Sol−Gel Processing of Ordered Multilayers To Produce Composite Films of Controlled Thickness

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Received April 8, 2000. Revised Manuscript Received June 16, 2000

Sol−gel processing of a multilayered film formed by the alternate adsorption of poly(diallyldimethylammonium chloride) and a synthetic silicate sheet mineral, Laponite RD, resulted in an interpenetrating composite network. Kinetic data indicate that the amount of material added due to sorption and gelation of tetraethyl orthosilicate (TEOS) reached a steady-state value within a day. Sol−gel growth occurred within the multilayer, with very little silicate being deposited at the surface. The resulting composite film showed the same order as an untreated multilayer, indicating that sorption and gelation did not disrupt the structural order of the multilayer. Curing the TEOS-treated films at 175 °C for 24 h to drive off excess water and complete the gelation process again resulted in an ordered composite structure. Cured films exposed to various levels of relative humidity demonstrated a dramatic decrease in swellability compared to an untreated multilayer.

Introduction

Combining different materials to form composites can result in unique systems with enhanced characteristics due to synergies between the properties of the components. One popular method for the preparation of both pure and composite materials is the sol−gel process, which typically involves the controlled hydrolysis of metal or semi-metal alkoxides to form inorganic oxide networks.[1,2] Sol−gel composites containing organic modifiers have been reported to have improved mechanical, optical, and sorption properties.[3−6] Such inorganic−organic composite materials have been investigated for potential use as sensors[7] and optical materials[8] (e.g., in second-order nonlinear applications,[9] lasers,[10] and light-emitting diodes[11]). A related method of depositing silica particles within a network structure involves swelling a matrix with orthosilicate monomers and subsequent exposure to hydrolysis conditions.[12−17]

The use of sol−gel processing for optical applications, such as reflective or antireflective coatings, often requires control of the thickness and refractive index—the optical path length—of the resulting film as well as

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10.1021/cm000291a CCC: $19.00

of the architecture of the film to avoid undesirable scattering.[1−3] Although refractive index can be adjusted using additives, and internal structure can be controlled by choice of processing conditions, precise control of thickness at the nanometer scale of length remains an important goal of research.[1,18,19] We have succeeded in developing a method that allows control of the thickness of a thin film by the sorption of a sol−gel precursor into a preformed multilayer film and then hydrolyzing it in situ to form a cross-linked network.[20] This method represents a significant advance in the preparation of composite thin films for optics and complements methods reported by others for the preparation of ultrathin (nanometers) films of inorganic oxides, including surface[21−23] and Langmuir−Blodgett sol−gel processes,[24] oxidation of silicon monolayers,[25] and the thermal conversion of self-assembled oxide films.[26]

Recently, our research group developed a method for the stepwise formation of ordered multilayer films by the alternate adsorption of cationic polymers and anionic clay sheets.[27,28] For example, films prepared from poly(diallyldimethylammonium chloride) (PDDA) and Laponite RD, a synthetic form of hectorite, were sufficiently ordered in the direction normal to the substrate surface to diffract X-rays. These films can be formed quickly, with a single adsorption cycle taking ∼2 min and the thickness of the films increasing linearly as a function of the number of adsorption cycles.[29] The films produced by this and related methods are, however, "soft" materials that swell readily and are easily damaged mechanically.[27,30−32] Early in our investigations, for example, we observed that the color of these films (due to optical interference) changed when they were exposed to humid air, indicating that the thickness and/or refractive index of the film had changed.[27,30] These observations prompted our investigation of the potential use of these films as humidity sensors.[30,31] The results of these studies indicated that both the thickness and the refractive index of these films change rapidly and reversibly in response to variations in relative humidity (RH). While this swelling/deswelling behavior is advantageous from the standpoint of sensor design, it is problematic for optical coatings. By forming a sol−gel network within a preformed film, we hoped to obtain films whose thickness would be less sensitive to RH.

