In-Situ Fluorescence Imaging of Sol-Gel Thin Film Deposition

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F. NISHIDA AND B. DUNN

Department of Materials Science and Engineering, UCLA, Los Angeles, CA

J.M. MCKIERNAN AND J.I. ZINK

Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA

C.J. BRINKER AND A.J. HURD

Sandia National Laboratories, Albuquerque, NM

Abstract. Pyranine was used as a fluorescence probe to monitor the chemical evolution in-situ during thin film deposition by the dip coating process. The sensitivity of the pyranine luminescence to protonation/deprotonation effects was used to quantify changes in the water/alcohol ratio in real time within the depositing film as the substrate was withdrawn from the coating reservoir. The spatially resolved spectral results clearly showed that preferential evaporation of alcohol occurred with increasing distance from the reservoir and that the maximum water content reached rather high values near the drying line. Correlation of the luminescence results with the interference pattern of the drawn films allows the solvent composition in the film to be mapped as a function of film thickness. These experiments demonstrate for the first time that luminescent organic molecules may be applied to the processing science of sol-gel thin film deposition.

Keywords: fluorescence probe, luminescence, thin film processing

1. Introduction

Sol-gel films belong to a broad class of coatings where the material is applied via a liquid carrier. This approach has been known and well studied for over 50 years [1] and in recent years a number of applications have emerged in a wide range of areas [2]. Of the several different methods used to produce sol-gel films, dip coating is perhaps the most important one from a technological perspective since a uniform coating can be deposited onto substrates of large dimensions and complex geometries [3]. In the dip coating process the substrate is immersed into the coating solution and then withdrawn at a controlled rate. Brinker and co-workers have carried out extensive work, both experimental and theoretical, and established how various physical and chemical parameters involved in dip coating affect the structure and properties of the final film [4].

In the dip coating process, a substrate is withdrawn slowly at constant speed from a colloidal or polymeric sol. A film of liquid becomes entrained on the surface.

This film thins from gravitational draining, capillary-driven flows and evaporation. When the upward moving flux is balanced by that of evaporation, a steady wedge-shaped film profile, 1–2 cm in height, is established which terminates in a well defined drying line. Above the drying line exists a nearly dry film. The structural evolution in sol-gel thin films is very complex. Unlike the bulk gel systems, the drying stage of the sol-gel process overlaps the gelation and aging stages. During the final part of the deposition (drying) process, large capillary pressures can develop, causing the network to collapse. The greater capillary pressure is one reason that there is greater compaction of films as compared to bulk gels. The final film structure represents a competition between phenomena which collapse the film, such as evaporation and capillary pressure, and phenomena which tend to stiffen the structure, such as condensation and aggregation.

Determining the composition of the film at different stages during film formation is central to understanding the film's properties and microstructure. The

changes in film chemistry which occur during film formation will affect the surface tension, capillary pressure and, therefore, the densification of the network. At the present time, there is relatively little experimental work which addresses the issue of chemical evolution. The characterization of sol-gel thin films has generally been limited to the characterization of the final dried film. One exception to this has been the imaging ellipsometry measurements of Hurd and Brinker which allowed *in-situ* monitoring of film thickness and refractive index during film pulling [5].

This paper reports new results on the use of an organic molecule as a luminescent probe to monitor the chemical evolution *in-situ* during thin film deposition by the dip coating process. The incorporation of organic, organometallic and biological molecules in sol-gel matrices has been well established over the past few years [6, 7]. This synthesis approach has led to a number of new optical materials. However, another important direction for the work has been to use fluorescent molecules to probe local chemical and structural changes which occur during the sol-gel process. A number of such studies have been reported with bulk materials [6, 7]. Because of the shorter optical path, there is the question of whether the optical probe techniques can be adapted to thin films. The work presented in this paper clearly establishes that these methods may be applied to sol-gel dip-coated thin films.

