average layer thicknesses from ellipsometry with X-ray data. The indexes of refraction were determined to be ~1.50 for all samples reported here (*cf.* $n = 1.544$ for bulk Hf–DBP). This is somewhat surprising, given that all samples had significantly different average layer thicknesses.

All of these data taken together suggest that Hf–DBP films grown layer-by-layer onto a hafnium-functionalized silicon oxide surface are significantly structurally different than the structure generally accepted for bulk Hf–DBP or Zr–DBP based on the α-ZrP structure. In particular, a departure from the metal–phosphonate oxygen binding motif of α-ZrP is necessary to account for average layer thicknesses larger than ~17 Å. A structural model for these films is proposed to account for variation of layer thickness and absence of a Bragg reflection from individual layers. This model is based on a domain structure, in which the lateral spacing of bis(phosphonate) chains, the alkyl chain tilt angle, and the individual layer thickness vary from one domain to the next. Preliminary calculations based on this model suggest that a variation in individual domain organic layer thicknesses on the order of ±4 Å is necessary in order to broaden the Bragg reflection so that it is not observed.

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