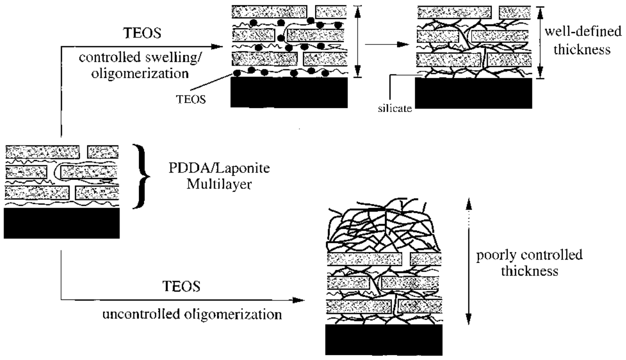

Figure 1. Schematic representation of in situ formation of a composite network by sol−gel processing of TEOS within a PDDA/Laponite multilayer film. Controlled sorption and gelation of TEOS should produce films having well-defined thicknesses, whereas uncontrolled gelation would result in films having poorly controlled thicknesses due to deposition of silicate on top of the film.

Tetraethyl orthosilicate, ($Si(OEt)_4$, TEOS) is a commonly used sol−gel precursor for the formation of silica.[1−3] Partial hydrolysis of the orthosilicate occurs to form $Si(OH)_n(OEt)_{4-n}$ and EtOH, and condensation between silanols or between silanol and silylethoxy groups then results in gelation. The hydrolysis reaction can be catalyzed by base, leading to a high degree of branching, or by acid, leading to linear molecules with infrequent cross-linking.[1−3] We expected that the uncatalyzed reaction, with unbuffered water, would allow the greatest control over the polymerization reaction and thus the thickness of the film (Figure 1).

A central goal in these studies was to achieve internal cross-linking without sacrificing control over the overall thickness of the film. This problem was challenging because withdrawing a sample from a solution of the monomer would leave the surface covered with a thin layer of this solution with an ill-defined thickness. Rinsing would not only remove the layer of solution but also remove some of the sorbed monomer from within the structure. Similarly, sorption from the gas phase could result in uncontrolled condensation on the outer surface of the film, and evaporation could remove some of the sorbed monomer. Our experimental results demonstrate, however, that the slow kinetics of gelation, relative to sorption, allowed controlled growth primarily within the multilayer "scaffolding". This paper describes the results of this approach, as well as the characterization and swelling properties of the composite-network films produced. A second focus of this work was to distinguish between two possible modes of swelling: intercalation into ordered domains versus sorption into amorphous regions.

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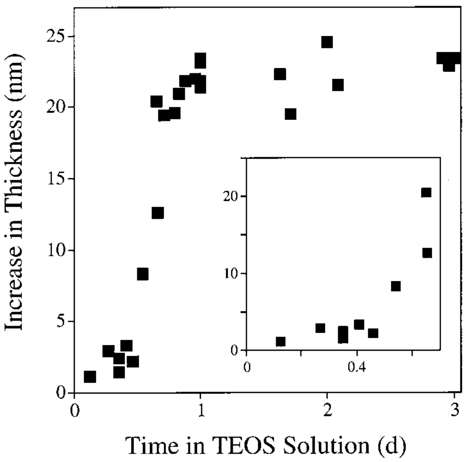

Figure 2. Kinetics of sorption and gelation of TEOS within 25-cycle multilayer films. Each data point represents an individually prepared sample. The abrupt increase in thickness that occurs between 11 and 15 h is shown expanded in the inset.

Results and Discussions

Synthesis and Characterization of the Composite Networks. Multilayered films were formed by sequential adsorption of PDDA and Laponite RD (25 cycles) from aqueous solutions, as described previously,[27] and had initial thicknesses of approximately 62–67 nm. Separate samples were suspended horizontally, face down, into a 1.1 M solution of TEOS in ethanol/water (3:2) for various lengths of time, followed by rinsing with EtOH (95%) and drying with a jet of nitrogen. The thickness of the films was then measured ellipsometrically at a relative humidity of 7–10% to minimize the effect of sorption of ambient water vapor (Figure 2).[33] Each data point represents an individually prepared sample. These data indicate that after a short induction time an abrupt increase in film thickness occurred between 11 and 15 h, with a steady-state value reached within 24 h. The initial shape of the curve (Figure 2, inset) suggests that small silicate oligomers formed within the multilayer film early in the process can easily migrate out, but upon further condensation, higher molecular weight products are trapped within the multilayer framework.

