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In Situ Fluorescence Probing of Molecular Mobility and Chemical Changes during Formation of Dip-Coated Sol−Gel Silica Thin Films

Michael H. Huang,[†] Hermes M. Soyez,[‡] Bruce S. Dunn,*[,‡] and Jeffrey I. Zink*[,†]

Departments of Chemistry and Biochemistry and Materials Science and Engineering, University of California, Los Angeles, California 90095

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Pyranine (trisodium 8-hydroxy-1,3,6-pyrenetrisulfonate) and PRODAN (6-propionyl-2-(dimethylamino)naphthalene) are used as in situ fluorescence probes to monitor the molecular mobility and chemical evolution during sol−gel silica thin film deposition by the dip-coating process. Measurements are made on the evolving film as it emerges from the sol at thicknesses changing from <4 μm for the starting film to 300 nm for the final film. The thickness is monitored by interferometry. Results of the spatially resolved fluorescence depolarization for films withdrawn from a fresh sol show that the tumbling motion of both probes is retained until the final deposition stage when an extensive cross-linking silica framework forms. Intermediate probe mobility occurs at an earlier time in films pulled from an aged sol. A comparison between thin film deposition and monolith formation is made.

Introduction

One of the advantages of the sol−gel process is the versatility of fabricating the materials derived from this process into different forms, including bulk monoliths, fibers, and films.[1,2] Among these, sol−gel thin films are perhaps technologically the most important, due to their applications in optical and electronic coatings. Extensive studies have been devoted to these areas and have been reviewed.[3] While the properties of the final dried and solidified films are important for their particular applications, a better understanding of the dynamic structural and chemical changes during the film formation process can lead to better ways of preparing these films to give them the desired properties. However, only a few studies have focused on in situ observation of the dip-coated thin film formation process.[4,5] Film thickness and refractive index were measured during film deposition using imaging ellipsometry,[4] and aspects of the chemical composition were measured using a fluorescent probe molecule.[5]

In this paper, films formed by the dip-coating process are examined. A sketch of this process is shown in Figure 1. In the dip-coating process, a substrate is withdrawn slowly at a constant speed from a sol that contains monomeric or oligomeric silicate species.[6] The moving substrate entrains the sol forming the liquid film. This film thins by solvent evaporation, gravitational draining, and possibly surface tension gradient driven flow. When the upward moving flux is balanced by that of evaporation, a wedge-shaped steady film profile, 1−2 cm in height, is established. Preferential evaporation of alcohol creates a water-rich film, which subsequently dries to form the deposited film.[5]

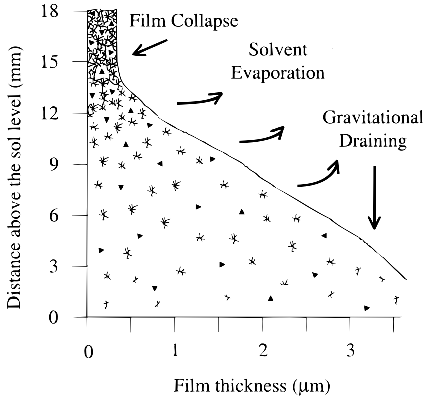

Figure 1. Sketch of the dip-coating process. The structural evolution shown is obtained from the fluorescence depolarization measurements. The triangles represent the probe molecules, and the irregular symbols represent the sol particles.

The structural evolution during film deposition is very complex and rapid; the sol to gel to xerogel transformation is complete within 30 s. The result is the overlap of the drying stage with hydrolysis and condensation reactions. Several parameters affect the structure of the final sol−gel thin films. Determining the chemical and structural changes at different stages during film formation, including film deposition from fresh and aged sols, is central to the understanding of the chemical and physical conditions of the sol affecting the properties and microstructure of the final film. Monitoring film

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[‡] Department of Materials Science and Engineering.

