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# CONTROL OF THIN FILM PROCESSING BEHAVIOR THROUGH PRECURSOR STRUCTURAL MODIFICATIONS

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## ABSTRACT

In the sol-gel processing of ceramic thin films it has been frequently noted that the processing behavior, microstructure and properties of the films are dependent on the nature of the coating solution. In an attempt to understand such thin film processing-property relationships, we have systematically investigated the effects of varying the precursor nature on thin film densification and crystallization for $ZrO_2$ and $TiO_2$ films.

Metal alkoxide starting compounds, e.g., zirconium *n*-butoxide•*n*-butanol and titanium *i*-propoxide, were reacted with acetic acid and 2,4-pentanedione to prepare coating solutions for thin film deposition. The use of these chelating ligands resulted in solution oligomeric species of different nature. Studies of thin film processing indicated that film processing characteristics, i.e., consolidation, densification and crystallization, were strongly dependent on solution precursor nature. Ligand steric size, pyrolysis behavior, extent of chelation, and precursor reactivity were found to be key variables in controlling film processing characteristics.

## INTRODUCTION

Sol-gel processing has been widely used for the fabrication of ceramic thin films in numerous material systems. Single component films, such as silicates, are under investigation for use as ultramicroporous membranes for gas separation,[1] while porous and dense titania thin films are of interest for sensor applications[2] and dielectric layers,[3] respectively. Multicomponent thin films prepared by sol-gel processing are also of interest. For example, lead zirconate titanate thin films are under development for a variety of electronic applications, ranging from decoupling capacitors[4] to optical storage discs.[5]

In all of these applications, the successful development of sol-gel derived thin films into devices requires that thin film processing be controlled to the extent that either, tailored pore structures, or specific ceramic microstructures, be

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developed. Since as-deposited sol-gel coatings are typically porous and contain significant amounts of organic species, control of pore structure development requires control of thin film consolidation, densification, and pyrolysis behavior.[6] Effective control of ceramic microstructural evolution requires control of the processes discussed above, as well as control of crystal nucleation and growth.

Many investigators have noted that the nature of the coating solution impacts on film processing characteristics.[1,7] In previous studies, we have seen that one solution property that can affect film processing behavior is the nature of the solution precursor species.[8,9] Because of these observations and the results of other investigators, we are interested in understanding the relationships between precursor properties and thin film processing characteristics. As a means of developing this understanding, we have reacted metal alkoxide compounds with different chelating ligands to prepare precursors with intentionally introduced structural differences. The species formed in these reactions have been referred to as molecularly modified alkoxides by several investigators,[9-11] but there is a surprising scarcity of reports on the effects of such modifications on film processing in the literature. After precursor synthesis, we fabricated thin films and systematically studied the relationships between precursor structure and film consolidation, densification and crystallization. Our goal in understanding such relationships is to be able to utilize intentionally introduced precursor variations to tailor thin film consolidation, densification, and crystallization as required for different applications.

The two chelating ligands we used to prepare our precursors are acetic acid (acetate) and 2,4-pentanedione (acetylacetone; acac), shown in Figure 1. When mixed with metal alkoxide starting compounds, the two ligands react with, or chelate, the metals, forming species with different molecular structures than the parent alkoxides.[12,13] It is also known that these ligands interact differently with the metal alkoxide compounds. For example, while both ligands are bidentate (i.e., they coordinate through both oxygens to the metal center), acac is a non-bridging

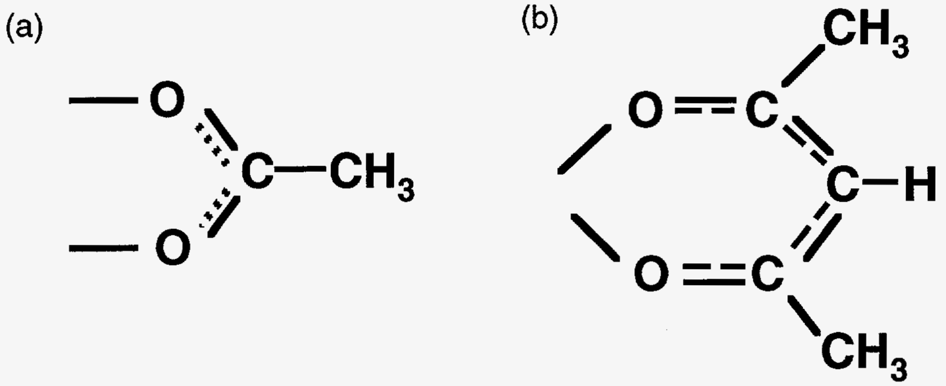

Figure 1. Structures of the (a) acetate and (b) acac modifying ligands used in the present study.

ligand,[11,12] whereas acetic acid is frequently a bridging ligand.[9,10,15] Other characteristics of the ligands, e.g., steric size, may also be expected to affect precursor properties and thereby, thin film processing behavior.

In addition to using different ligands to obtain precursors with different structures,[6] it is also possible to simply vary the ligand/metal alkoxide ratio. Illustrated in Figure 2 are structures for two titanium oxo-acetate-alkoxide compounds prepared by reacting titanium *i*-propoxide with different amounts of acetic acid.[12] It can be seen that while the general nature of the species is similar, i.e., both possess two types of bridging oxygen species, bridging acetate groups, and bridging and terminal alkoxy groups, the product formed from the 1:1 reaction (Figure 2a) has fewer bridging acetate groups and more terminal alkoxy groups than the product formed from the 1:2 reaction (Figure 2b). Since these two precursors have different numbers of reactive species we would expect that when used in coating solutions, thin films with different processing behaviors would be obtained.

