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

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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was used to quantify changes in the water/alcohol ratio in real time within the depositing film as the substrate was withdrawn from the coating reservoir.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 In the dip coating process the substrate is immersed into the coating solution and then withdrawn at a controlled rate.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In the dip coating process, a substrate is withdrawn slowly at constant speed from a colloidal or polymeric sol.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 H₂O/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: