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In Situ Probing by Fluorescence Spectroscopy of the Formation of Continuous Highly-Ordered Lamellar-Phase Mesostructured Thin Films

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Continuous highly-ordered mesostructured lamellar-phase thin films are formed by a rapid dip-coating method. The films are made by a dip-coating process from a sol consisting of tetraethoxysilane and the surfactant sodium dodecyl sulfate (SDS). XRD patterns give sharp peaks extending to 14 orders, indicative of a highly-ordered structure. Film thickness is measured in real time by using interferometry; interference fringes remain constant in height above the sol on the continuously-moving silicon substrate. In situ fluorescence spectra of probe molecules were recorded to trace both the formation of the micelles and the solvent composition of the films as they are pulled in real time. Micelles are formed, break up, and re-form to produce the final structure in 12 s, and the water content smoothly increases from 2% to 60% in the same amount of time.

Recent developments in the preparation of mesostructured templated sol−gel silica materials have extended the morphology from the originally discovered powders, with particle sizes on the order of microns,[1] to continuous thin films.[2,3] This discovery not only allows macroscopic materials to be fabricated but also enables both the chemistry and the dynamics of the assembly of the structure to be probed in real time because the steps involved in the formation and solidification of the structure are separated both spatially and temporally.[3] In this Letter we report the development of a very high degree of long range order in continuous silicate films 1500 Å thick by using the surfactant sodium dodecyl sulfate (SDS) and a sol composed of tetraethoxysilane (TEOS). The film thickness, solvent composition, and micelle formation are measured in real time by simultaneously combining interferometry and spectroscopy of luminescent molecular probes.

The sol was prepared by refluxing TEOS ($(C_2H_5O)_4Si$), ethanol, water, and HCl (mole ratio: $1:3.8:1:5 \times 10^{-5}$) at 60 °C for 90 min. Water and HCl were added to increase the concentration of HCl to 7.34 mM. The sol was stirred for 15 min and then aged at room temperature for another 15 min, followed by a dilution with 2 equiv of ethanol. To the sol was then added 0.5−2 wt % (0.04−0.16 M) SDS. The final mole ratio of the constituents was 1:22.3:5.1: 0.004:0.022−0.089 TEOS/ethanol/H_2O/HCl/SDS. Films were prepared by the dip-coating method in which clean Si(100) wafers with dimensions of about 8 cm × 1 cm were immersed in the sol and withdrawn at a speed of about 5−6.8 cm/min. The films made with ≤1.0 wt % SDS are uniform in color (blue) and are 1500 Å thick, as measured by profilometry. Films made from sols with surfactant concentrations ≥1.5 wt % contain some radial spots and stripes.

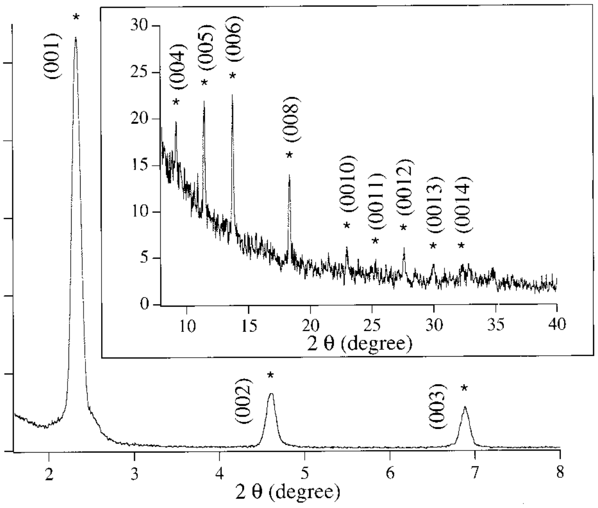

Figure 1. X-ray diffraction pattern of a mesostructured silicate thin film made with 1.7 wt % SDS at a pulling speed of 6.8 cm/min. The peaks from the lamellar phase structure are indexed and labeled with asterisks.