The fluorescent probe molecule, trisodiumtrisulfonatehydroxypyrene, or pyranine, is sensitive to proton transfer phenomena. The fluorescence spectrum of the molecule changes as the proton is added or removed, with the protonated form having an emission maximum of 430 nm and the deprotonated form having a maximum of 515 nm [8, 9]. The photochemistry of the molecule is well known and it has found wide use as a pH indicator. In previous studies with sol-gel materials, pyranine was used successfully to measure the water/alcohol content of aluminosilicate bulk gels during the sol-gel-xerogel transformation and to study the effect of pH on water consumption during gelation of a silica system [10, 11]. The present work extends the use of pyranine fluorescent probes to real time measurements within the depositing film. The combination of interferometry with luminescence spectroscopy has been used to provide a number of new insights concerning composition evolution during film pulling.

2. Experimental Methods

2.1. Materials Preparation

The sols used in this study were designed to contain varying amounts of "excess" water in the sol. Silica sols in the system tetraethoxysilane (TEOS)/ethanol/water were prepared with the mole ratio of $H_2O/Si = 4$ and using equal volumes of TEOS and ethanol. The mixtures were refluxed at 65°C for 1.5 hours. The volume of the mixture was then reduced by 50% by rotary evaporation and an equivalent amount of absolute ethanol added. The evaporation step was repeated 4 times to remove any excess water (as the azeotrope) and acid. Immediately prior to the film drawing experiments, the sol was combined with an equal volume of absolute ethanol containing pyranine (2×10^{-4} M), and then the desired amount of "excess" water was added. The films investigated in this study were prepared with 2.5, 5, 12.5 and 25 volume% of water added. From this series of sols, it was possible to examine the effect of excess water content on film composition. In addition to the silica sols, a series of standard solutions of ethanol/water containing pyranine (1×10^{-4} M) were prepared.

The films were drawn using the same apparatus as that described by Hurd and Brinker [5]. The substrates were polished silicon strips (10 cm × 1 cm × 1 mm) cleaned with Chromerge, rinsed with deionized water and then methanol and acetone. The substrate was withdrawn in a convection-free drying chamber which was closed to the atmosphere except for a small aperture required for the excitation laser and the collecting lens. A film drawing rate of 5 cm/min (± 10%) was used for all experiments. Equilibrium conditions were established within 15 seconds, creating a steady wedge-shaped film, 1–2 cm in height depending upon water content. Spectra were collected at various heights above the reservoir to determine how the composition of the pore fluid changed due to differential evaporation of alcohol and water. Several spectra were obtained during a given substrate withdrawal.

2.2. Optical Measurements

Figure 1 indicates the experimental arrangement which combines interferometry with luminescence spectroscopy. Interferometry was used to monitor film thickness (h) according to the relation:
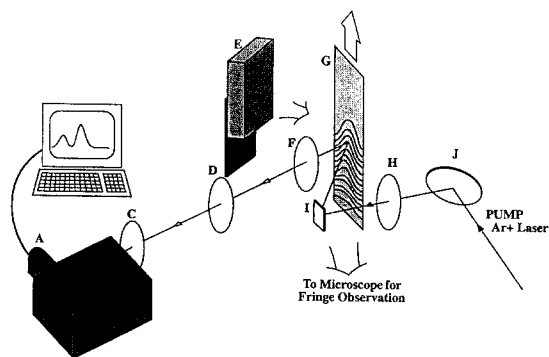
Fig. 1. Experimental arrangement combining interferometry with fluorescence spectroscopy. Components are as follows: A. optical multichannel analyzer; B. monochromator; C. focusing lens; D. aperture; E. mercury lamp w/filter (546 nm); F. objective lens; G. substrate (silicon wafer); H. focusing lens; I. and J. mirrors.

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

where $\lambda = 546.1$ nm (filtered Hg lamp), θ is the illumination/viewing angle of the interference pattern ($\theta = 65°$ to the substrate normal) and m is the interference fringe number ($m = 0$ corresponds to the drying line). The fringe number not only relates to film thickness, it also provides a convenient vertical scale to identify the distance between the drying line and the film reservoir or bath meniscus ($m \approx 10$–15 depending upon drawing rate).