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evolution requires in situ observation methods. Real time monitoring by fluorescent probes has been demonstrated to be a feasible method for sol–gel-based films.[5,7,8]

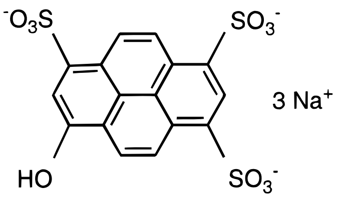
In this paper we report measurements in real time of the structural evolution of thin film formation. The dip-coating process separates the changes that occur both temporally and spatially. We simultaneously use both interferometry and fluorescence depolarization. Interferometry takes advantage of the interference of light rays reflecting off the top and bottom surfaces of a thin film and allows us to measure the changing thickness of the film as it is being formed on the substrate. Fluorescence depolarization measures the degree to which the orientation of polarized light is maintained after emission from a fluorescent molecular probe; the probes report the relative rotational mobility and provide a measure of the structural rigidity of the film on the nanometer scale. We use these nondestructive optical methods to map the structural changes as a function of processing time. The origins of the structural changes and comparisons to monolith formation are discussed.

Experimental Section

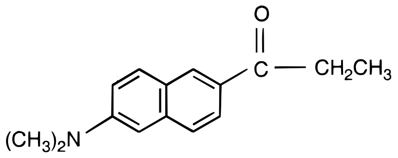
I. Materials Preparation. The sol used for this study follows the formulation used in an earlier study (MeOH, TMOS sol, and pH 4.25 acetate buffer with a volume ratio of 4:5:1) that produces a high optical quality thin film.[9] For our experiments the TMOS sol was prepared by mixing 15.27 g of TMOS (Aldrich), 3.38 g of deionized water, and 0.22 g of 0.04 N HCl. The TMOS sol was sonicated in an ice bath for 10 min. Typically 15 mL of the TMOS sol, 12 mL of MeOH, and 3 mL of the buffer were used to prepare the starting sol. To this sol 0.0157 g of pyranine (trisodium 8-hydroxy-1,3,6-pyrenetrisulfonate, Sigma Chemical Co.) was added such that the pyranine concentration in the final sol is 10^{-3} M. In the PRODAN (6-propionyl-2-(dimethylamino)naphthalene) experiment, 0.0020 g of PRODAN (Molecular Probes) was added to the sol such that the PRODAN concentration in the final sol is 3×10^{-4} M.

The films were drawn using the apparatus described previously.[5] This approach uses hydraulic motion to produce a steady and vibration-free withdrawal. Polished Si (100) substrates (9 cm × 1 cm × 1 mm) were cleaned with Nochromix (Godax Laboratories) and then rinsed with and stored in deionized water prior to use. These substrates were connected, through a ribbon, to a weighted float in a cylindrical water tank whose drainage rate was controlled by a flow valve. On top of the sol reservoir a transparent Pyrex cover was placed to reduce air currents. A small opening was used to pass the excitation laser beam and the emitted light. Convection-free drying was found to be critical to obtaining high optical quality films. The film pulling rate was ~6.9 cm/min for all experiments. This pulling rate makes good quality films. A steady-state fringe pattern was established within 15 s after the start of the experiment and persisted until the bottom of the substrate was pulled from the sol (~1.5 min). After deposition was complete, the thickness of some of the dried films was measured by surface profilometry (Alpha-Step 200; Tencor Instrument).

II. Probe Molecules. The fluorescent molecular probe molecules used in this work are pyranine



and PRODAN



The protonated form of pyranine has an emission maximum at 430 nm, and the deprotonated form has a maximum at 510 nm.[10,11] It has been used to monitor the alcohol/water ratios in sol–gel films.[5] PRODAN has an emission maximum at 505 nm in methanol and a maximum at 531 nm in water.[12] It has also been used to probe the microenvironment in the sol–gel matrix as a function of aging time[13] and in polymer-impregnated sol–gel composite monoliths.[14] These two probes were chosen because they have different shapes and charges (highly negatively charged for pyranine and neutral for PRODAN). It is of interest to compare a molecule that is planar with one that is elongated. It is also interesting to see if ion pairing plays a role in molecular mobility. Both probes are strongly luminescent.

