Evaporation induced self assembly and rheology change during sol-gel coating

Chang H. Lee
Department of Mechanical and Aerospace Engineering, Washington University, St. Louis, Missouri 63130

Yunfeng Lu
Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118

Amy Q. Shen
Department of Mechanical and Aerospace Engineering, Washington University, St. Louis, Missouri 63130

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Thin films with self-assembled nanostructures are important in applications such as catalysis and biosensor technology. A major technique used to prepare such films is sol-gel processing. This technique involves depositing a complex fluid on a substrate by dip, spin, or spray coating, followed by allowing the film to evaporate and form self-assembled nanostructures. Since the composition of the film during coating is central to understanding how changing chemical and physical conditions affect the properties and microstructures of the films, we investigate the rheological properties of the entrained fluid film and its subsequent impact on the steady state film thickness during the evaporation-induced self-assembly process. We perform systematic experiments to measure the meniscus shape and film thickness during sol-gel dip coating. We observe that the experimental data of film thickness lie way below the Landau-Levich-Derjaguin prediction from the classic film-coating results. To explain this discrepancy, we present a thin film model based on the lubrication approximation with an evaporation effect. Our results show that evaporation-induced self-assembly leads to rheological variations in the entrained film and, consequently, alters the film thickness. The predicted film thickness based on the evaporation-induced rheology variation model compares well with the experiments.
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I. INTRODUCTION

The development of modern technologies has come to depend more and more on novel materials with well-controlled structures and functionalities. Because they possess large surface areas and adjustable pore sizes and compositions, mesoporous films have become increasingly important in many exciting applications such as photonics, sensing, quantum electronics, energetic materials, and catalysis. The synthesis of these porous films relies on the cooperative assembly of organic structural directing agents (i.e., surfactants or block copolymers) with inorganic building clusters (i.e., silicate clusters) that form ordered lytropic liquid crystalline mesostructured phases. Removal of the surfactants or block copolymers creates mesoporous inorganic materials containing tunable pore structures. A major technique used to prepare such films is sol-gel coating. The sol solution normally starts with a solution consisting of a mixture of ethanol, water, and silica along with various surfactants. As the coating process proceeds, the ethanol evaporates, causing an increase in the surfactant concentration and thereby triggering micelle formation. The micellar aggregates then interact with the silica inorganic precursor, further self-assemble, and eventually form a well-ordered nanostructured film on the substrate (see Fig. 1).

For sol-gel dip coating, the coating speed must be sufficiently low (less than 0.5 cm/s) to ensure the proper balance of many simultaneous competing factors occurring over a short time scale (on the order of seconds). These factors include the evaporation of the solvent, self-assembly of the micelles and the inorganic phase, and condensation of the inorganic (i.e., silicate) network (see Fig. 1). The rapid kinetics of organization also makes it challenging to understand the fundamental mechanisms underling the synthesis; thus, it is equally challenging to control the film structure and make rational design decisions to improve the process quality and rate.

Many research groups have explored using different chemical compositions and experimental techniques to synthesize new mesoporous materials. For example, Brinker's group, Zink's group, and Stucky's group have presented extensive experimental and theoretical work[1–11] on synthesizing nanostructured films and particles by dip coating or aerosol processing, with various pore sizes and structures such as one-dimensional hexagonal (pores parallel to the surface), two- and three-dimensional hexagonal, lamellar and cubic with different initial surfactant concentrations and types. Ozin's group[3] has developed a procedure for the synthesis of mesoporous silica in acidic conditions, which can produce exotic shapes such as shell- and rope-like morphologies.

Despite the present knowledge concerning sol-gel coating, many important questions still remain open. For example, little is known about how the local rheology of the sol and the film thickness changes during the evaporation-induced self-assembly process or how the film thickness

