Rapid, Reversible Sorption of Water from the Vapor by a Multilayered Composite Film: A Nanostructured Humidity Sensor

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Composite films prepared by alternate adsorption of poly(diallyldimethylammonium chloride) and exfoliated sheets of a synthetic sheet-silicate mineral (Laponite RD) respond in a dramatic way to changes in ambient humidity. The structural order in these films and the ability to prepare them to precisely controlled thicknesses provided unique opportunities to study this behavior. Ellipsometric and gravimetric evidence indicates that initially some water fills void spaces in the films, giving rise to a relatively small increase in overall film thickness; further uptake of water then causes greater swelling of the film. This behavior is rapid: water penetrates to depths greater than 139 nm within seconds and desorbs from the films at a similar rate. The rapid and reversible response of this system makes it interesting from the standpoint of molecular sensing.

Interest in the design and development of sensors has increased dramatically in recent years.[1] Thin films offer unique promise for use in sensors due to their large area/mass ratio and the ease with which they can be incorporated into electronic and microelectronic devices. Advances in this area have included the use of Langmuir−Blodgett multilayered films in various types of sensors[2] and layered metal−phosphonates, which have demonstrated shape selectivity.[3] The molecular-sieving ability of thin zeolite layers, either attached directly to quartz-crystal microbalances or deposited in a silica matrix onto surface acoustic wave devices, has also been used for chemically selective sensing.[4]

We have recently described a new method for the formation of ordered ultrathin films by controlled, stepwise adsorption of a cationic polyelectrolyte and single exfoliated sheets of a silicate mineral onto solid surfaces.[5] Early in this work, we observed that the films underwent dramatic, reversible changes in interference color when exposed to humid air. We have also noticed small variations in the ellipsometric growth per adsorption cycle from day to day that may reflect changes in the ambient humidity.[6] Motivated by these observations, we have used ellipsometric and gravimetric measurements to gain additional insight into the sorption of water by the films[7,8] and to explore the use of the films as sensors. The order, uniformity, and pre-
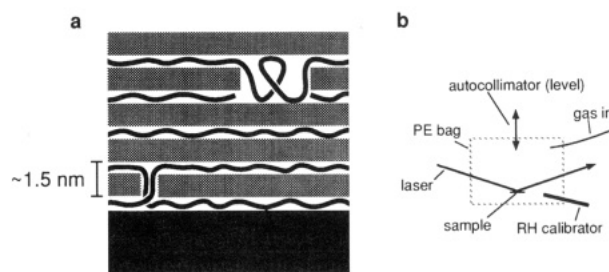
Figure 1. Schematic diagrams of (a) the structure of PDDA/hectorite multilayered films and (b) the setup used for ellipsometric measurement of film thickness and refractive index as a function of relative humidity.

cisely controllable thickness of these films make them attractive for fundamental studies of sensor design and function.

Results and Discussion

Alternate adsorptions of poly(diallyldimethylammonium chloride) (PDDA) and hectorite form multilayered films with thicknesses that grow linearly with the number of adsorption cycles and that possess order in the direction perpendicular to the substrate surface (Figure 1a).[5] As these PDDA/hectorite films grow in thickness on silicon substrates, they display a series of vivid colors due to constructive and destructive interference between the light reflected from the surface of the film and that reflected from the silicon substrate.[5,9,10] The interference color of a coating depends upon its thickness and its refractive index. The changes in color of particular PDDA/hectorite films in response to

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(2) For a review, see: Ulman, A. *An Introduction To Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*; Academic: New York, 1991.

(3) Brousseau, L. C.; Aoki, K.; Garcia, M. E.; Cao, G.; Mallouk, T. E. *Multifunctional Mesoporous Inorganic Solids*; Sequeira, C. A. C., Hudson, M. J., Eds.; Kluwer Academic: Netherlands, 1993; p 225. Cao, G.; Garcia, M. E.; Alcalá, M.; Burgess, L. F.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992,** *114,* 7574.

(4) For examples, see: Yan, Y.; Bein, T. *J. Phys. Chem.* **1992,** *96,* 9387. Bein, T.; Brown, K.; Frye, G. C.; Brinker, C. J. *J. Am. Chem. Soc.* **1989,** *111,* 7640.

(5) Kleinfeld, E. R.; Ferguson, G. S. *Science* **1994,** *265,* 370.

(6) Kleinfeld, E. R.; Ferguson, G. S., unpublished results.

(7) For detailed studies of the sorption of water by montmorillonite, see: Mooney, R. W.; Keenan, A. G.; Wood, L. A. *J. Am. Chem. Soc.* **1952,** *74,* 1367, 1371.

(8) Swelling of polyelectrolyte films by water has also been noted. See, for example: Decher, G.; Lvov, Y.; Schmitt, J. *Thin Solid Films* **1994,** *244,* 772.

(9) Pliskin, W. A.; Conrad, E. E. *IBM J. Res. Dev.* **1964,** *8,* 43.

(10) The similarity in refractive index between the multilayered film and the native or thermal oxide of silicon minimizes the reflected intensity at this interface.

differences in relative humidity (RH) thus indicated rapid and reversible swelling of the films. For example, a 67-cycle multilayered film with a thickness of 223 nm (assumed index of refraction, $n = 1.5$), prepared on a wafer bearing a native oxide, appeared deep gold in color. When the sample was held in the vapor above water in a small vial, its interference color rapidly changed to fuchsia, indicating an increase in the film thickness and/or refractive index.[9] As the sample was removed from the vial, the color began to revert to gold, and this change was complete by the time the entire sample had been removed from the vial. The sample could be cycled into and out of the humid environment many times with no apparent change in its response. Using a video camera operating at 30 frames/s, we examined the time necessary for this same sample to respond to a moving jet of humid air. When the videotape was viewed frame by frame, no trailing of the pink interference color was apparent behind the jet, indicating that the time needed for the sample to undergo this reversible change in color was shorter than the residence time of a single frame (33 ms). The speed of this reversible behavior makes the system quite promising from the standpoint of molecular sensing.[11]

Ellipsometry was used to quantify the effect of changes in RH on the thickness and refractive index of the multilayered films. A 25-cycle film on silicon was placed into a controlled-atmosphere chamber on an ellipsometer stage, along with a commercial RH calibrator (Figure 1b), and the film's thickness and index of refraction were determined as a function of the RH. The thickness increased monotonically with increasing RH, from 67.2 nm at 0.5% RH to 82.1 nm at 87% RH. Measurements taken 5 and 10 min after the calibrator had equilibrated always agreed to within 0.4 nm. The index of refraction also changed systematically as a function of RH. A plot of ellipsometric thickness vs RH is shown in Figure 2a, with corresponding refractive indexes given in Figure 2b. Taken together, the changes in thickness and refractive index provide insight into the sorption of water into the films. Upon going from 0.5% to 20% RH, for example, the film underwent a sudden increase in refractive index, with a relatively small increase in thickness, indicating that some of the sorbed water entered void spaces in the structure (e.g., spaces between platelet edges and interlamellar spaces). In contrast, upon going from 20 to 87% RH, the film underwent a gradual decrease in refractive index concomitant with a relatively large increase in thickness, suggesting that in this regime, swelling of the film was occurring due to sorption of water into the interlamellar galleries, void spaces in the structure having been filled. We infer that the refractive index drops because the refractive index of water ($n = 1.333$) is lower than that of the film. A small hysteresis was observed (compare solid and dotted lines in Figure 2a), which is common for adsorption and desorption of water by smectite minerals.[7,12] A different 25-cycle sample showed behavior nearly identical with that shown in Figure 2. The changes in ellipsometric thickness observed for the 25-cycle samples as a function of RH are sufficient to
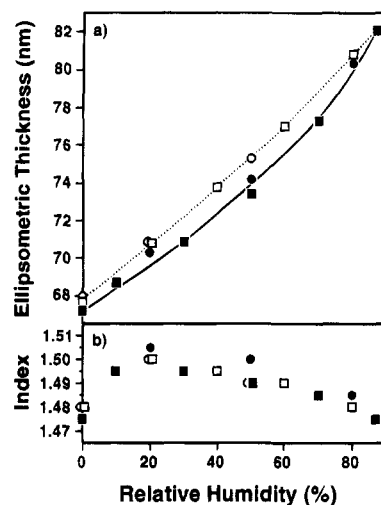
Figure 2. (a) Ellipsometric thickness of a 25-cycle multilayered film on silicon as a function of relative humidity. The filled symbols (solid line) correspond to thicknesses measured in order of increasing RH; the open symbols (dashed line) correspond to thicknesses measured in order of decreasing RH. The squares represent data obtained during the first cycle; the circles represent data obtained during the second cycle. The lines are guides for the eye. (b) Refractive index of the film, rounded to the nearest 0.005, as a function of RH. With the exception of the point at 87% RH, all data were obtained at multiples of 10% RH (±0.5%); some data points have been offset slightly in the horizontal direction for clarity of presentation.

