

## Effects of Solution Precursor Nature on Sol-Gel Derived PZT Thin Film Crystallization Behavior and Properties

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### Introduction

In the fabrication of lead zirconate titanate (PZT) films for non-volatile memories and decoupling capacitors, a variety of deposition techniques including sputtering, pulsed laser ablation, metal organic chemical vapor deposition, and sol-gel have been investigated. Each of these processes has been demonstrated to generate films with acceptable dielectric and ferroelectric properties. In particular, sol-gel methods offer excellent control of film stoichiometry and coating uniformity.

The sol-gel approaches used for PZT film fabrication fall into one of two categories: processes that use 2-methoxyethanol as a solvent<sup>1,2</sup> and processes that use chelating agents,<sup>3,4</sup> such as acetic acid, for reducing the hydrolysis sensitivity of the alkoxide compounds. Due to concerns regarding the toxicity of 2-methoxyethanol, we have concentrated on the development of sol-gel methods that fall into the second category mentioned above. We have found that, in addition to reducing the hydrolysis sensitivity of the metal alkoxides, the use of chelating agents serves to define the processing behavior of the films, i.e., film consolidation after deposition, and densification and crystallization during heat-treatment.<sup>5</sup> In this paper, we discuss the relationships between precursor structure, as defined by the reactions between the chelating agents and the metal alkoxide starting reagents, and film consolidation, densification and crystallization.

### Experimental

PZT thin films were fabricated using an inverted mixing order (IMO) method that has been described previously.<sup>4-7</sup> Solutions were prepared by combining the appropriate amounts of zirconium butoxide-butanol\* and titanium isopropoxide\* and allowing 5 minutes for reaction. Acetic acid,† ~ 4 mols/mol alkoxide, was then added and after 5 minutes, methanol was added. Subsequently, lead (IV) acetate\* was added, and the solution was heated to ~ 85°C for dissolution of the lead precursor. Solution preparation was completed with further additions of methanol, acetic acid, and water. Typically, 0.4 M, 50 ml batches were prepared, and 10 mol % excess lead acetate was added. For selected samples, a second chelating agent, 2,4-pentanedione‡ (acetylacetone; acac) was added to the solution approximately 15 minutes prior to film deposition.<sup>6</sup>

Thin films were deposited onto Pt/Ti/SiO<sub>2</sub>/Si substrates by spin-casting at 3000 rpm for 30 seconds. After deposition, the films were heated for 5 minutes at 300°C on a hot plate. Fired thicknesses, per layer, varied from ~ 900 to 1000Å, depending upon the acac/PZT molar ratio. Thicker films were fabricated by a multi-layering approach, and typically, four layers were deposited and pyrolyzed prior to crystallization, which was accomplished by heat-treatment at 650°C for 30 minutes.

For film consolidation experiments, films were deposited onto Si substrates (with native oxide) and thickness and refractive index were measured using a Gaertner L-116C ellipsometer. The pyrolysis behavior of films deposited on platinum coated Si substrates was measured using a Nicolet Magna 550 FTIR spectrometer with diffuse reflectance attachment. Optical scattering losses were measured using a spectrally resolved reflectance technique<sup>8</sup> and film microstructures were characterized by scanning electron microscopy (Jeol 6400).

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## Results and Discussion

Film consolidation behavior was characterized by measuring the changes in film thickness and refractive index at room temperature after deposition. Results presented in Figure 1 illustrate typical behavior for single layer, IMO derived PZT 40/60 films prepared with and without acetylacetone. Both films display extensive consolidation (a decrease in thickness) as well as densification (an increase in refractive index) with "drying" time after deposition, as observed previously for other sol-gel derived films.<sup>9,10</sup> Considering the molar volumes of the acetate and acac ligands are 57.2 and 103.0 cm<sup>3</sup>/mol, respectively, it may also be observed that the film prepared from the solution precursor modified with the sterically larger acac ligand displays less efficient precursor aggregation during deposition. This is evidenced as a greater initial thickness and a lower initial refractive index. Interpretation of precursor effects on initial film properties and film consolidation behavior are discussed further in references 5 and 10.