To demonstrate that this increase in thickness was due to the sorption and gelation of TEOS within the film, and not to accumulation of it on the top of the film, the following experiment was performed. Multilayered samples of various thicknesses—2-, 5-, 10-, 17-, 25-, 30-, 40-, and 60-cycle films—were prepared and treated with the TEOS solution for 24 h. A plot of the increase in thickness after treatment with TEOS as a function of the number of adsorption cycles used to prepare the original film was linear in the range of 2–30 cycles (Figure 3) but showed less growth than anticipated beyond 30 cycles. For these thicker films, the condensation of silicate species may form a barrier or "shell" that could impede the diffusion of monomer more deeply into the film. This reduced growth was not the result of insufficient sorption time, as two 40-cycle films soaked for an additional 24 h (48 h total, Figure 3) showed no

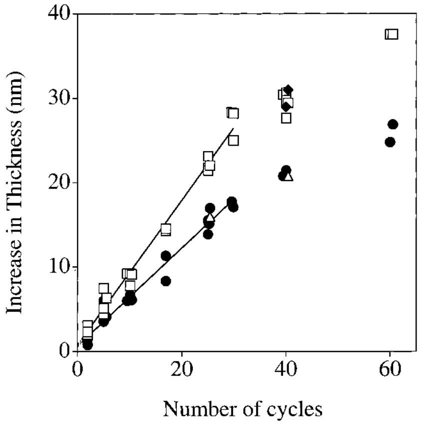

Figure 3. Increase in ellipsometric thickness of multilayer films after soaking in TEOS solution for 24 h (squares) and after subsequent heating in air at 175 °C for 24 h (circles). Diamonds represent films soaked in TEOS solution for 48 h, and triangles represent films soaked in TEOS solution for 24 h and then heated in air at 175 °C for 48 h. Some data points are offset slightly in the horizontal direction for clarity.

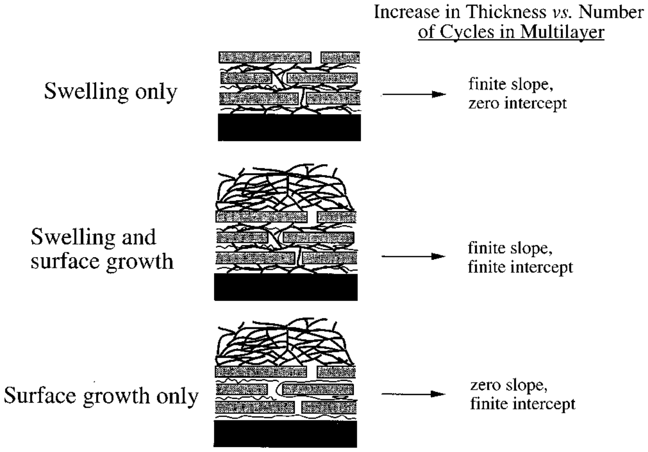

Figure 4. Schematic representation depicting the possible modes of growth in film thickness during sol–gel processing and the corresponding features expected for plots of increase in thickness versus the number of cycles used to prepare the film (i.e., Figure 3).

additional growth. A least-squares fit of the data for films in the linear range had a slope of ~0.9 nm/cycle, indicating a ~34% increase in thickness of the multilayers due to swelling and gelation. The near-zero intercept (0.7 nm) is consistent with sorption/swelling and gelation *within* the films but not with growth of oligomeric silicates on the outer surface of the film. As summarized in Figure 4, if both sorption/swelling and growth on the surface had occurred, we would have expected the linear plot to have a large, positive intercept representing the average amount of material deposited on the surface during the treatment. If growth had occurred exclusively on the surface, we would have expected a large, positive intercept and a slope of zero in this plot.

We evaluated the effect of the sorption and gelation of TEOS on the structural order of these films by comparing X-ray diffractograms of treated and untreated 30-cycle multilayered films (Figure 5a,c). The (001) reflection in the diffractogram of the untreated film occurred at 6.2° (2θ), corresponding to a d spacing of 1.42 ± 0.01 nm, while for the TEOS-treated film the

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(33) Ellipsometric data were obtained asumming a refractive index of 1.5 for the film.

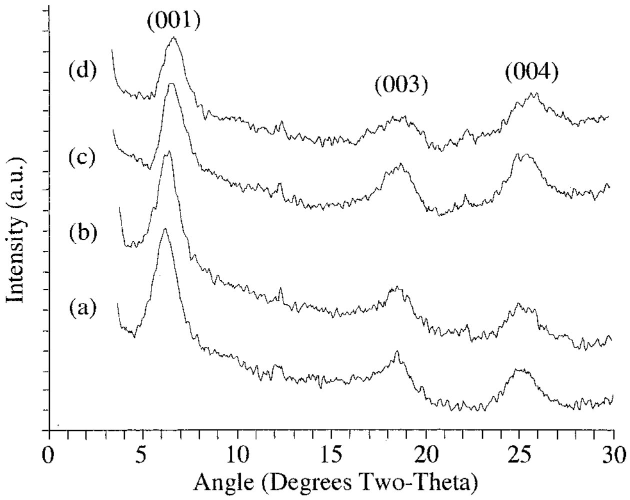

Figure 5. X-ray diffractograms comparing various 30-cycle PDDA/Laponite multilayer films: (a) an untreated film, (b) untreated/cured film, (c) a TEOS-treated film, and (d) a TEOS-treated/cured film.

