



Effect of Solution Processing on PZT Thin Films Prepared by a Hybrid MOD Solution Deposition Route

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Abstract. Lead zirconate titanate, $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT), thin films were prepared by a hybrid metalorganic decomposition (MOD) solution deposition route; the effects of processing conditions on the film structure and properties were investigated. Solutions were synthesized by mixing and reacting Zr acetylacetonate and Pb acetate trihydrate with a solution prepared from Ti isopropoxide, acetic acid and water. Chemical changes in the solution during preparation and solution storage (i.e., aging) were investigated by visual observation and FTIR, and were evidenced by changes in phase content and properties of the final PZT films. Results suggest that Zr acetylacetonate and Pb acetate trihydrate react with a Ti oxoacetate-based precursor, and that this reaction continues during aging at room temperature. The PZT film quality and properties improved with aging time of the solution before deposition. To achieve good properties and design a convenient processing route, an accelerated aging scheme, including a brief aging at 60°C and freezing to prevent further reaction, was developed. PZT films prepared from these solutions had average dielectric constants of ~ 1040 , loss tangents of ~ 0.05 , remnant polarizations of $\sim 26 \mu\text{C}/\text{cm}^2$, and coercive fields of $\sim 39 \text{ kV}/\text{cm}$.

Keywords: thin film, ferroelectric, PZT, processing, microstructure

Introduction

The electromechanical properties of lead zirconate titanate, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), make it an excellent material for microactuators and microsensors in microelectromechanical systems (MEMS). Of particular interest are PZT compositions near the morphotropic phase boundary ($x \approx 0.52$) where dielectric, ferroelectric and piezoelectric parameters are greatest. MEMS devices incorporating PZT thin films include room temperature pyroelectric detectors, pressure sensors, and microactuators [1–5]. In these MEMS applications, PZT thin films are integrated with conducting electrodes (e.g., Pt, RuO_x), structural materials (e.g., poly-Si, silicon nitride) and sometimes Si-based signal processing and amplification circuitry. For preparation of PZT thin films, solution deposition

routes can provide molecular level mixing, low cost processing, and compatibility with Si batch processing techniques.

Solution deposition routes have been used for a variety of ceramic films and many routes have been developed for the preparation of PZT [6–12]. A common processing scheme involves Ti and Zr alkoxides and Pb acetate trihydrate dissolved and reacted in 2-methoxyethanol (2MOE) [7]. This process is considered a “sol-gel” route as the alkoxide precursors undergo hydrolysis (reaction with H_2O) and condensation (polymerization) reactions to form metal-oxygen-metal bonds and with continued reaction the solution becomes a gel. The 2MOE sol-gel route is popular due to the level of understanding of the processing variables and solution chemistry [13,14] as well as the very good properties of the resulting materials. However, alternatives to the carcinogenic 2MOE solvent are needed. For example,

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solution deposition routes have been reported using metalorganic species based on carboxylate and β -diketonate chelating ligands; these precursors are water insensitive, can be prepared in a variety of solvents and do not undergo polymerization reactions [10–12]. Routes using these precursors are described as metalorganic decomposition (MOD), because the precursors simply decompose to the oxide(s) on heating. In general, MOD processes require less time for solution preparation and less atmospheric control during processing, compared with sol-gel processes. However, problems associated with pyrolysis of the organic ligands (e.g., cracking and stress development caused by shrinkage) and the large number of depositions required to reach a desired film thickness reduce the effectiveness of MOD routes.

A hybrid MOD route is a process in which metal alkoxides are combined with metalorganics precursors which are less sensitive to water [6]. Hybrid MOD routes retain MOD's advantages of ease of preparation, use of less toxic solvents and insensitivity to water and sol-gel's advantage of greater oxide thickness per layer of deposited solution. However, the complex make-up of hybrid MOD solutions, particularly the presence of alkoxides with water and other reactants, leads to the chance that reactions will continue over time after the solutions have been prepared. For example, Boyle and co-workers [15] found that the size of molecular species in their hybrid solution grew with time. This change resulted in thicker films with poorer optical quality, but very similar electrical performance.