account for the small variations we have seen in ellipsometric growth per adsorption cycle from day to day. As a control experiment, ellipsometric measurements were made of a bare wafer having a thermal oxide 61 nm in thickness (assumed index of refraction, $n = 1.465$) at 0.5% and 88% RH. The difference in thickness at these two extremes of RH was less than 1 nm, indicating that the changes in thickness of the multilayered samples were due mainly to intercalation of water and not to condensation onto a hydrophilic surface. The measurements in Figure 2 reflect reproducible changes in a film under conditions of controlled humidity and do not appear to depend upon the absolute refractive index, which varies from sample to sample and with the thickness of individual samples.

A more elaborate control experiment allowed us to determine how deeply into the film the water molecules penetrated and to conclusively rule out surface condensation as the dominant mechanism for these changes in thickness/refractive index. Five samples were prepared having different thicknesses of adsorbed multilayer and underlying native or thermal oxide (SiO_2), but having approximately the same combined thickness and thus the same interference color. These samples are depicted schematically in Figure 3, and details of their composition are given in Table 1. The final step in the preparation of all five samples was adsorption of hectorite, which ensured that all their *surfaces* should have the same affinity for H_2O. The response of these samples to water vapor was compared to that of sample 1, whose behavior was described at the beginning of this section. The extent of the change in interference color (i.e., from gold to peach, pink, or fuchsia) was used as a qualitative measure of the increase in thickness and/or refractive index of the film and thus the amount of water sorbed. Samples **2–5** were held over water in a

(11) The change in interference color in the path of the jet of humid air was not as dramatic as when the sample was allowed to equilibrate in a static humid atmosphere.

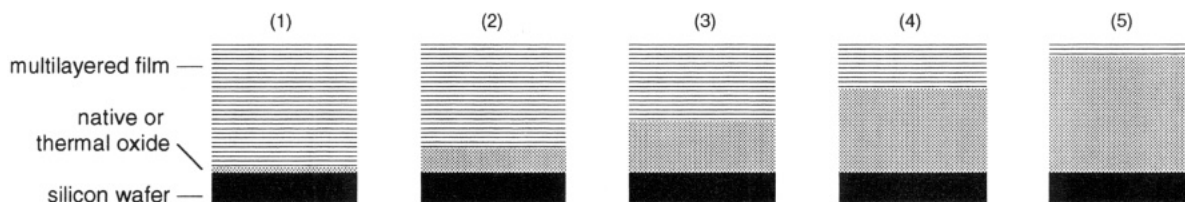(12) Barrer, R. M.; MacLeod, D. M. *Trans. Faraday Soc.* **1954**, *50*, 980.

Figure 3. Schematic diagram of the composition of samples **1**–**5**; details are given in the text and in Table 1.