In this paper, we report on the use of both of the approaches discussed above to prepare different precursors for the fabrication of titania and zirconia thin films. Ellipsometry was the primary characterization tool used to monitor the effects of precursor structure on thin film processing. After deposition, film thickness and refractive index variations were studied as a function of time. Such variations give an indication of the consolidation behavior of the film. Changes in densification behavior with precursor structure were evaluated by measuring the refractive indices of heat-treated films. Changes in film crystallization behavior (crystallization onset temperature) were monitored by X-ray diffraction. We were particularly interested in characterizing the magnitude of the variations in processing behavior, so that the utility of using precursor structural variations to control thin film processing could be determined.

## EXPERIMENTAL

Titanium *n*-butoxide* and zirconium *n*-butoxide•*n*-butanol* were used as the starting compounds for the synthesis of the solutions. Two different chelating ligands, i.e., acetic acid* or 2,4-pentanedione‡ (acac: $CH_3COCH_2COCH_3$), or different chelating ligand to metal ratios, were used to generate different solution precursor species for thin film fabrication. Four types of deposition solutions were prepared: (i) titanium butoxide with acac; (ii) titanium butoxide with acac and water; (iii) zirconium butoxide with acetic acid; and (iv) zirconium butoxide with acac and water. Water was used as an additive to prepare larger, more reactive oligomeric species.

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* Aldrich Chemical Company, Inc.; Milwaukee WI.

‡ Fisher Scientific, Pittsburgh, PA.

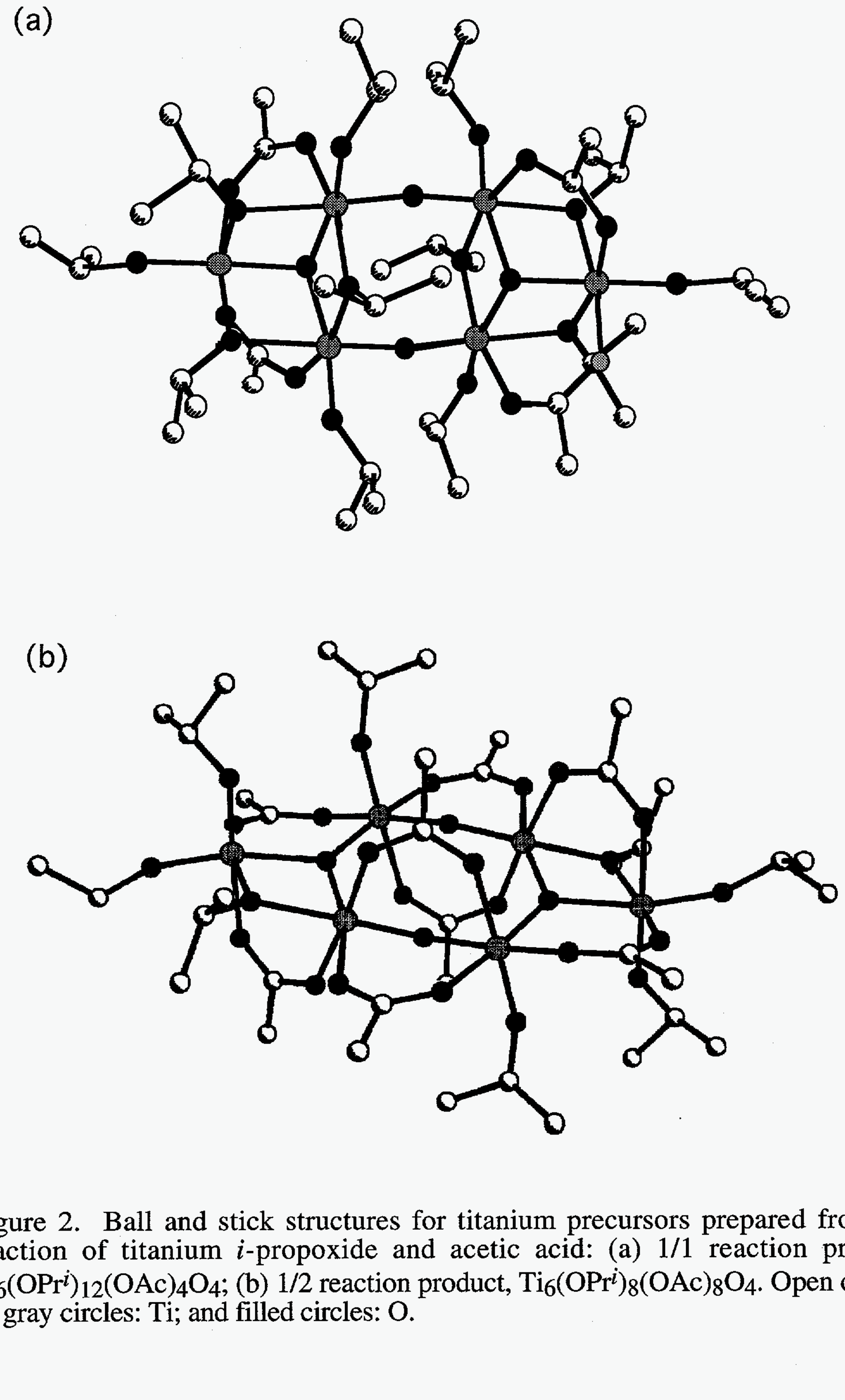

Figure 2. Ball and stick structures for titanium precursors prepared from the reaction of titanium *i*-propoxide and acetic acid: (a) 1/1 reaction product, $Ti_6(OPr^i)_{12}(OAc)_4O_4$; (b) 1/2 reaction product, $Ti_6(OPr^i)_8(OAc)_8O_4$. Open circles: C; gray circles: Ti; and filled circles: O.

The titanium/acac precursor solutions were prepared by first measuring out the correct amount of titanium *n*-butoxide, and then adding the required amount of purified[16] acac while stirring. Solution preparation was completed by diluting the reaction mixture to 0.25 M (Ti) with dry *n*-butanol. Solutions with r ratios (r = mols acac/mol Ti) ranging from 0 to 3 were synthesized.