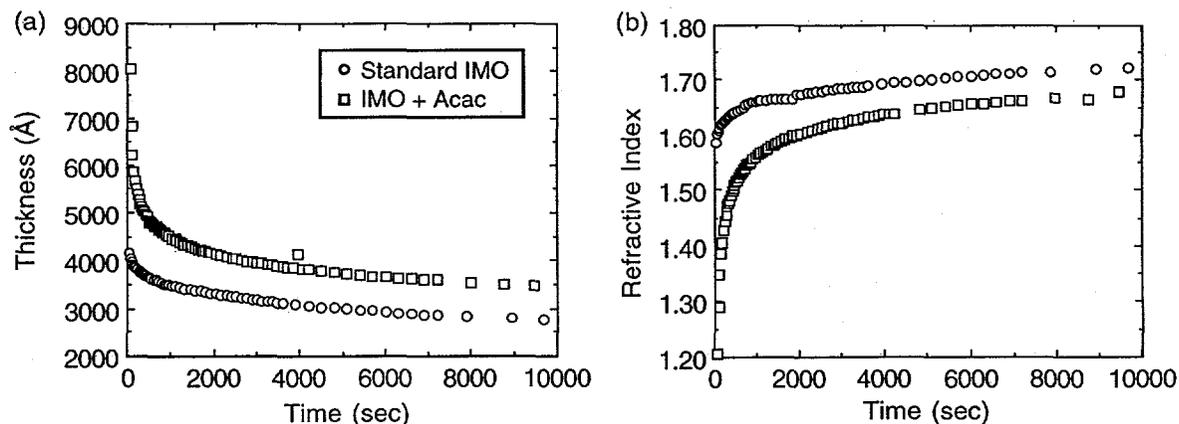


Figure 1. Ellipsometry measurements of (a) thickness and (b) refractive index for standard IMO and acac-modified IMO (3 mols acac/mol PZT) films; single layer PZT 40/60 deposited on Si.

Film consolidation behavior at room temperature is of interest because it is typically paralleled by film densification during conversion to the crystalline ceramic. For example, films prepared from less reactive precursors, which exhibit greater consolidation at room temperature, usually display greater densification during crystallization. This is believed to be due to the fact that precursors of lower reactivity yield films that are more physical gel in nature than chemical gel.<sup>9</sup> This allows for continued rearrangement of the oligomeric species during low temperature processing and delays the formation of the metal - oxygen - metal skeletal network, which serves to inhibit densification due to the corresponding increase in film modulus. We have seen in the preparation of zirconia films that by proper control of precursor nature and heating rate, film density may be increased from ~ 88% to 96%.<sup>9</sup>

In addition to precursor reactivity, pyrolysis behavior may also play a role in defining film densification during heat treatment. The impact that different chelating agents can have on film pyrolysis behavior is illustrated in Figure 2. The FTIR spectra show the carbon - oxygen (1300 - 1700 cm<sup>-1</sup>) and metal - oxygen (400 - 800 cm<sup>-1</sup>) bonding regions.<sup>5</sup> The C-O spectral region is indicative of organic content in the films, due either to the presence of acetate or acac. Comparing the two spectra, it is evident that the film prepared from the acetate precursor retains little organic matter after heat treatment at 300°C, while the film prepared from the acac-modified precursor still has a significant organic component. These results are in agreement with those for zirconia thin films prepared from acetate and acac precursors.<sup>9</sup> In this material system, we found that the acac-based precursor also displayed a higher pyrolysis temperature than the acetate precursor.

Interestingly, for the zirconia films, film crystallization temperature and densification also appeared to be related to pyrolysis behavior. Films that retained organic fractions to higher temperatures displayed higher temperature crystallization onsets, and higher film densities.<sup>10</sup> In

contrast, films that displayed lower crystallization temperatures exhibited lower densities, presumably because the onset of crystallization is accompanied by the impingement of crystalline inclusions in the film, which retard densification by processes such as viscous flow. For these films, densification must occur by solid state diffusion, an energetically less favorable process.<sup>11</sup>

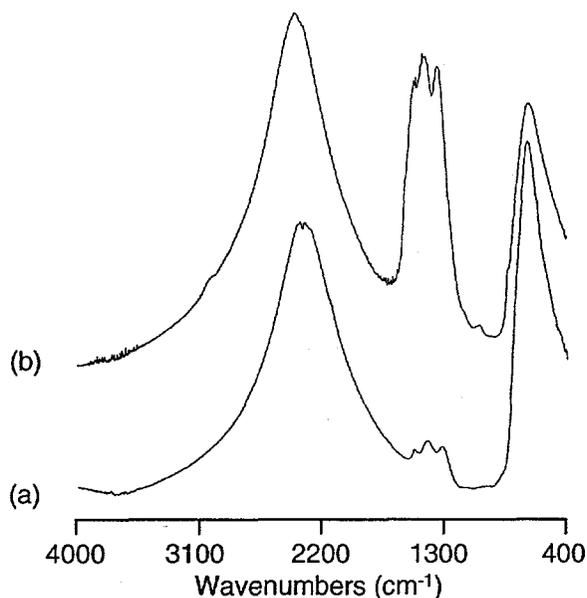


Figure 2. FTIR diffuse reflectance spectra of (a) standard IMO and (b) acac modified IMO PZT 40/60 4-layer films deposited on platinum coated Si and heat-treated on a hot plate at 300°C for 5 minutes (each layer). The intense, broad peak at  $\sim 2300\text{ cm}^{-1}$  is believed to be due to  $\text{CO}_2$  entrapped within the pores of the film.<sup>12</sup>

In developing precursors that display enhanced film densification behavior, it is difficult to state whether precursor reactivity or pyrolysis behavior is more critical in the preparation of high density materials. To date, the sterically demanding (large) ligands utilized in precursor synthesis also displayed higher pyrolysis temperatures. Therefore, it has not been possible to separate these effects. To evaluate which of these parameters is more important will require the synthesis of precursors from sterically non-demanding ligands that possess high pyrolysis temperatures.