Table 1. Thickness of Native or Thermal Oxide on Silicon and of Multilayered Film Adsorbed on Each Substrate

sample	oxide thickness (nm) assumed $n = 1.465$	multilayer thickness (nm) assumed $n = 1.5^a$	overall thickness (nm)
1	1.4	223 (67 cycles)	224
2	64	167 (53 cycles)	231
3	88	139 (46 cycles)	227
4	149	80 (27 cycles)	229
5	216	16 (6 cycles)	232

^{a} For any one film, growth has always appeared to be a linear function of the number of adsorption cycles when a constant refractive index is assumed. We have, however, observed variations in refractive index during the growth of individual films and from one film to another. For the films on samples **1**–**5**, the measured thicknesses (t) and refractive indexes (n) were (**1**) $t = 206$ nm, $n = 1.57$; (**2**) $t = 168$ nm, $n = 1.50$; (**3**) $t = 144$ nm, $n = 1.47$; (**4**) $t = 70$ nm, $n = 1.61$; (**5**) $t = 16$ nm, $n = 1.53$.

vial and compared to sample **1** in a separate but identical vial. The samples gave a range of responses that corresponded to the thickness of the multilayered films: sample **5**, having the thinnest film, acquired only a slightly peachy color; sample **2**, having the second-thickest film, turned the same deep fuchsia as sample **1**. Samples **3** and **4** displayed behavior between these two extremes. These observations indicate that water can be rapidly sorbed into the films to depths greater than 139 nm (sample **3**) and confirm that the changes in color cannot be due primarily to condensation of water vapor onto the samples' surfaces.

Although ellipsometry was useful in measuring the changes in thickness and refractive index of the films that produced visible responses to changes in humidity, this method does not provide a direct measure of the amount of water sorbed. To address this question, we used a quartz-crystal microbalance (QCM). The magnitude of the change in the resonant frequency of the crystal is directly proportional to the change in the mass of the film during sorption of water.[13] A 10-cycle film was adsorbed onto a gold-coated, AT-cut quartz crystal, and its resonant frequency was recorded after it had equilibrated for several minutes in atmospheres of chosen RH. The response of the film to changes in RH (Figure 4) resembles that of bulk montmorillonite, a mineral similar in structure to hectorite.[7] Others have correlated the inflection point in such curves for montmorillonite with discrete jumps in d spacing, revealed by X-ray diffraction, and ascribed it to the completion of intercalation of one layer of water in the interlamellar space and the beginning of the uptake of a second layer.[7] The multilayer-coated crystal responded rapidly to these incremental changes in RH (in fact, more rapidly than the commercial RH calibrator); after the flow rates of wet and dry nitrogen were set to desired values, the
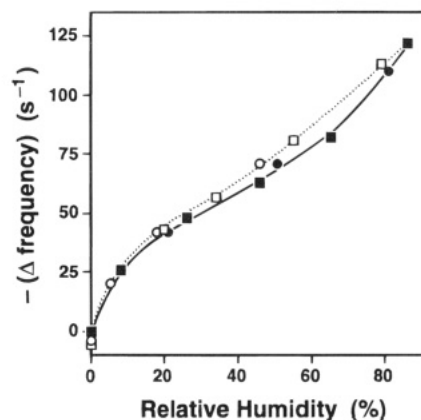

Figure 4. Change in resonant frequency of an oscillating quartz crystal coated with a 10-cycle film of PDDA and hectorite as a function of relative humidity. The filled symbols (solid line) correspond to changes measured in order of increasing RH; the open symbols (dashed line) correspond to changes measured in order of decreasing RH. Data obtained during the first cycle are represented by squares; data obtained during the second cycle are represented by circles. The lines are guides for the eye.

QCM often equilibrated to within ±1 Hz in under 1 min. For the multilayered samples, measurements taken 5 and 10 min after the calibrator had equilibrated always agreed to within 1 Hz.