The titanium/acac/$H_2O$ solutions were prepared by reacting titanium *n*-butoxide with an *n*-butanol solution containing the acac ligand. After allowing 30 minutes for the chelation reaction, a solution of water in *n*-butanol of equal volume to the titanium-acac reaction mixture was added. Solutions were stirred during both phases of the preparation. Final solution concentration was 0.25 M (Ti). Solutions with r = 2 and h = 2 (mols $H_2O$/mol Ti) were prepared. The coating solution was used for film fabrication the same day it was prepared.

A similar procedure was used for the preparation of zirconium/acac/$H_2O$ coating solutions. Zirconium *n*-propoxide•*n*-propanol* was used as the metal alkoxide starting reagent. To prepare oligomers of different nature, two samples were prepared: acac-H: r = 2.0, h = 0.5; and acac-L: r = 0.5, h = 2.0. Final solution concentration was 0.4 M (Zr). It is expected that the acac-L precursor would be significantly larger due to more extensive hydrolysis and condensation reactions. Solution viscosity measurements were in apparent agreement with this prediction.[6] Due to a higher concentration of residual OH groups, this precursor is also expected to be more reactive than the acac-H precursor.

Acetate precursor solutions for zirconia film fabrication were prepared by reacting zirconium *n*-propoxide•*n*-propanol with purified[16] acetic acid in a molar ratio of 1:1.5 in a dry box. After approximately 5 minutes, sufficient dry *n*-propanol was added to yield a 0.4 M (Zr) solution. Prior to use, the solution was aged for 3 days at 25°C under argon. This sample will be referred to as HOAc.

Films were fabricated onto silicon wafers by spin-casting at 3000 rpm. Continuous uniform films were prepared from each of the coating solutions discussed above. As-deposited film thicknesses ranged from ~ 900Å to ~ 3000Å. Gelation times of the depositing films (i.e., the time required for stabilization of the interference colors during deposition) were under 10 seconds. Film thickness and refractive index were determined using a Gaertner L-116C rotating analyzer ellipsometer ($\lambda$ = 6328Å). Gaertner GC4A software for single layer, non-absorbing films was used to convert the measured psi and delta values to film thickness and index. Multiple angle measurements, typically 50 and 70° incidence, were used to confirm the phase period of the film i.e., first, second, or third order thickness. Results presented are for 70° measurement. For film drying experiments, film thickness and refractive index were monitored as a function of time after deposition. Ambient humidity was typically between 25 and 45%. Multiple trials were conducted to confirm the effects of precursor structure on film thickness and refractive index variations. In general, ellipsometry measurements were very reproducible. Thickness measurements of the L-116C ellipsometer have an accuracy of ±3 Å; refractive index measurements have and accuracy of ±0.005. Pyrolysis of organic species from the films was determined using a Nicolet Magna 550 spectrometer with diffuse reflectance attachment. Crystalline phase identification was carried out using a Siemens D500 X-ray diffractometer, Cu $K_\alpha$ radiation, and a 4° grazing incidence angle.

## RESULTS AND DISCUSSION

### Ligand Effects on Film Consolidation Behavior

Our initial studies focused on determining the effects of precursor structure on consolidation at room temperature. These results are of particular interest in the preparation of porous films. Figure 3 illustrates the variations in film thickness, shrinkage, and refractive index for films prepared from Ti/acac precursors. As the acac to Ti molar ratio increases from 0 to 2, initial film thickness increases from ~875Å to ~2800Å. Concurrently, the initial refractive indices of the films decrease as the extent of acac modification is increased.

The observed results may be explained by considering: (i) the nature of the acac ligand on precursor structure; (ii) the properties of the modifying ligand compared to the parent ligands (butoxy groups); and (iii) the physical processes that occur during film formation. Compared to the alkoxy groups it is replacing, acac is sterically bulkier and less susceptible to hydrolysis.[14] During the spin-off stage of deposition,[17] the concentration of the precursor species increases dramatically. As the precursor species come together during film formation, they begin to interact. Precursor properties governing this interaction include size, shape (fractal nature),[1] and reactivity. Since the viscosities of the solutions are similar, we believe that the increase in initial film thickness with acac addition is due to a decrease in packing efficiency of the more highly modified precursor species during aggregation, most likely as a result of increased precursor/oligomer bulkiness. In addition to the differences in initial film thickness, another indication of the lower packing efficiency of the more highly substituted precursors is the observed decrease in initial refractive index. With no acac modification, an initial refractive index of 1.629 is observed. For the r = 1 sample, the initial refractive index is 1.594 and for the r = 2 sample, the refractive index has decreased to approximately 1.336.

In addition to differences in aggregation behavior, film consolidation behavior also depends on precursor properties, i.e., size, shape and reactivity. Precursors that are less reactive (toward hydrolysis and condensation) are termed "transparent," since they interpenetrate during aggregation and consolidation; those which tend to react are referred to as "opaque".[1,18] As greater amounts of acac are used as a structural modifier, less reactive, more transparent precursors are formed. This is not only due to the fact that the acac ligand is less susceptible to hydrolysis than the butoxy ligand, but being sterically large, it can inhibit accessibility to any remaining (reactive) alkoxy species. Acac derived films prepared from more highly modified precursors (r = 2) should therefore consolidate to a greater extent that those prepared from more reactive species (r = 0) because the precursors are more transparent, and do not crosslink to as great an extent during drying. An indication of this behavior may be the fact that even though, initially, the r = 2 film is significantly thicker that the r = 0 or r = 1 films, after drying at 25°C for about 2 hours, the films display similar thicknesses. Shrinkages for hte r = 0, 1, and 2 films during drying at 25°C were 46%, 54%, and 78%, respectively. In the present case, more pronounced differences in film consolidation may not have been observed because the butoxy ligand itself is fairly insensitive to hydrolysis and