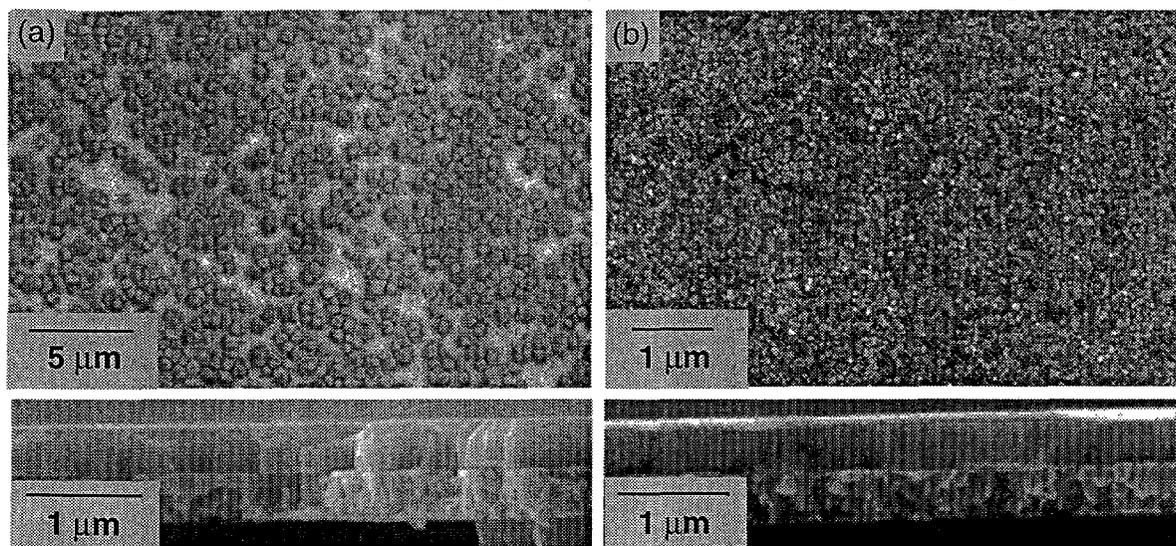


Figure 3. (a) Plan-view and cross-sectional SEM photomicrographs of a four layer PZT 40/60 film prepared from a standard IMO solution aged 60 days; (b) plan-view and cross-sectional SEM photomicrographs of a four layer PZT film prepared from the same 60 day old solution to which 3 mols acac /mol PZT were added prior to film fabrication. For cross-sectional views: lower layer - Pt bottom electrode; second layer - PZT thin film; upper layer - Pt top electrode ((b) only).

For sol-gel derived PZT films, changes in film pyrolysis behavior due to acac additions were also accompanied by changes in film crystallization behavior. While films derived from fresh IMO solutions typically display uniform, columnar microstructures with nucleation of the perovskite phase occurring at the lower electrode, films derived from aged IMO solutions also exhibit large, surface nucleated grains, as shown in Figure 3a. While both grain types are perovskite in nature, the "di-phasic" microstructure results in a degradation in ferroelectric properties and an increase in optical scattering.<sup>8</sup> Acac additions can eliminate surface nucleation in films derived from aged solutions, as shown in Figure 3b. This film was prepared from the same IMO solution used for the film shown in Figure 3a, but 3 mols acac/mol PZT were added to the solution shortly before film deposition. Potentially, the higher pyrolysis temperature of the acac film causes a delay in the nucleation of the perovskite grains at the film surface, allowing growth of the interface-nucleated columnar grains to dictate the microstructure. However, it is possible that changes in the organic content of the precursor or the structural free energy of the resulting amorphous phase might also be responsible for the observed change in nucleation behavior. Further experimentation is required to elucidate which of these effects is most important.

The elimination of surface nucleation results in a much more uniform microstructure and improved ferroelectric and optical properties. The acac-derived film was characterized by higher  $P_r$  and  $P_s$  values,<sup>6</sup> and significantly less optical scattering.<sup>8</sup> The enhanced optical properties of these films make them more suitable for applications such as optical storage devices.

## Conclusions

In the preparation of ceramic thin films by sol-gel processing, precursor structure/nature can have a significant impact on the consolidation, densification, and crystallization behavior of the films. Two key precursor properties which define film processing behavior are reactivity and precursor pyrolysis temperature. Film crystallization temperatures and microstructures can be affected by the nature of the precursor, impacting electrical and optical properties.

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