reflection occurred at 6.5° (2θ), corresponding to a *d* spacing of only 1.36 ± 0.01 nm. The (003) and (004) reflections were also observed, though at the same positions for both films (18.6° and 25.2°, respectively), indicating a layer spacing of 1.45 ± 0.02 nm. The similarity of the position and intensities of the reflections (particularly the higher-order reflections)[34] in these two diffractograms indicates that the sorption and oligomerization of TEOS within the PDDA/Laponite multilayers did not disrupt their structural order and that these processes occurred primarily within the amorphous regions of the film. Hence, the blocklike components in Figure 1 should be interpreted as comprising crystalline domains of PDDA/Laponite within the film, described previously,[27] separated by swellable amorphous material.

The increase in thickness of our multilayers upon treatment with TEOS and after rinsing indicates that some oligomerization of the TEOS had occurred during and/or after swelling. To drive off excess water and complete the gelation process, samples were heated in air at 175 °C for 24 h. This temperature was chosen to cause condensation of silanol groups in the gel, while minimizing shrinkage and avoiding any carbonization of the polymer.[1,2,35] This curing treatment caused only a small decrease (∼8%) in *overall* film thickness. The thickness of the cured films increased linearly with increasing number of absorption cycles, as was the case prior to curing, in the range of 2−30 cycles (Figure 3). The slope of this growth, however, was lower than that prior to curing by about a third. In a control experiment, an untreated 30-cycle film was heated at 175 °C for 24 h and also showed an 8% decrease in thickness. This result indicated that the shrinkage in our TEOS-treated samples was due primarily to the multilayer itself and not to the sorbed sol−gel material. Curing of 25- and 40-cycle films for twice as long did not cause further shrinkage (Figure 3).

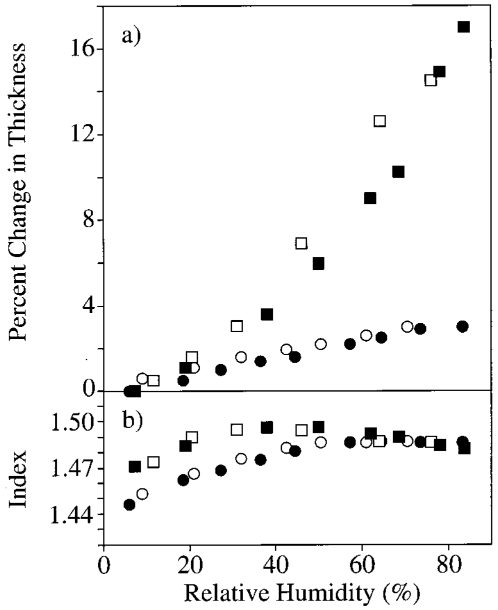

Figure 6. (a) Percent change in ellipsometric thickness of a 25-cycle multilayer film (squares) and a 25-cycle treated/cured multilayer film (circles) as a function of relative humidity (RH). Filled symbols represent data obtained with increasing RH, and open symbols were obtained with decreasing RH. (b) Refractive index of the films as a function of RH.

The (001) reflection in the XRD of a 30-cycle TEOS-treated film revealed that the lattice spacing had decreased only slightly, from 1.36 ± 0.01 nm before curing to 1.34 ± 0.01 nm (6.6°, 2θ) after the curing step (Figure 5c,d). The (003) and (004) reflections, found at 18.5° and 25.6°, indicate layer spacings of 1.45 ± 0.02 and 1.43 ± 0.02 nm, respectively, compared to 1.45 ± 0.02 nm reported above for an uncured sample. A 30-cycle multilayer that had not been treated with TEOS was also heated under these conditions for comparison (vide supra), and the *d* spacing indicated by its (001) reflection decreased only slightly, from 1.42 ± 0.01 nm (6.2°, 2θ) to 1.39 ± 0.01 nm (6.4°, 2θ) (Figure 5a,b). Higher-order reflections for this control sample occurred at 18.6° (003) and 25.5° (004), indicating spacings of 1.45 ± 0.02 and 1.43 ± 0.02 nm, respectively. The similarity of the *d* spacings for samples before and after curing, as well as with and without treatment with TEOS, indicates that these processes did not significantly disrupt the packing of the PDDA/clay crystallites within the film. Furthermore, these data indicate that film shrinkage occurs primarily in the amorphous regions of the film, consistent with those being the locations of the original sorption and polymerization.