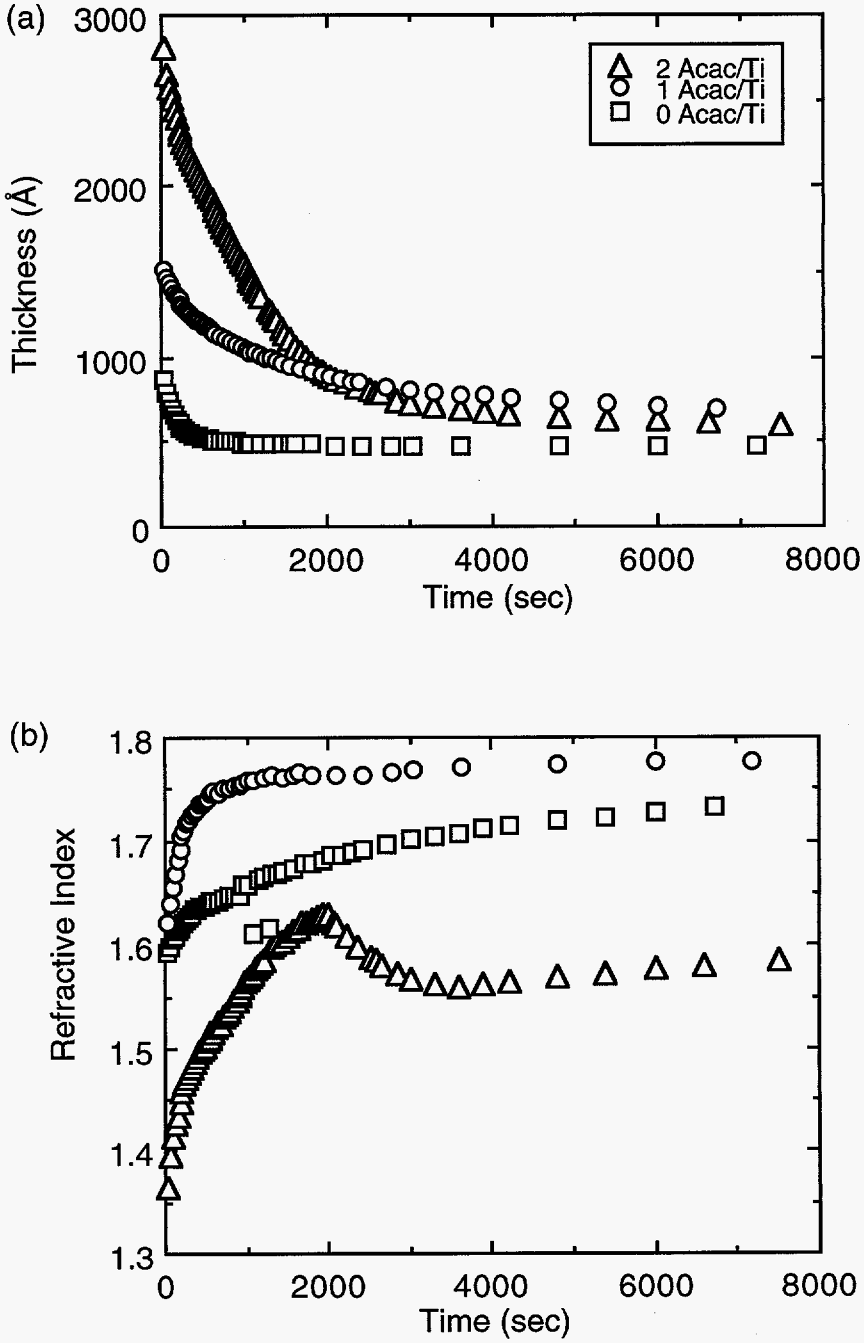

Figure 3. Ellipsometry results for (a) thicknesses and (b) refractive indices of titania thin films as a function of time after deposition. Solution precursors prepared by reaction of Ti(OBu$^n$)$_4$ and acac; modifying ligand ratio indicated in legend.

condensation, much less so than many typically used alkoxy groups, e.g., ethoxy or *i*-propoxy.

Variations in film consolidation behavior can also be induced through the use of different chelating ligands, rather than by changing the modifying ligand/alkoxide ratio. Typical results are shown in Figure 4 for zirconia thin films prepared from acetate and acac-modified zirconium *n*-propoxide precursors. Acetate is a sterically smaller, more reactive ligand than acac.[14] The predicted outcome of these differences in ligand properties is that the acetate-based films should display smaller initial thicknesses, higher initial refractive indices, and less extensive consolidation with time at room temperature. These predictions are agreement with the observed results shown in Figure 4. The acac-derived film has an initial thickness of ~2380Å, while the acetate-derived film has an initial thickness of ~2170Å. The initial refractive index of the acac film was 1.455, while that of the acetate film was 1.480. These results thus parallel those for the acac modified titaniua films; the film prepared from the less reactive, sterically bulkier acac precursor had a greater initial thickness and lower initial refractive index than the film prepared from the more reactive acetate precursor. Also in accordance with predictions for the effect of decreased precursor reactivity, the acac-derived film consolidated to a greater extent, 40%, versus 26% for the acetate-derived film. Enhanced precursor reactivity for the acetate system was also noted in other experiments.[6] Attempts to redissolve the acetate-derived films in the parent solvent (*n*-propanol) were unsuccessful, indicating that more extensive chemical crosslinking between precursor species occurs. In contrast, it was possible to dissolve films prepared from the acac-based precursor in the parent solvent immediately after deposition.[6]

## Effects Of Water Incorporation on Film Consolidation Behavior

Changes in film consolidation behavior may also be introduced through the addition of water to the coating solutions, as shown in Figure 5. Water additions result in more extensive hydrolysis and condensation during formation of the precursor species. Because of this, it is expected that the precursor species are characterized by more hydroxyl (OH) groups. The presence of the reactive OH sites causes the precursor species to become more opaque in nature, i.e., to display a greater tendency toward chemical crosslinking (M-O-M bond creation between precursors) during film formation. The more extensive crosslinking produces a film of greater initial thickness. These same chemical crosslinks, together with those formed during film drying, result in a higher modulus network that is more resistant to consolidation. The result is a film that consolidates to a lesser extent, as indicated by the greater film thickness after drying shown in Figure 5. Such variations in film network structure and processing behavior are important in the definition of pore structure[1] and also in the preparation of crack-free materials.