X-ray diffraction (XRD) patterns of the films, taken using Cu Kα radiation with $\lambda = 1.5418$ Å, revealed a high degree of long range order with peaks extending to 14th order (Figure 1). The average 2θ spacing is 2.3° (37.9 Å d-spacing). Small peaks at $2\theta = 28.50°$ and 34.83° probably arise from packing of the hydrocarbon chains within the layers.[4] The absence of segregated crystalline SDS is indicated by the absence of its strong (110), (111), and (200) peaks at the 2θ values 20.31°, 20.67°, and 21.84°, respectively. The XRD pattern is most consistent with a

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(1) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710−712. (b) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834−10843.

(2) (a) Ogawa, M. *J. Am. Chem. Soc.* **1994**, *116*, 7941−7942. (b) Yang, H.; Kuperman, A.; Coombs, N.; Maniche-Afara, S.; Ozin, G. A. *Nature* **1996**, *379*, 703−705. (c) Yang, H.; Coombs, N.; Sokolov, I.; Ozin, G. A. *Nature* **1996**, *381*, 589−592. (d) Aksay, I. A.; Trau, M.; Manne, S.; Honma, I.; Yao, N.; Zhou, L.; Fenter, P.; Eisenberger, P. M.; Gruner, S. M. *Science* **1996**, *273*, 892−898. (e) Tolbert, S. H.; Schäffer, T. E.; Feng, J.; Hansma, P. K.; Stucky, G. D. *Chem. Mater.* **1997**, *9*, 1962−1967. (f) Martin, J. E.; Anderson, M. T.; Odinek, J. G.; Newcomer, P. P. *Langmuir* **1997**, *13*, 4133−4141. (g) Ryoo, R.; Ko, C. H.; Cho, S. J.; Kim, J. M. *J. Phys. Chem. B* **1997**, *101*, 10610−10613.

(3) Lu, Y.; Ganguli, R.; Drewien, C. A.; Anderson, M. T.; Brinker, C. J.; Gong, W.; Guo, Y.; Soyez, H.; Dunn, B.; Huang, M. H.; Zink, J. I. *Nature* **1997**, *389*, 364−368.

(4) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147−1160.

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lamellar-phase structure with alternating surfactant and silica layers.[1b,4] The Scherrer formula[5] was used to estimate the size of the ordered region; on the basis of the width of the (001) peak, the lower limits are greater than 660 and 885 Å for films made with 1.7 and 1.9 wt % SDS, respectively. Calcination of the films at 400 °C for 4 h to remove all the organic species destroys the structure and leaves behind only the inorganic silica matrix. XRD patterns of the calcined films show loss of all the peaks. Mesostructured SDS sol−gel powders have also been reported to display lamellar structure with a *d*-spacing of 35 Å and the surfactant−silicate interactions discussed.[6,7] Figure 1 shows the XRD pattern of a 1.7 wt % SDS sol−gel film. Increasing the surfactant concentration gives progressively sharper XRD peaks but poorer quality films.

The combination of interferometry and fluorescence spectroscopy is used to characterize spatially the physical and chemical changes during film pulling.[8] Film thickness is monitored in real time by interferometry. 546-nm light from a filtered mercury lamp illuminated the film at an angle of 35° to the substrate normal. A telescope at an angle of 35° to the substrate normal was used to observe the interference fringes. Each fringe above the sol represents a decrease in the thickness of about 2200 Å; this value varies with height because the refractive index increases during processing. Interference fringes remain constant in height above the sol at a constant pulling speed and are reproducible from sample to sample under identical pulling conditions. The fringe numbers thus provide information on the film thickness. The distance from a particular fringe to the sol meniscus is directly proportional to the processing time. The highest dark fringe is labeled as the first fringe; film thickness is essentially constant beyond that fringe.