The fluorescence was excited by the 351 nm line from a coherent Innova 90 Ar$^+$ laser at a power of approximately 20 mW. The spot size of the excitation beam was less than 50 μm, allowing for excellent spatial resolution. The spectra were recorded using an EG&G model 1420 OMA and a 0.32 m Jobin-Yvon/ISA monochromator for dispersion. The slit width was 200 μm and the integration time was 1 second. The laser spot did not affect the pattern of the interference fringes.

3. Results and Discussion

This paper reports the use of pyranine emission to determine the solvent composition in sol-gel thin films as they are withdrawn from the sol reservoir. The emission spectra of pyranine depend on whether or not the molecule is protonated [8–10]. The molecule is deprotonated in water but protonated in ethanol. The luminescence spectra for a series of reference ethanol/water
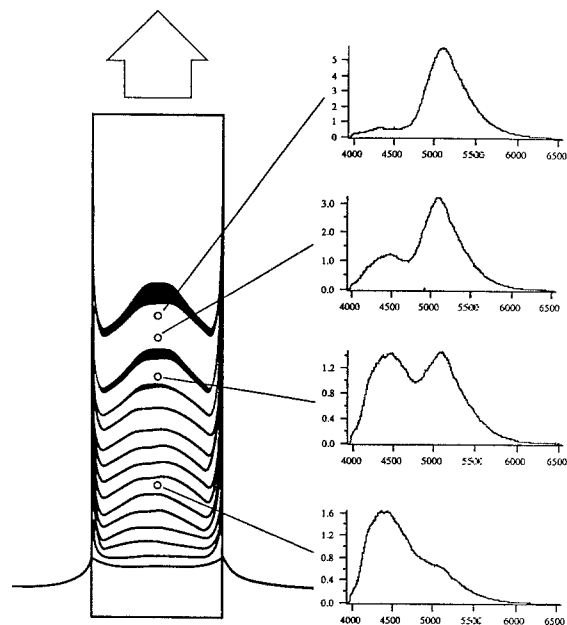

Fig. 2. Sketch of a typical interference pattern and the corresponding luminescence spectra at the different interference fringe positions.

solutions were analogous to those shown in Figure 2 of reference 10. The luminescence of a pure water solution of pyranine had almost no peak at 430 nm, while in an absolute ethanol solution of pyranine the peak at 515 nm was not visible. Adding water to an alcohol solution increases the number of deprotonated pyranine species and, therefore, the intensity of the luminescence peak at 515 nm. From this protonation/deprotonation behavior, we have been able to quantify chemical changes in the solvent during film pulling, to spatially map the ethanol/water ratio in films in real time and to investigate how the solvent composition in the film is influenced by the overall composition of the sol.

The characteristic interference pattern for the sol-gel film as it is withdrawn from the reservoir is shown in Figure 1 and 2. The dynamics of the dip coating process and the sequential stages of structural development in sol-gel films from this technique have been well reviewed [4, 12]. The first fringe marks the drying line, beyond which lies a nearly dry film. The fringes offer a convenient vertical scale between the sol reservoir and the drying line, and a series of emission spectra of pyranine in silica sols of known composition were obtained at different fringe positions. The spectra were obtained as the silicon substrate was withdrawn from the sol reservoir and after the interference pattern had achieved a steady-state position.
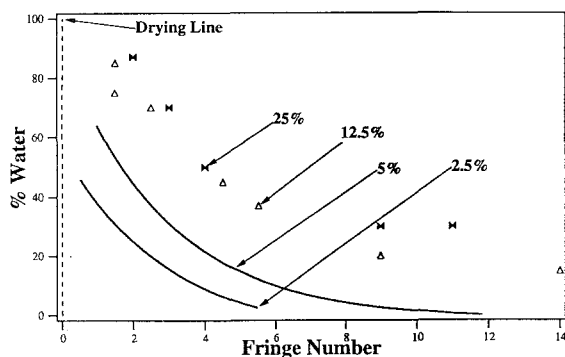
Fig. 3. Water content in the film as a function of fringe number for sols containing different amounts of excess water; 2.5%, 5%, 12.5%, 25%. The drying line is at $m = 0$. Curves are shown for the 2.5% and 5% sols rather than data points for the sake of clarity.