## Film Densification and Crystallization Behavior

We have discussed how variations in precursor structure may be used to control precursor aggregation behavior during film formation, as well as thin film

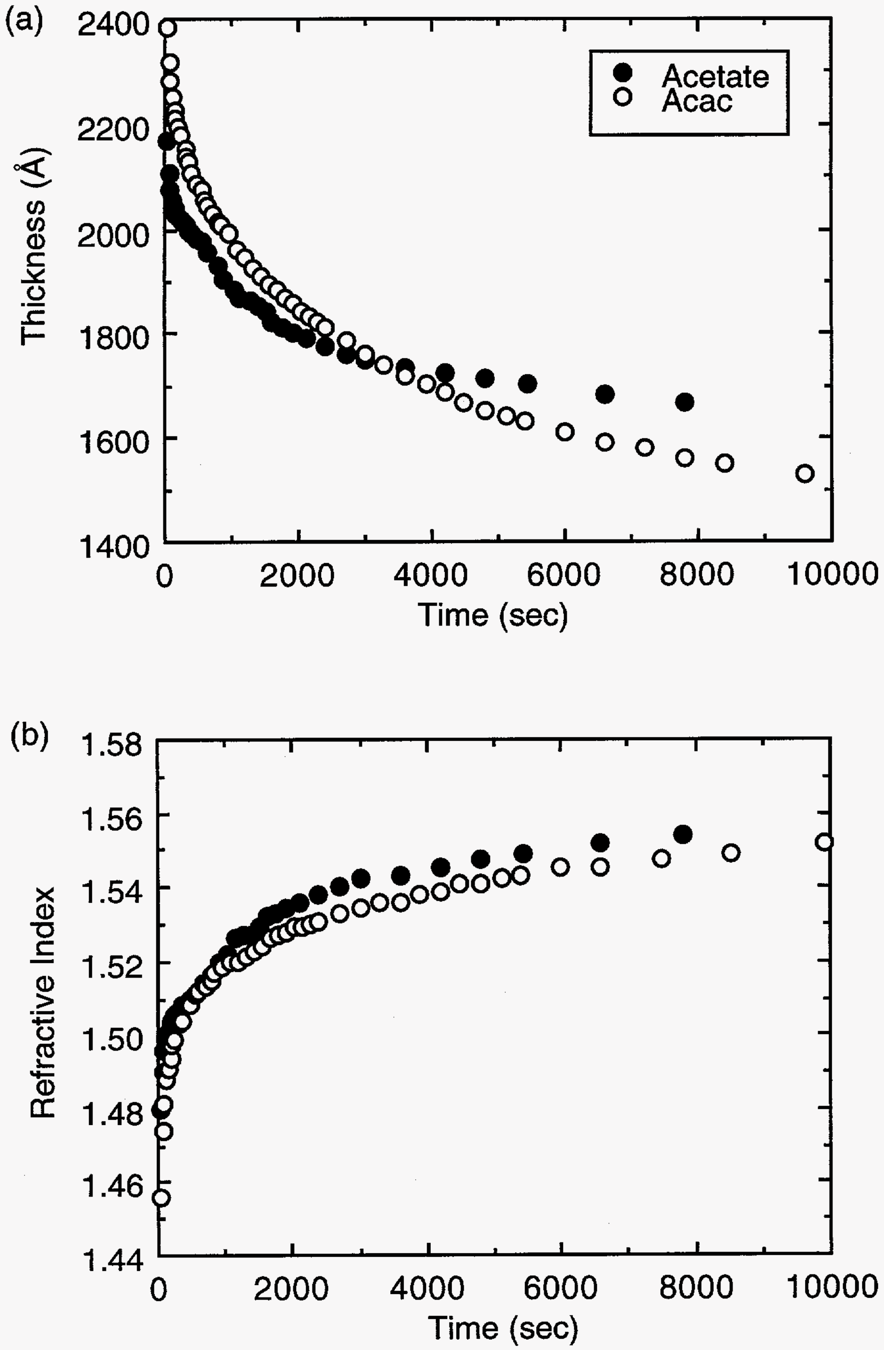

Figure 4. Ellipsometry results for (a) thicknesses and (b) refractive indices of acetate and acac-H (acac) derived zirconia thin films as a function of time after deposition.

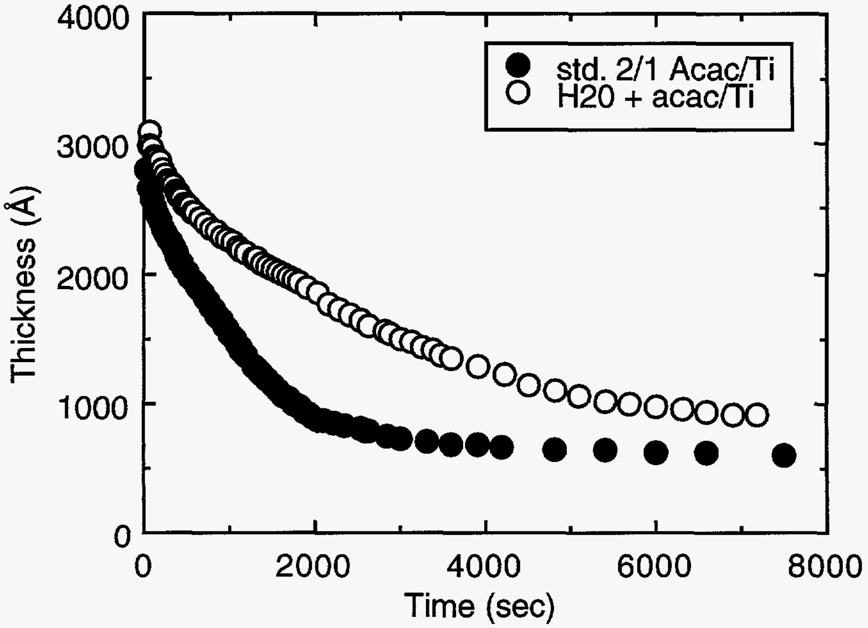

Figure 5. Effect of water addition on titania thin film drying behavior as measured by ellipsometry.