The dynamics of the physical and chemical changes that occur during film formation are monitored by using in situ fluorescence spectra of suitable probe molecules. Micelle formation is probed during film formation by the vibronic band intensity ratios in the emission spectrum of pyrene that have been used previously to distinguish surfactant concentrations below and above the critical micelle concentration (cmc) in aqueous solutions.[9] The incorporation of pyrene in spin-coated surfactant-templated sol−gel silica films has also been examined,[10] and its use as a probe of the pore environment in sol−gel materials has been reviewed.[11] The variation in the water/ethanol ratio during the film development is monitored by blue (430 nm) to green (510 nm) luminescence band intensity ratios from the protonated and deprotonated forms of pyranine.[8] In both cases the probe molecule was dissolved in the sol (1×10^{-4} M pyranine or between 1×10^{-4} and 2×10^{-4} M pyrene). The fluorescence was excited by the 351-nm line from an Ar^+ laser focused to a spot of about 100 μm. The laser did not affect the interference fringe pattern, thus indicating that local heating did not influence the film quality. The spectra were recorded by using an EG&G model 1420 optical multichannel analyzer and a 0.32 m Jobin-Yvon/ISA monochromator for dispersion. The slit width was 150 μm, and the integration time was 1 s. The results of the measurements for 1 wt % SDS sol−gel films using a pulling speed of 5 cm/min are summarized in Figure 2.

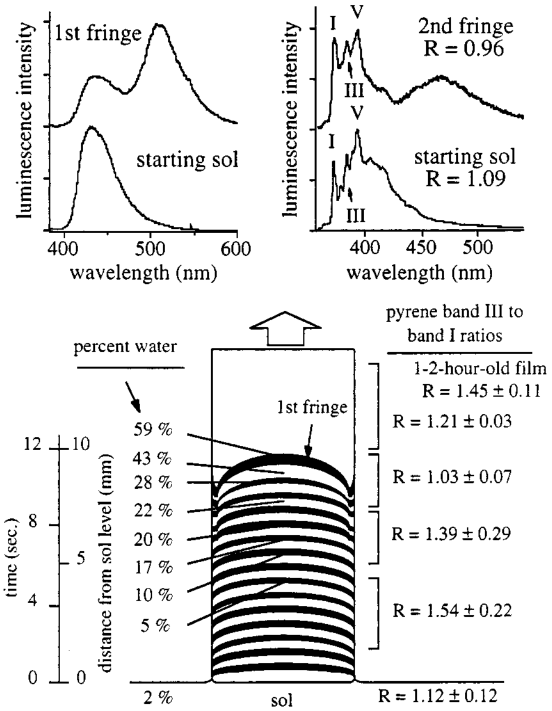

Figure 2. Schematic diagram of the results of the interferometry and spectroscopy. The distance from the sol in millimeters and the processing time in seconds are shown at the left. The steady-state fringes that develop on the moving substrate are shown by dark bands and monitor the film thickness (see text). The percent water as a function of thickness and time are shown to the left of the film. Representative spectra of the pyranine probe that are used to calculate the percent water at two different positions on the film are shown at the top left. The pyrene vibronic band intensity ratios *R* that are used to determine polarity are shown on the right. Pyrene spectra from which *R* values are obtained are shown at the top right. Note the increase, decrease, and final increase in *R* as a function of time, indicative of micelle formation followed by breakup and re-formation.

The water to alcohol ratio increases continuously during film development because of the higher vapor pressure and faster evaporation of alcohol.[8] In the sol, the water content is about 2%, but about halfway through the processing (6 s, seventh fringe) it has increased to about 10%. By the time the film has shrunk to nearly its final thickness (first fringe, 12 s), it has increased to almost 60%.