The mass of water intercalated into the multilayered film can be calculated using a form of the Sauerbrey equation:[13]

$$M = -(f - f_0)\rho v A / 2(f_0)^2$$

where M is the mass of water; f is the frequency of the crystal in an atmosphere at a given RH; f_0 is the frequency of the crystal in an atmosphere at ~0% RH; ρ is the density of quartz, 2.65 g/cm³; v is the shear-wave velocity for an AT-cut quartz crystal, 3.34×10^5 cm/s; and A is the active area of the crystal. Because the active area of the crystal is difficult to define,[13] the areal density of water (i.e., M/A) was calculated instead. From the data shown in Figure 4, at 86% RH, the film sorbed 1.53×10^{-6} g of water per square centimeter of active area. This value is larger (on a per-cycle basis) than would be estimated from the increase in thickness measured ellipsometrically, for at least two reasons. First, the ellipsometric data indicate that some of the water fills void spaces, not causing swelling (vide supra) and therefore not resulting in an increase in ellipsometric thickness. Second, uptake of water by any excess film on the back of the quartz crystal[14] would artificially inflate the results generated by the QCM. This excess film does not affect ellipsometric measurements, which are obtained within a limited area on one side of the substrate.

Time-resolved QCM experiments allowed measurement of the speed with which water was sorbed by the

(13) Lu, C., Czanderna, A. W., Eds. *Applications of Piezoelectric Quartz-Crystal Microbalances; Methods and Applications* 7; Elsevier: New York, 1984; pp 26–31.
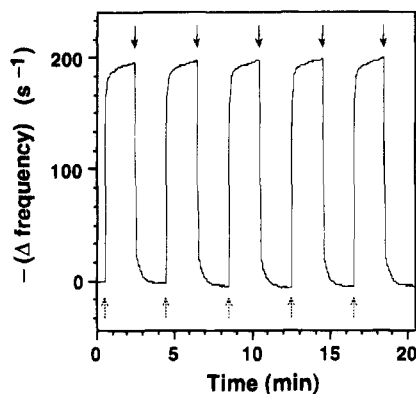
Figure 5. Change in resonant frequency of a quartz crystal coated with a 10-cycle multilayered film, as a function of time of exposure to a jet of dry or wet nitrogen. Dashed arrows (pointing up) indicate when the jet was switched to wet nitrogen, solid arrows (pointing down) indicate when the jet was switched to dry nitrogen.

films. A 10-cycle film, nominally 30 nm in thickness,[15] was adsorbed onto a gold-coated quartz crystal and exposed to a jet of nitrogen that was switched back and forth between ~0% and ~95% RH at 120-s intervals. The resonant frequency of the crystal was recorded at 1.5-s intervals (Figure 5). The sorption traces show that when the jet was switched to dry nitrogen, the frequency changed by more than 82% of its total range within the first 3 s. Likewise, each time the jet was switched to wet nitrogen, the frequency changed by more than 77% of the total frequency range within the same period. These results explain why the visible changes in interference color appeared complete within seconds when a wafer was cycled into and out of a humid atmosphere (vide supra). The path of water molecules diffusing through the film is probably tortuous due to the presence of the hectorite sheets (diameter 25–35 nm). Nevertheless, the initial kinetics of sorption are faster than our ability to take measurements, as would be expected based upon the kinetics of sorption of water by similar systems (zeolites[16] and hydrophilic polymers[17]). Approximately 1 min appeared to be sufficient for the sample to equilibrate to within 1 Hz after the jet had been switched to 0% RH. The kinetics of adsorption mirrored those of desorption; the final phase of equilibration at 95% RH, however, was somewhat slower than at 0% RH.[7] The tailing in the response curves at longer exposure times to either dry or wet nitrogen is probably due not only to the finite time needed for atmospheric turnover in the glass cell but also to changes in the heat of desorption of water as a function of the amount of water in the film. The heat of desorption of water from various clay minerals

increases as the amount of water in the sample decreases,[7,18] which makes the sorbed water in a nearly dry film more difficult to remove. By the same argument, the much lower heat of adsorption of water into a nearly saturated film causes further net adsorption to proceed more slowly due to competitive desorption. Intercalation of water by clays has been reported to exhibit a slow approach to equilibrium, with desorption being more reproducible than adsorption.[7]