consolidation behavior. During conversion of the amorphous thin film to the crystalline phase, we have oberved that the differences in film processing behavior at room temperature persist in subsequent processing at higher temperatures. Results are presented in Table I for the refractive indices and densities of titania and zirconia thin films heat-treated to 700°C. Film densities were calculated from the measured refractive indices using the Lorentz-Lorentz relationship[19] and assuming refractive indices of 2.530 for dense $TiO_2$ (anatase), and 2.150 for dense $ZrO_2$ (cubic), the phases into which the films crystallized. It may be noted that, in general, higher density films are prepared from precursors which are more highly substituted ($r = 2$ acac modified titania), or which are modified by sterically larger ligands (acac derived zirconia compared to acetate). For the titania films, the $r = 0$ and $r = 1$ (acac/Ti) films displayed densities of ~85%, while the $r = 2$ film displayed a density of 88%. For the zirconia thin films, the acac-derived film displayed a density 7% greater than the acetate-derived film; 95% versus 88%.

Interestingly, the variations in film density are apparently related to variations in precursor reactivity. In going from acetate to acac modification, or from less to more highly substituted precursors, the reactivity of the precursors decreases. Higher density films are prepared from less reactive precursors. The smaller variation in film density with acac substitution for the titania films may be related to the fact that the parent butoxy ligands of $Ti(OBu^n)_4$ are relatively unreactive groups. Replacement of these butoxy groups by acac therefore does not have as important an effect on precursor reactivity as does replacement of *n*-propoxy groups by acetate or acac in the fabrication of the zirconium *n*-propoxide derived films.

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Table I.

Density and refractive index data for sol-gel derived titania and zirconia thin films.

Titania Thin Films§

| Precursor | Fired $n_f$ | Density (%) |
|---|---|---|
| 0/1 acac/Ti$(OBu^n)_4$ | 2.147 | 85 |
| 1/1 acac/Ti$(OBu^n)_4$ | 2.146 | 85 |
| 2/1 acac/Ti$(OBu^n)_4$ | 2.208 | 88 |
| 3/1 acac/Ti$(OBu^n)_4$ | 1.941 | 75 |
| 2/2/1 $H_2O$/acac/Ti$(OBu^n)_4$ | 2.056 | 81 |

Zirconia Thin Films†

| Precursor | Fired $n_f$ | Density (%) |
|---|---|---|
| HOAc | 1.943 | 88 |
| acac-H | 2.064 | 95 |

§ Titania thin film heat-treatment conditions: 700°C for 1 hour; 50°C/min ramp rate. Conventional firing using tube furnace.

† Zirconia thin film heat-treatment conditions: 700°C, no hold time; 300°C/min ramp rate. Rapid thermal processing using AET Addax RMV 4.

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It is also interesting to note that the effects of precursor reactivity on high temperature processing behavior (densification) parallel those of room temperature processing (consolidation): decreased precursor reactivity increases both consolidation and densification. Thus, the relatively transparency or opacity of the precursors and their tendency toward crosslink formation at room temperature are important considerations for both condolidation and densification behavior.

The observed variation in film densification with water addition to the coating solution also appears to be well described by the changes in precursor reactivity associated with this modification. The addition of water to the 2/1 acac/Ti$(OBu^n)_4$ solution generates precursors of higher reactivity. In Figure 5, the observed outcome of this change in precursor reactivity was an increase in initial film thickness and a decrease in the extent of consolidation. As shown in Table I, accompanying this decrease in consolidation is a decrease in densification. Compared to the standard r = 2 film, which is 88% dense, the water modified sol yields a film that is only 81% dense. Thus, again in this instance, as precursor reactivity increases, the density of the crystallized film decreases.

In addition to the effects of precursor reactivity, changes in film densification behavior may also be related to variations in the crystallization behavior, as influenced by precursor/ligand modifications. Figure 6 shows results of ellipsometry measurements and X-ray diffraction analysis of acetate and acac-based films heat-treated to various temperatures by rapid thermal processing. At lower firing temperatures (T < 500°C), films prepared from both precursors display a gradual increase in refractive index. As organic pyrolysis becomes important (T ~ 550°C) the refractive indices for films prepared from both precursors increase. However, with heat treatment at still higher temperatures (T > 700°C), the refractive indices of the acetate films decrease, while those of the acac-derived films continue to increase. Thus, compared to the acetate-based films, the acac-derived films display continued densification at higher firing temperatures. Analysis of the films fired at 700°C by X-ray diffraction indicate that while the acetate-derived film is crystalline (cubic zirconia), the acac-derived film is still amorphous. For the acetate-based film, when the formation of crystallites within the film reaches the point where they begin to interact, densification must occur by solid state sintering.[20] The continued densification of the acac-derived films is most likely due to the retention of the lower viscosity amorphous structure to higher temperatures. This permits further densification by structural relaxation and viscous flow, which possess more favorable energetics than solid state diffusion.[21-23] Thus, while precursor reactivity may be important in determining film densification, control of crystallization onset temperature, which is influenced by the modifying ligand employed, also appears to be critical.