The results of the probe of micelle formation are surprising: micelle formation occurs almost immediately above the sol, but the micelle is broken up about halfway through the film formation and only forms the final lamellar structure at the very end of the processing. The III/I ratio of pyrene in the starting sol is 1.12 ± 0.12. The same value is measured when the surfactant is absent. The value in pure ethanol is 0.91, and that in pure water is 0.63.[9] Thus, micelles are not present in the starting sol and pyrene is responding to a polar environment. Between about 2 and 5 s during the film formation, the ratio dramatically increases to 1.54 ± 0.22, as shown in Figure 2. This increased value is indicative of a nonpolar environment and signals micelle formation. (The ratio is 1.65 in hexane.)[9] The solvent composition outside of the micelle has not changed dramatically, but the film

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[5] West, A. R. *Solid State Chemistry and its Applications*; John Wiley & Sons: New York, 1996; pp 173−175.

[6] Yada, M.; Kitamura, H.; Machida, M.; Kijima, T. *Langmuir* **1997**, *13*, 5252−5257.

[7] Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176−1191.

[8] Nishida, F.; McKiernan, J. M.; Dunn, B.; Zink, J. I.; Brinker, C. J.; Hurd, A. J. *J. Am. Ceram. Soc.* **1995**, *78*, 1640−1648.

[9] Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039−2044.

[10] (a) Ogawa, M. *Langmuir* **1995**, *11*, 4639−4641. (b) Ogawa, M. *Chem. Mater.* **1998**, *10*, 1382−1385.

[11] Dunn, B.; Zink, J. I. *Chem. Mater.* **1997**, *9*, 2280−2291.

thickness has shrunk from about 3 to 2 μm, the surfactant concentration has increased, and the cmc is exceeded.

The most startling result is that as film development proceeds, the ratio *decreases* back to a value about that of the original sol. This transition begins about 6 s into the development at about the seventh fringe. In this region the film thickness continues to decrease, and the percent water concentration markedly increases. A likely explanation of the decrease in the ratio is that the originally-formed micelle is disrupted and the structure is undergoing a phase change, typical of surfactant behavior in aqueous solution as the surfactant concentration increases.[12] As these changes occur, the pyrene is re-exposed to the solvent and the ratio reports the significant increase in polarity.

Finally, at and above the first fringe, the pyrene again becomes contained in a nonpolar environment as the final lamellar phase is formed. The large values do not occur immediately at the final fringe (where the film almost reaches its final thickness) but rather require an additional 5−15 min. There are still dynamic processes occurring during this time such as continued solvent evaporation and/or flexibility of the surfactant in the lamellar structure. The ratio measured after 1−2 h is 1.45 ± 0.11. The final ratio of the fully developed film measured after several weeks is 1.67.

The spectra of the pyrene probe provide a second measure of these dynamics; a broad excimer peak caused by dimerization in the excited state grows and then declines during this time. The excimer peak appears when the laser excites the molecules in the region of the second fringe, grows in intensity as the laser is moved further up the film, and then slowly decreases. (The excimer intensity decreases to half its original intensity in about 60 min and continues to decrease for as long as several hours.) These results suggest that at the second fringe the pyrene concentration becomes high enough to allow excimer formation because of the reduction in the film volume. As the lamellar structure forms, the pyrene molecules become immobilized and isolated; the continuous decrease in mobility with time inhibits excimer formation.[13]

XRD patterns taken at 8-min intervals over 2 h were used to investigate whether long-time structural changes occurred. No significant changes were observed. These results suggest that the long range order of the lamellar structure is established at about the time the final thickness is reached even though more local dynamics persist for several hours.

In summary, sol−gel silica films templated by SDS form highly ordered lamellar films by dip-coating. In situ interferometry and fluorescence spectroscopy of probe molecules simultaneously trace in real time both the continuous enrichment of water in the solvent of a depositing film and the formation of micelles. Micelles are formed, break up, and re-form into the final lamellar structure in 12 s, and the molecular motion in the film continues for several hours.

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[12] (a) Ross, S.; Morrison, I. D. *Colloid Systems and Interfaces*; John Wiley & Sons: New York, 1988; pp 173−177. (b) Raman, N. K.; Anderson, M. T.; Brinker, C. J. *Chem. Mater.* **1996**, *8*, 1682−1701.

[13] Kaufman, V. R.; Avnir, D. *Langmuir* **1986**, *2*, 717−722.