III. Optical Measurements. The experimental measurements combined interferometry with fluorescence depolarization to characterize spatially the probe mobility and the chemical changes during film formation. The experimental setup used is similar to that described earlier.[5] Interferometry is based on the production of interference fringes when light illuminates a thin film of varying thickness. A mercury lamp filtered to emit 546 nm light was placed at an angle of 65° to the substrate normal to illuminate the film. On the other side of the film, a telescope, placed at an angle of 65° to the substrate normal, was used for fringe observation. Interference occurs at a thickness corresponding to

$$h = \frac{(2m + 1)\lambda}{4(n^2 - \sin^2 \theta_L)^{1/2}} \qquad (1)$$

where h is the film thickness, m is the interference fringe number ($m = 1$ for the first observed fringe below the dried film for agreement with the measured dried film thickness), θ_L is the illumination/viewing angle of the interference pattern, and n is the refractive index.[15] The interference fringes were reproducible under the same pulling conditions. In addition to providing an estimate of the film thickness, the fringe pattern also gives a convenient vertical scale to identify the distance between the sol reservoir level and a particular fringe and the time to reach that particular fringe.

The fluorescence depolarization technique uses polarized light to excite a fluorescent probe molecule.[16] The probe molecules in the proper orientation absorb and then emit on

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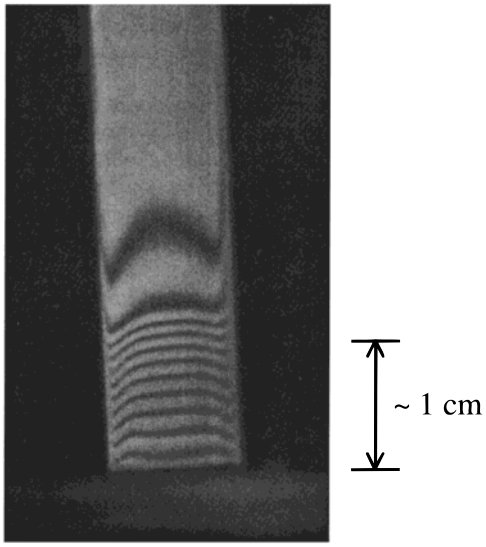

Figure 2. Photograph of an interference fringe pattern observed on a sol−gel thin film. The substrate is being withdrawn from a sol reservoir and is moving, but the fringe pattern is constant.

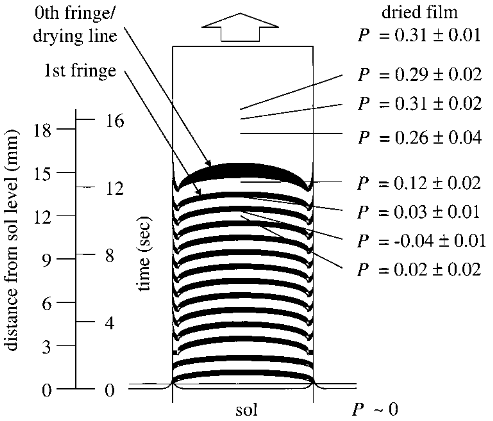

Figure 3. Schematic diagram of the results of the interferometry and of the fluorescence depolarization of pyranine. The distance from the sol in millimeters and the processing time in seconds are shown at the left. The steady-state fringes that develop on the moving substrate are shown by dark bands and monitor the film thickness (see text). The values of the degree of polarization, P, and the standard deviations of the mean are shown to the right of the film.

a time scale determined by the emission lifetime. The random tumbling motions of the probes in the excited state during this time lead to the depolarization (or scrambling of the direction of the polarization) of the resulting emission. The scrambling of the emission polarization is expressed as P, the degree of polarization:

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \tag{2}$$

where $I_{\parallel}$ and $I_{\perp}$ are the emission intensities parallel and perpendicular to the polarization of the exciting light. When the excited probe freely tumbles before emitting at a later time, $I_{\parallel} = I_{\perp}$ and $P = 0$. When the emitter is immobilized or its motion is considerably constrained, P can have a maximum value of 0.5. This technique, therefore, can be used to provide information on the immediate environment of the probe.