Although the samples prepared for the QCM experiments each behaved in a consistent and reproducible manner, significant differences were observed from sample to sample. For example, whereas one crystal exhibited a difference of 125 Hz between limiting frequencies at ~0% and ~86% RH, another with the same nominal surface area and composition exhibited a difference of 170 Hz. This variability probably results from differences in sample preparation,[14] which might be minimized by optimization of the adsorption conditions. Given this uncertainty, a more detailed analysis of the absolute mass of water sorbed per structural unit of the multilayered film is not justified. Nonetheless, as was true for the ellipsometric study, the use of these films in practical applications would simply require the calibration of individual samples.

In conclusion, PDDA/hectorite multilayered films sorb water rapidly and reversibly. Ellipsometric and gravimetric studies indicate that, at first, some water fills void spaces in the structure, swelling the structure to a relatively small extent; further uptake of water into the interlamellar galleries causes greater swelling of the film. Due to the order in these films and corresponding orientation of the constituent silicate sheets (Figure 1a), we expect that this swelling occurs primarily in the direction normal to the surface. This anisotropy is important because it maximizes changes in thickness measured ellipsometrically and minimizes differential stress at the film/substrate interface as the sample is cycled repeatedly between dry and wet atmospheres. This study has not only provided insight into the sorption of water into these composite films but has also demonstrated the feasibility of using these unique materials as sensors. The method for preparing these films is flexible with respect to the choice of component materials;[19] this versatility may allow design of sensors that are selective for various classes of vapors.

Experimental Methods

Materials. Poly(diallyldimethylammonium chloride) was obtained from Polysciences as a 20% (w/w) aqueous solution and was diluted with Millipore Milli-Q water (15–17 MΩ cm) to 5% (w/w) before use. Laponite RD (synthetic hectorite) was obtained from Laporte Industries, Ltd., in powder form. It was added to Milli-Q water with stirring to form a 0.5% (w/w) dispersion; stirring was continued until the dispersion appeared clear (typically for several hours). The dispersion was then allowed to stand overnight without stirring to allow complete exfoliation of the precursor, and was diluted to 0.2% (w/w) before use. The individual silicate sheets in the suspension are 0.96 nm thick and approximately 25–35 nm in diameter; the composition of Laponite RD [66.2% SiO_2, 30.2%

(14) Multilayered films formed from PDDA and hectorite appear to adsorb readily onto a great variety of surfaces (Kleinfeld, E. R.; Ferguson, G. S., manuscript in preparation); it was therefore difficult to limit the growth of the film to the front face of the crystal, and the extent of the growth on the back face may vary from one crystal to another. Application of a removable mask to the back face of the crystal was not considered due to the risk of contamination of the film during formation of the film or upon removal of the mask.

(15) We have determined that, when films are adsorbed onto gold, the ellipsometric growth and film structure are identical or nearly identical to those of films formed on the native oxide of silicon (see ref 14).

(16) Karger, J.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*; Wiley: New York, 1992; pp 203, 400.

(17) Vieth, W. R. *Diffusion In and Through Polymers*; Hanser: New York, 1991; pp 209–211.

(18) Grim, R. E. *Clay Mineralogy*; McGraw-Hill: New York, 1968; p 270.

(19) Kleinfeld, E. R.; Ferguson, G. S. *Mater. Res. Soc. Symp. Proc.* **1995**, *369*, 697. For analogous organic/inorganic composite multilayers from other polyelectrolytes see: Keller, S. W.; Kim, H.-N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 8817.