Effect of Relative Humidity on Film Thickness. The effect of the sol−gel treatment on the swellability of the multilayer films by water vapor was evaluated by studying the changes in ellipsometric thickness (Figure 6a) and index of refraction (Figure 6b) as a function of relative humidity (RH) for both an untreated 25-cycle film (squares) and a 25-cycle film that had been treated with TEOS and then cured (circles). At 10% RH, the untreated film had a thickness of 70.5 nm, and the treated/cured film had a thickness of 85.8 nm. As the humidity was increased (filled symbols) and then de-

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creased (open symbols) in the range of 10−84% RH, the thickness of the untreated sample rose dramatically, and its refractive index rose to a broad maximum at intermediate RH and began to decrease at higher RH, as reported earlier.[30] In contrast, the thickness of the treated/cured sample rose only slightly, and its refractive index reached a plateau at ∼50% RH. The decrease in the full range of swellability of the treated/cured film from 17.5% to 3.5% upon sol−gel processing was consistent with the anticipated increase in rigidity of the composite, a central goal of this work. Nearly identical results were obtained using a second treated/cured 25-cycle film.

The differences in the shapes of the curves for the untreated and sol−gel-processed films, particularly in the refractive index data, are also significant. The thickness of the untreated film rose monotonically with RH, whereas that of the treated/cured film appeared to level out at high RH. Another difference in these curves is the presence of a hysteresis in the measurements for the untreated film and its near absence in those of the treated/cured film. These data demonstrate the decreased swellability of films upon sol−gel processing. Such hysteresis is characteristic not only of the untreated multilayers[30,31] but also of smectite minerals in general.[36,37] The refractive index of both films initially increased as water presumably displaced air in void spaces within the structures. After this initial increase, however, the refractive index of the untreated film decreased at relative humidities above ∼40% as water (with a lower refractive index) swelled the multilayer. The index of the sol−gel-processed film, in contrast, simply plateaued at ∼50% RH, indicating that swelling of this sample was minimal.

Conclusions

Multilayer films formed by alternate adsorption of PDDA and Laponite RD readily sorb orthosilicate monomers, allowing sol−gel processing in situ to form an ordered composite network. The change in thickness of the multilayers upon sorption and gelation is controlled and indicates that irreversible growth occurs only within the multilayers and not on the surface of the film. Kinetically, a steady-state value of thickness is reached within about 24 h. Curing the composite drives off excess water and allows the completion of the gelation process. X-ray diffractograms of films that had been treated and cured show similar order to untreated films, indicating that the sorption and oligomerization processes do not disrupt the order characteristic of the PDDA/Laponite system.

Upon exposure to various levels of relative humidity, the thickness of the treated/cured films changed very little, compared to the behavior of the untreated films. These results show promise for utilizing this system for optical applications because the overall thickness of the film can be predicted and controlled and the swellability of the film minimized. Use of a preformed multilayer as a "scaffolding" or template[38] for thin film formation[39] affords precise control over film thickness and refractive index by minimizing the shrinkage that normally accompanies condensation.[1,2,35] Expanding our methodology to include other sol−gel systems is an area of continuing interest.

Experimental Section

Materials. Poly(diallyldimethylammonium chloride) (20 wt % solution in water, MW 200 000−350 000) was obtained from Aldrich and diluted to 5% (w/w) with Millipore Milli-Q water (15−16 MΩ). Absolute ethanol (McCormick), ethanol (95%, Pharmco), and tetraethyl orthosilicate (TEOS, 98%, Acros) were used as received. Laponite RD (Southern Clay Products, INC., Gonzales, TX) was obtained in powder form and added to Milli-Q water and stirred overnight to form a clear 0.2% (w/w) dispersion.