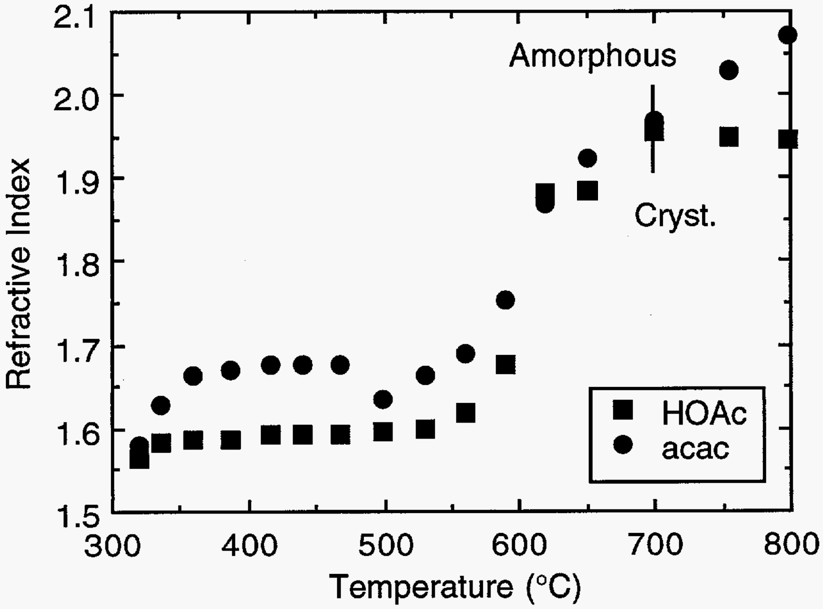

Figure 6. Refractive indices of acetate and acac derived zirconia thin films heat-treated to various temperatures using the AET Addax RTP furnace; no hold at temperature, 50°C/min ramp rate. Crystallization determined by X-ray diffraction analysis.

Since crystallization temperature appears to play a key role in sol-gel thin film processing, it is important to understand which aspects of precursor structure define this temperature. Analysis of the heat-treated films by FTIR diffuse reflectance spectroscopy, shown in Figure 7, indicates that the pyrolysis characteristics of the precursors may be one important property. In this figure, results are presented for the spectral region from 1200 - 1800 $cm^{-1}$, where vibrations associated with the acetate and acac organic groups are most intense. The zirconia films derived from the acetate precursor display a much lower pyrolysis temperature. Analysis of peak areas in this spectral region show that at 620°C the acetate-based film has lost more than 99% of its initial organic (acetate) content. In contrast, the acac film at 650°C still retains approximately 40% of its initial organic (acac) content. Retention of organic species may thus delay conversion to the crystalline phase, as indicated by the combined FTIR (Figure 7) and X-ray diffraction (Figure 6) results. In addition to precursor reactivity, precursor or ligand pyrolysis behavior is therefore another key consideration in the processing of thin films from molecularly modified alkoxide compounds.

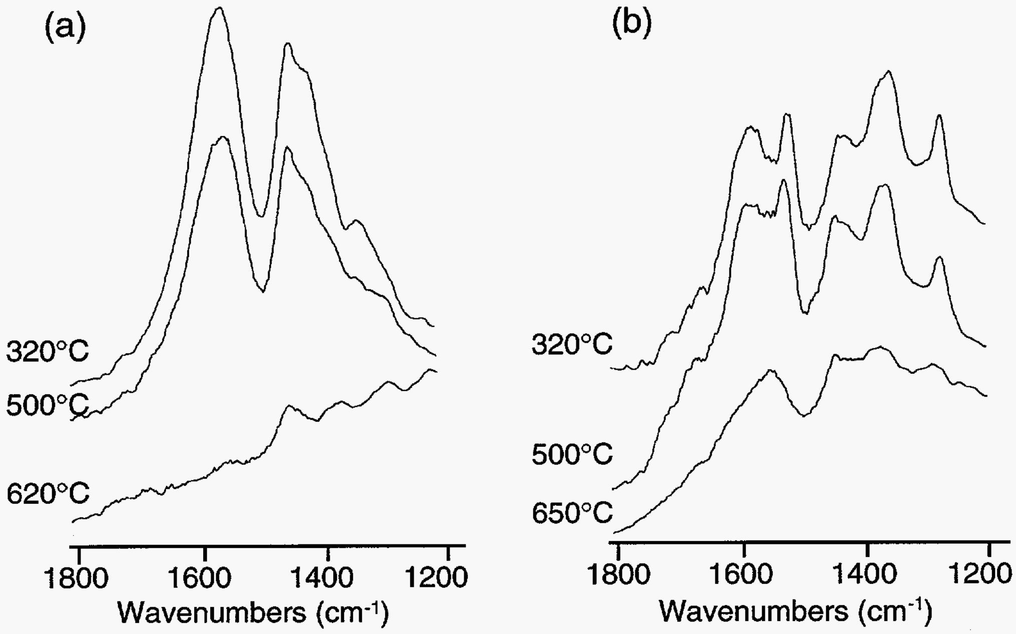

Figure 7. FTIR diffuse reflectance spectra for (a) acetate and (b) acac derived zirconia thin films heat-treated to various temperatures using the AET Addax RTP furnace; no hold at temperature, 50°C/min ramp rate.

## CONCLUSIONS

Titania and zirconia thin films were prepared from alkoxide compounds modified by different chelating ligands. Films displaying a range of processing characteristics were obtained from the various precursor solutions. Modifying ligand steric size, precursor reactivity, and pyrolysis behavior were found to be key variables for control of film consolidation, densification, and crystallization behavior. It was also possible to control thin film processing behavior through tailoring other process variables such as chelating ligand to metal alkoxide ratio and pre-hydrolysis of precursor species. Further studies are in progress to better elucidate the relationships between precursor structure and crystallization behavior.