For all experiments the excitation source is the 351 nm polarized light from a Coherent Innova 90 Ar^+ laser (50:1 vertical polarization). The laser spot size is about 100 μm, permitting excellent spatial resolution. The laser spot did not affect the interference fringe pattern. Fluorescence of the probe passes through a Glan-Thompson polarizer into a monochromator (Model 82-410, Jarrell-Ash Co.), which is set at the emission maximum of the fluorescent probe in methanol (430 nm for pyranine and 505 nm for PRODAN). The slit width is 300 μm. A depolarizer is placed in front of the slit to eliminate the polarizing effect of the monochromator. The signal is collected by a photomultiplier (C31034/76), processed by a photon counter (SR400, Stanford Research Systems) and displayed on a computer. During the experiment the polarizer is set parallel to the polarization of the laser light and $I_{\parallel}$ is measured for about 15 s. During the 15 s measurement period 30 data points were taken, allowing good signal averaging. The polarizer is then rotated 90° and $I_{\perp}$ is measured for about the same amount of time. The process is repeated until the substrate is completely withdrawn from the sol reservoir. Emission intensities of the fresh sol were measured within $1^1/_2$ h after sol preparation, whereas measurements of the aged sol were made about 4 h after sol preparation.

Results

I. Interferometry and Film Thickness. A photograph of a characteristic fringe pattern for the sol−gel film as it is withdrawn from the reservoir is shown in Figure 2. A sketch of the pattern is shown in Figure 3 on which the processing time and the height from the sol reservoir to a particular fringe are shown. The film deposition reaches steady state, so that the pattern is constant in time although the substrate is actually moving. In this paper, the dark fringe furthest from the sol reservoir is called the zero fringe. This fringe has also been called the drying line.[5] In this paper it corresponds to $m = 1$ in eq 1. Beyond this fringe the film thickness is essentially constant and is comparable to that of the dried film. The lower fringes are called the first fringe, second fringe, and so on. The thickness of the dried film is approximately 3000 Å, as determined by profilometry. The difference in thickness between adjacent fringes, calculated using eq 1, is about 2500 Å. The film shrinks from <4 μm for the starting film to about 3000 Å above the zero fringe. The film thickness at various fringes is estimated assuming that there is a linear increase in the index of refraction between the sol and the dried film. The index of refraction of the starting sol is estimated as 1.35 based on the components of the starting sol, and that of the final film is 1.43.[5] There is a 5% uncertainty in the estimation of film thickness at the last dark fringe (the zero fringe) if the index of refraction is assumed to be 1.39 instead of 1.43.

The appearance of the fringe pattern is very similar for both fresh and aged sols. However, as the sol ages and approaches gelation, the fringes became more curved, and the lower and middle fringes are more closely spaced. A set of 25−30 fringes is observable, and the fringe height is elongated to more than 3 cm. This is due to a much greater extent of condensation occurring in the sol and a slower solvent evaporation rate, resulting in a more viscous sol and a much thicker dried film that often cracks. All of the fluorescence depolarization studies are done when the sol is fully fluid.

II. Fluorescence Depolarization of Molecular Probes. Figure 3 shows the results of the degree of polarization, P, for pyranine in the sol−gel film drawn from a fresh sol. P is approximately zero in the sol and surprisingly remains small until just below the zero fringe. P is 0.12 just below the zero fringe and dramati-

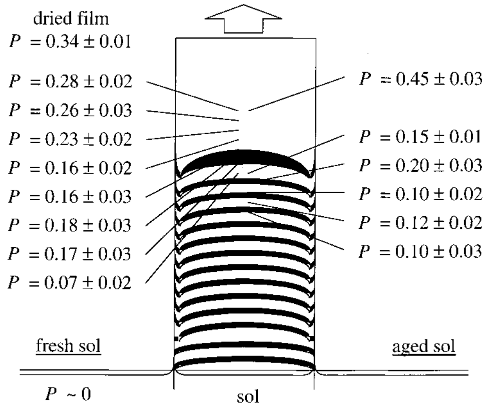

Figure 4. Schematic diagram of the results of the interferometry and of the fluorescence depolarization of PRODAN. The values of the degree of polarization, *P*, and the standard deviations of the mean for the fresh sol are shown to the left of the film. The corresponding *P* values for the aged sol are shown on the right.

cally increases to around 0.3 above the zero fringe. The dried films tested days later also have a *P* value of about 0.3. The experimental uncertainties in the *P* values represent the standard deviation of the mean. There are intensity fluctuations associated with these measurements because of the dynamic nature of the experiment.