Silicon (100) substrates (p-doped) were obtained from WaferNet, Inc., or Submicron Systems Corp., cut into ∼1 cm × ∼2.5 cm pieces, swabbed with absolute ethanol to remove silicon dust, and cleaned in piranha solution (1:2 (v/v) 30% H_2O_2 and concentrated H_2SO_4). *Caution: piranha solution reacts violently with organic material and should be handled carefully.* The clean wafers were rinsed thoroughly with Milli-Q water and dried with nitrogen. The wafers had a native oxide thickness of 1.8−2.1 nm.

Ellipsometric Analysis. The ellipsometric data were obtained on a Rudolph Auto-EL III nulling ellipsometer with a HeNe laser ($\lambda = 632.8$ nm) at an angle of incidence of 70°. Three to four spots were measured at 7−10% relative humidity,[30] unless otherwise noted, and averaged for each sample. The thickness of the native oxide of silicon and the multilayer film were measured assuming a refractive index of 1.5 ($k = 0$ because the multilayer is nonabsorbing) for these overlayers[27] and a standard refractive index for the silicon substrate ($n = 3.858$, $k = 0.018$). To determine the thickness of the multilayer, the thickness of the native oxide was subtracted from the measured overall thickness of the film (oxide and multilayer).

X-ray Diffractometry. X-ray diffractograms were obtained on a Philips APD 3720 powder diffractometer, in $\theta/2\theta$ mode, with monochromatized Cu Kα radiation ($\lambda = 0.154$ nm), operating at 45 kV and 30 mA. Data were obtained using a 0.05° step and 3 s/step collection time.

Multilayer Preparation. A clean silicon wafer was rinsed with Milli-Q water and dried with nitrogen. The 5% PDDA solution was dripped with a pipet onto the silicon wafer to cover its surface completely. After 5 s, the wafer was rinsed with Milli-Q water and dried with N_2. Rinsing and drying were then repeated. The same process was followed for the 0.2% Laponite dispersion. An adsorption of PDDA followed by an adsorption of clay constitutes one adsorption cycle. The average growth per such cycle was ∼2.9 nm. To minimize the effect of relative humidity (RH) on the measured thicknesses, all measurements were taken at between 7% and 10% RH, unless otherwise noted.

Sol−Gel Processing of Multilayer Films. Separate multilayer films were suspended horizontally, face down, in a 20 mL borosilicate scintivial containing 8 mL of a 1.1 M solution

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of TEOS in ethanol/water (3:2, v/v). After the indicated time period, the film was removed, rinsed with EtOH (95%), and dried with a jet of nitrogen. Within 15 min of removal, the thickness of the film was measured ellipsometrically at a relative humidity of 7–10% to minimize the effect of sorption of ambient water vapor.

Kinetics of TEOS Sorption/Oligomerization. The kinetics of TEOS sorption/oligomerization within Laponite/PDDA multilayers were measured by treating 25-cycle films with 8 mL of a 1.1 M solution of TEOS in ethanol/water (3:2, v/v) for various lengths of time. A separate sample was used for each time period to avoid any artifacts due to repeated cycling of samples in to and out of solution. These films were treated as described in the previous section.

Curing of TEOS-Treated Multilayers. A film treated with TEOS was placed in a scintivial with the film facing toward the bottom of the vial and heated in a Fisher Isotemp 500 series oven at 175 °C for 24 h. The film was then removed and allowed to cool to room temperature. Ellipsometric measurements were taken within 1 h of removal from the oven at a RH of 7–10%.

Swellability of Films in Humid Nitrogen. A 25-cycle film that had been treated with TEOS and then cured at 175 °C for 24 h, and a 25-cycle film that had been untreated and uncured, were exposed to various levels of RH. The RH was cycled between ~4% and ~86%, with ellipsometric measurements taken 5 and 10 min after the RH calibrator (Vaisala HMC 20) had equilibrated at each value of RH. The apparatus and this procedure have been described in more detail previously.[30]

Acknowledgment. We gratefully acknowledge support for this research from Southern Clay Products, Inc., as well as from the National Science Foundation (“Undergraduate Materials Education Initiative: Undergraduate Degree in Chemistry of Materials Synthesis and Processing”, #DMR-9218093), and Lehigh University (Presidential Scholarship, Roy Eckart College Scholar Program, and Althouse and Horner Fellowships for B.A.M., and Horner Fellowship for J.H.R.). We gratefully acknowledge the donation of the silicon wafers from WaferNet, Inc., and Submicron Systems Corporation (Allentown, PA). We also thank Elaine Kleinfeld and George Yasko for assistance and helpful discussions.

CM000291A