Typical luminescence spectra at different fringe positions (or fringe numbers) are shown in Figure 2. The emission spectrum of the pyranine probe changes with the position of the excitation beam. In the region close to the reservoir, the 430 nm emission dominates indicating low water content. The 515 nm emission becomes more prominent in the regions closer to the drying line, i.e., with increasing distance from the reservoir surface. Just below the drying line, this emission dominates, signalling a very significant water content.

The spectral data shown in Figure 2 can be converted to a more quantitative form by using the pyranine reference spectra [10]. In this way it is possible to observe how the water content in the film varies between the reservoir and the drying line. Figure 3 illustrates two important features; there is a gradient in water content near the drying line and the maximum water content (in the vicinity of the drying line) varies with the excess water added to the sol.

The sharp gradient in water content is comparable for all the sol/water systems investigated. These results are the first ones to definitively show that differential evaporation of water and alcohol causes the composition of the entrained sol to become progressively enriched in water with increasing distance from the reservoir surface. This effect has been widely assumed and even used in developing models for the dip coating process [13]. The present experiments clearly prove the effect and quantify the gradient produced.

The increase in the water content of the solvent is due to physical processes (i.e., preferential loss of ethanol) rather than chemical processes associated with the production or consumption of water during condensation or hydrolysis. Calculations have shown how

preferential evaporation of EtOH leaves behind a water-rich film in the vicinity of the drying line [13]. The results for TEOS/EtOH/H$_2$O sols (Figure 3) are consistent with this model. From the chemical perspective, hydrolysis was complete after the sols were synthesized and any water produced from condensation during synthesis was removed by rotary evaporation. Even if the 4 : 1 (H$_2$O : Si) sol had no condensation until film deposition, the water produced by condensation will not exceed more than a few volume percent in the sol. This amount is insignificant compared to the large increase in water content observed within the first few fringes of the drying line.

The second aspect to be considered in Figure 3 is that the maximum water content in the immediate vicinity of the drying line depends upon the excess water content initially present in the sol. The measured values range from 50% with 2.5% excess water to 85% at 25% excess. Interestingly, there is nearly no change in maximum water content or the composition gradient for the sols prepared with 12.5% and 25% excess. The water content in the vicinity of the drying line has significant implications for sol-gel films prepared by dip coating. The greater surface tension of water causes a corresponding increase in capillary pressure [4]. The capillary pressure exerted at the final stage of the deposition process has an enormous effect on compaction of the film. Thus, by controlling the water content at the drying line it will be possible to have a prominent influence on the structural development of sol-gel thin films.

The measurements of film water content are also quite significant in that the composition information is obtained spatially and in real time (i.e., as the film is being pulled). Through the use of Equation 1, the fringe number can be used to accurately calculate film thickness and the composition profile can be derived as a function of film thickness. Although not shown here, this curve is analogous to that of Figure 3 except that now the solvent composition at a given thickness is known [14].

4. Conclusions

This paper has demonstrated that pyranine may be used as a fluorescence probe to monitor the chemical evolution *in-situ* during sol-gel thin film deposition of silica by the dip coating process. The results have significant implications for sol-gel film deposition in two different

ways. First, the measurement provide a number of new insights concerning the chemical changes which occur during film pulling. The results conclusively show a sharp gradient in water content near the drying line, that the maximum water content reaches rather high values near the drying line and that it is possible to map the solvent composition as a function of film thickness. The second contribution is the applicability of this work to thin film process control. The use of an optical signal to monitor the chemical composition and film thickness provides an opportunity to rigorously control film processing through automated computer-based methods. Although the results are obtained for dip coating, it is evident that these methods may be readily adapted to other solution based materials preparation processes.

Acknowledgments

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