Figure 4 shows the *P* values and their uncertainties for PRODAN in sol–gel films drawn from fresh and aged sols. For the fresh sol again the *P* values are close to zero in the starting sol to near the first fringe. Intermediate *P* values were measured around the zero fringe. *P* is 0.18 at the zero fringe, and above the zero fringe *P* increases continuously to close to 0.28. The *P* value of the dried film measured days later is about 0.34.

The aged sol has a greater degree of silicate condensation than in the fresh sol; intermediate *P* values were measured at lower fringes, or at an earlier time of the film formation process. The third fringe has a *P* value of 0.1. *P* goes up to 0.2 at the first fringe. A very large *P* value was recorded several fringe distances above the zero fringe.

Discussion

The sol–gel thin films formed by the dip-coating process are made by withdrawing a substrate (in this paper silicon) from a fluid sol. Continuous gravitational draining and solvent evaporation, accompanied by the condensation and gelation of the inorganic silicates, results in the deposition of the solid film.[6,17] Oligomeric species are formed at the early stage of the film-forming process by hydrolysis of the TMOS precursor and condensation. These oligomers then concentrate, by shrinkage of the film thickness through solvent evaporation, to produce an extensively cross-linked silicate network near the final stage of film deposition. At this stage, the branched network should still be flexible and filled with solvent, but very little is known about when and where this stage exists. At the end of the film deposition process, the silicate solidifies to form a dense porous network. The median pore radius is <20 Å in films withdrawn from an unaged sol.[6]

To probe in real time the changes that occur during film formation, fluorescent molecules are used. The fluorescence signal reports information about the molecules' surroundings on the 1 nm length scale. Extensive studies of sol–gel monolith formation using luminescence probes have been done and reviewed.[18,19] Of specific interest in this study is the mobility of the molecular probes in films and how the developing film changes the mobility. The molecular length used here is 6–8 Å, and the dynamic structural changes leading to the formation of the highly branched porous silica film is monitored at these dimensions. Simultaneously, the changes in the thickness of the film are monitored on the 10^2–10^3 nm scale by using interferometry. The thickness varies from <4 μm directly above the sol to 300 nm in the final film. All of these changes take place on the 13–14 s time scale.

The rotational freedom of the probe molecules is eventually restricted by the size of the pores. A consideration of the relative sizes of the pores and the probe molecules is instructive. The average pore diameter in the film near the end of the film formation process (the region between the zero fringe and first fringe) is on the order of 40 Å. The probes are small relative to the average pore and will retain their mobility if they are away from the silica walls. Restriction of the motion will occur when the molecules are trapped in constricting regions, i.e., necks and channels with dimensions of a few angstroms in the larger pores.[18] In addition, loss of solvent will lead to loss of mobility. The experimental results reveal at what time during the film formation and at what thickness of the film the restriction occurs.

The results for both pyranine and PRODAN in films made from fresh sol are similar. *P* values are around zero until the film has shrunk to about 500 nm after about 12 s of processing (i.e. between the zero fringe and first fringe). This suggests that both probes experience and report similar environmental conditions and mobility. These probes rotate freely in the solvent until the film is about 500 nm thick (above the first fringe). Formation of the silicate oligomers in the early stages of film formation (up to about 10 s) has practically no effect on the motion of the probes. These oligomers may still be too far apart compared to the sizes of the probes to hinder their tumbling mobility. The probe molecules are apparently not trapped in the oligomers. Intermediate *P* values measured in the region above the first fringe to the end of the zero fringe indicate the formation of an extensive silica framework that begins to restrict the probe motion. This region is shown in Figure 1. In this region the film thickness has shrunk to nearly that of the dried film by continuous and preferential evaporation of alcohol.[5] The solvent should still allow probes residing in the center of the pores rapid free rotation, but the probe molecules located near or interacting with the surrounding silica walls have constrained mobility. Thus intermediate *P* values are measured.