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## REFERENCES

1. C. J. Brinker, T. L. Ward, R. Sehgal, N. K. Raman, S. L. Hietala, D. M. Smith, D.-W. Hua, and T. J. Headley, "'Ultramicroporous' Silica-based Supported Inorganic Membranes," *J. Membrane Sci.*, **77**, 165 (1993).
2. W. J. Kaiser and E. M. Logothetis, "Exhaust Gas Oxygen Sensors Based on $TiO_2$ Films," SAE Technical Paper Series, No. 830167.
3. K. Fukushima and I. Yamada, "Electrical Properties of $TiO_2$ Films Deposited by a Reactive-Ionized Cluster Beam," *J. Appl. Phys.*, **65** (2), 619 (1989).
4. R. W. Schwartz, D. Dimos, S. J. Lockwood, and V. M. Torres, "Electrical Properties of Sol-Gel PZT Thin Films for Decoupling Capacitor Applications," in Ferroelectric Thin Films III, Eds., E. R. Myers, B. A. Tuttle, S. B. Desu, and P. K. Larsen, (*Mat. Res. Soc. Symp. Proc.*, Pittsburgh, PA, **310**, 1993) pp. 59-64.
5. C. E. Land, "Optical Information Storage in PLZT Thin Films," *Ceramic Trans.*, **11**, 343 (1990).
6. R. W. Schwartz, J. A. Voigt, C. D. Buchheit, and T. J. Boyle, "Densification and Crystallization of Zirconia Thin Films Prepared by Sol-Gel Processing," *Ceramic Trans., Ferroic Materials: Design, Preparation and Characteristics*, **43**, 145 (1994).
7. Y.-J. Kim and L. F. Francis, "Processing and Characterization of Porous $TiO_2$ Coatings," *J. Am. Ceram. Soc.*, **76** (3), 737 (1993).
8. R. W. Schwartz, B. C. Bunker, D. B. Dimos, R. A. Assink, B. A. Tuttle, D. R. Tallant, and I. A. Weinstock, "Solution Chemistry Effects in $Pb(Zr,Ti)O_3$ Thin Film Processing," *Integrated Ferroelectrics*, **2**, 243 (1992).
9. R. A. Assink and R. W. Schwartz, "$^1H$ and $^{13}C$ NMR Investigations of $Pb(Zr,Ti)O_3$ Thin-Film Precursor Solutions," *Chem. of Mater.*, **5** (4), 511 (1993).
10. S. Doeuff, M. Henry, C. Sanchez, and J. Livage, "Hydrolysis of Titanium Alkoxides: Modification of the Molecular Precursor by Acetic Acid," *J. Non-Cryst. Sol.*, **89**, 206 (1987).

11. P. P. Phule and F. Khairulla, "Molecularly Modified Alkoxide Precursors for Synthesis of Dielectric Ceramics," in Better Ceramics Through Chemistry IV, Eds., B. J. J. Zelinski, C. J. Brinker, D. E. Clark, and D. R. Ulrich (*Mat. Res. Soc. Symp. Proc.*, **180**, Pittsburgh, PA) pp. 527-532.
12. T. M. Alam, T. J. Boyle, C. D. Buchheit, R. W. Schwartz, and J. W. Ziller, "Formation, Structure, and Material Properties from the Reaction Product of $M(OCHMe_2)_4$ (M = Ti, Zr) and HOAc," in Better Ceramics Through Chemistry VI, Eds., A. K. Cheetham, C. J. Brinker, M L. Mecartney, and C. Sanchez, (*Mat. Res. Soc. Symp. Proc.*, **346**, Pittsburgh, PA, 1994). pp. 35-40.
13. C. Sanchez and M. In, "Molecular Design of Alkoxide Precursors for the Synthesis of Hybrid Organic-Inorganic Gels," *J. Non-Cryst. Sol.*, **147&148**, 1 (1992).
14. C. Sanchez, F. Babonneau, S. Doeuff, and A. Leaustic, "Chemical Modifications of Titanium Alkoxide Precursors," in Ultrastructure Processing of Advanced Ceramics, Eds., J. D. Mackenzie, D. R. Ulrich (Wiley Interscience, New York, 1988) pp. 77 - 87.
15. K. H. Von Thiele, and M. Panse, "Contributions to the Chemistry of Transition Metal Alkyl Compounds. XXVII. Preparation of Titanium Acetates from Tetramethyl and Tetrbenzyl Titanium," *Z. Anorg. Allg. Chem.*, **441**, 23 (1978).
16. D. D. Perrin and W. L. F. Armarego, Purification of Laboratory Chemicals 3rd Edition (Pergamon Press, New York, 1988) Chapter 2.
17. D. E. Bornside, C. W. Macosko, and L. E. Scriven, "On Modeling of Spin Coating," *J. Imaging Tech.*, **13**, 122 (1987).
18. R. W. Schwartz, T. J. Boyle, S. J. Lockwood, M. B. Sinclair, D. Dimos, and C. D. Buchheit, "Sol-Gel Processing of PZT Thin Films: A Review of the State-Of-The-Art and Process Optimization Strategies," *Integrated Ferroelectrics*, accepted for publication (1994).
19. M. Born and E. Wolf, in Principles of Optics (Pergamon Press, New York, 1975) p. 87.
20. G. W. Scherer, "Effect of Inclusions on Shrinkage," in Better Ceramics Through Chemistry IV, Eds., B. J. Zelinski, C. J. Brinker, D. E. Clark, and D. R. Ulrich, (*Mat. Res. Soc. Symp. Proc.*, Pittsburgh, PA, **180**, 1990) pp. 503-514.
21. C. J. Brinker, W. D. Drotning, and G. W. Scherer, "A Comparison Between the Densification Kinetics of Colloidal and Polymeric Silica Gels," in Better Ceramics Through Chemistry, Eds., C. J. Brinker, D. E. Clark, and D. R. Ulrich, (*Mat. Res. Soc. Symp. Proc.*, Pittsburgh, PA, **32**, 1984) pp. 25-32.
22. J. L. Keddie, P. V. Braun, and E. P. Giannelis, "Interrelationships Between Densification, Crystallization, and Chemical Evolution in Sol-Gel Titania Thin Films," *J. Am. Ceram. Soc.* **77** (6), 2669 (1993).
23. J. L. Keddie and E. P. Giannelis, "Effect of Heating Rate on the Sintering of $TiO_2$ Thin Films: Competition between Densification and Crystallization," *J. Am. Ceram. Soc.*, **74**, 2669 (1991).