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MgO, 2.9% Na_2O, 0.7% LiO_2 (w/w)] and the structure of the exfoliated suspension have been described elsewhere.[20] Silicon wafers [p-doped, (100)-oriented] were manufactured by Wacker Siltronic and had a native oxide approximately 1.5 nm in thickness, unless stated otherwise.

Sample Preparation. Silicon substrates were cleaned shortly before use by immersion for at least 30 min in a 30:70 (v/v) solution of 30% H_2O_2 and concd. H_2SO_4 (**Caution:** *This "piranha" solution reacts violently with organic materials!*) and were rinsed thoroughly with Milli-Q water and dried with a jet of nitrogen. For one experiment discussed in this paper, wafers were oxidized thermally in an oxygen atmosphere for various periods of time. These wafers were subjected to an additional cleaning step after treatment with piranha solution: immersion in a 50:50 (v/v) solution of 30% H_2O_2 and concentrated NH_4OH for 5 min, followed by rinsing and drying. Multilayered films were formed, as previously described,[5] by repeating a simple two-step cycle involving alternate adsorptions from a 5% (w/w) solution of poly(diallyldimethylammonium chloride) and a 0.2% (w/w) suspension of Laponite RD. No pretreatment of the substrates was used to promote adhesion of the multilayered films.

Ellipsometric Study of Water Sorption. A Rudolph Auto-EL III ellipsometer ($\lambda = 632.8$ nm, $\phi = 70°$) was used to measure thicknesses of the multilayered films using an assumed refractive index, or, if desired, to determine simultaneously both thickness and refractive index. The native or thermal oxide on silicon was always measured before adsorption of any multilayer and treated as a separate film. Unless noted otherwise, measurements were performed at ambient humidity and were always performed at room temperature (~22 °C). To study the response of the films to changes in RH, samples were placed on the ellipsometer stage which was enclosed in a polyethylene bag having small holes through which an RH calibrator (Vaisala HMC 20)[21] and a nitrogen flow of variable humidity were introduced and through which the laser beam was allowed to enter and exit (Figure 1b). The approximate volume of this cell was 2 L. The RH was cycled twice between ~0% and ~88%. In the first cycle, measurements were taken 5 and 10 min after the RH calibrator had equilibrated at a desired RH. In the second cycle, only one measurement was taken for each RH value, 5 min after the desired RH had been attained. In no case did the calibrator vary more than ±0.5% from this RH during the 10-min measurement period. Nitrogen of various relative humidities (RHs) was prepared by mixing dry nitrogen with nitrogen that had been passed through two gas dispersion bubblers filled with Milli-Q water; flow rates were $(5.0-20) \times 10^2$ sccm.

Gravimetric Studies of Water Sorption. A Sycon STM-100 MF quartz-crystal microbalance (QCM) was used to monitor mass changes resulting from the sorption of water by multilayered films. Gold-coated, AT-cut quartz crystals (6 MHz) were cleaned by rinsing with ethanol and water before use, and multilayered films were adsorbed according to the same procedure used on the silicon substrates.[5,15] The QCM sensor head and the RH calibrator were placed in a glass cell (approximate volume 0.45 L) into which a flow of nitrogen could be introduced. Measurements were performed at ambient temperatures (~22 °C). Nitrogen of various relative humidities (RHs) was prepared by mixing dry nitrogen with nitrogen that had been passed through two gas-dispersion bubblers filled with Milli-Q water. For measurement of water sorption as a function of RH, the resonant frequency of the crystal was determined 5 and 10 min after the RH calibrator had equilibrated. The RH was cycled twice, in steps, between ~0% and 88%. Flow rates were $(2.5-17) \times 10^2$ sccm. For measurements of water sorption as a function of time, data were taken at 1.5-s intervals as the gas flow was alternated between ~0% and ~95% RH (120 s each). Flow rates were $(6.9-9.3) \times 10^2$ sccm.

(20) Ramsay, J. D. F.; Swanton, S. W.; Bunce, J. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3919.

(21) The action of this calibrator is based on changes in capacitance of a polymer film as a function of RH.