The final stage of the film formation process is the formation of final dried and solidified silica film at the end of the fringe pattern. This stage occurs after about 14 s, and no further interference fringes are observed.

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Above the zero fringe, it is expected that the final silica framework is established and the solvent is essentially gone. A few millimeters above the zero fringe (corresponding to a few seconds of time), large P values (0.23−0.31) are measured indicating that the probes are trapped by the silica framework and that their mobility is constrained. The measurements support the structural collapse mechanism proposed for dip-coated films.[1,6,17]

It is of interest to compare the dynamics of films pulled from an aged sol with those from the freshly prepared sol. There should be a greater extent of oligomer formation in the aged sol and thus a greater amount of the solid components entrained in the film as it is pulled. This greater concentration of solid species in the film should hinder the probe motion at an earlier stage during the film formation process. Indeed, intermediate P values were measured at a thickness of about 1 μm (around the third fringe) in the aged sol films. The aged sol is only slightly more viscous than the fresh sol; the P values of zero just above the sol reservoir show that the probe molecule is unconstrained in the sol. The fact that the P values become nonzero at much earlier processing times and much greater film thickness (about the second or third fringe in the aged sol film compared to the zero fringe in the fresh sol film) suggests that the former probably has a more rigid and compact structure and/or contains pores with a larger number of constraining regions.

Finally, it is interesting to compare the deposition of sol−gel films with the formation of sol−gel monoliths. PRODAN has been used to probe the microenvironment of a monolithic TMOS sol−gel matrix as a function of aging time.[13] The changes in the fluorescence anisotropy, r, during the aging stage were monitored, where $r = (I_{\|} - I_{\perp})/(I_{\|} + 2I_{\perp})$. The r values used in the study of the monoliths and the P values used in this film study are related by the following equation:[16,20,21]

$$\frac{1}{r} = \frac{3}{2}\left(\frac{1}{P} - \frac{1}{3}\right) \tag{3}$$

Using the Perrin and the Debye−Stokes−Einstein equations that correlate r to microviscosity η,[12] the changes in the microviscosity during the long aging stage of the monoliths were calculated. The anisotropy r remained low ($r \sim 0.02$; microviscosity, 0.7 cp) from the monolith preparation to 95 h after the gelation point. Then r increased significantly during the alcohol removal period from 141 to 245 h ($r \sim 0.26$ or 140 cp at 245 h). Upon the onset of water expulsion at 573 h, the average r was about 0.26 or 140−150 cp.

Both similarities and differences in the dynamics of film deposition and monolith formation are evident from these results. The initial and final mobilities of the probes are similar. In both cases, the probe molecule is unconstrained in the sol ($r = 0.02$, or $P = 0.03$ for the sol before gelation) and in both cases similarly constrained in the final solid ($r = 0.26$, or $P = 0.34$ for both dried film and dried monolith). The major difference is that for monoliths the molecular mobility is high for a long time through the drying stage until the removal of alcohol, at which point intermediate mobility is observed. In the films the alcohol evaporation is continuous and is probably near completion at the first fringe. The mobility at the zero fringe where gelation takes place is intermediate (P value of 0.17). After a few more seconds (a few millimeters above the zero fringe) where almost all of the solvent has evaporated the probe finally becomes immobilized.

Summary

Fluorescence depolarization of the molecular probes pyranine and PRODAN are used to monitor the changes in the molecular mobility during the formation of dip-coated sol−gel silica thin films as the films are being pulled. At the same time, interferometry is used to measure the film thickness in real time. Similar results are obtained from both probes. The molecules tumble freely throughout most of the film deposition process until the film is about 500 nm thick after about 12 s of processing, indicating that the presence of scattered silicate oligomers at earlier times has little effect on their mobility. Probe motion is constrained after about 13−14 s and the films are about 350 nm thick; oligomer aggregation forms an extensive silicate framework. Shortly beyond the zero fringe where the solvent is mostly evaporated, the probe mobility is reduced to close to that in the dried film. In films pulled from an aged sol, PRODAN begins to experience constrained mobility when the film is 1 μm thick due to a higher degree of condensation/oligomer formation.

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