In this report, we describe a hybrid MOD solution deposition process for the preparation of PZT, and the microstructure and properties of the PZT thin films. The work was motivated by the need to develop a processing route that could be easily and conveniently used by a group of MEMS researchers. The solution processing procedure involves the mixing and reacting of Ti isopropoxide in acetic acid and water followed by the addition of Zr acetylacetonate and Pb acetate trihydrate. The solutions are easy to prepare; however, the microstructure and properties of the PZT films were found to change with the length of time that the solutions were stored. For this solution, the continued reaction appeared to improve the film microstructure and properties. Through an investigation of the solution chemistry and film properties, a procedure was established to overcome this disadvantage and develop a convenient process.

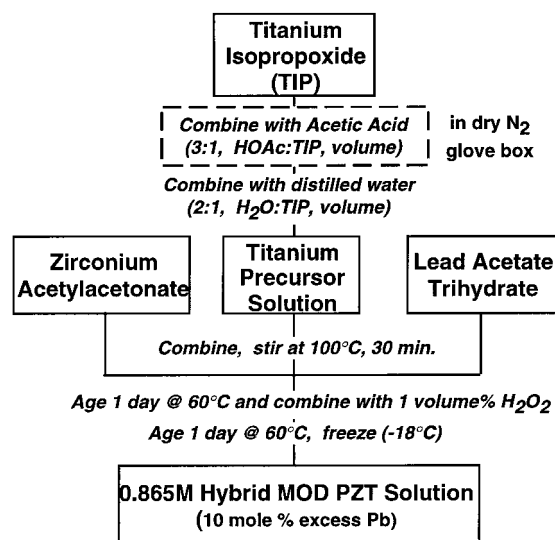


Fig. 1. Flow diagram for the preparation of hybrid MOD solution using the accelerated aging route.

Experimental Procedure

The hybrid MOD solution route used to prepare $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ thin films is shown schematically in Fig. 1. The route is a modified version of a method developed by Webb and co-workers [9]. A 0.865 M Pb—Zr—Ti (10 mole % Pb excess) solution was prepared by first combining titanium isopropoxide (TIP) with glacial acetic acid (HOAc) (3:1 volume ratio, HOAc:TIP) in a dry nitrogen atmosphere glove box. After 5 min of stirring, the TIP/HOAc solution was then combined with distilled water (2:1 volume ratio, H₂O:TIP). Upon water addition, a white precipitate with a polymeric appearance formed. The precipitate was dissolved under ultrasonic bath agitation for 30 min to form the Ti precursor solution. Zirconium acetylacetonate, $\text{Zr}(\text{OC}(\text{CH}_3)\text{CHCOCH}_3)_4$ ($\text{Zr}(\text{acac})_4$), and lead acetate trihydrate, $\text{Pb}(\text{OCOCH}_3)_2 \cdot 3\text{H}_2\text{O}$ ($\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$), powders were then added (sequentially) to the Ti precursor solution and dissolved by heating to a boil at 100°C in an open refluxing system. After constant stirring for 30 min, the solution was allowed to cool to room temperature. The solution color changed from golden yellow to yellow-orange with time; therefore, aging (i.e., storage time) was also considered a variable in the processing. The solution was then modified through

addition of 1 volume % hydrogen peroxide, H_2O_2 (30% assay in H_2O), prior to deposition.

An initial study of the effect of solution aging at room temperature was carried out. The number of days before addition of $\text{H}_2\text{O}_2(x)$ and the number of days after H_2O_2 addition but before coating deposition (y) were varied; the aging conditions investigated were $x-y = 1-1, 1-3, 1-5, 1-7, 3-1, 3-3, 3-5, 3-7, 5-1, 5-3, 5-5, 5-7, 7-1, 7-3, 7-5, \text{ and } 7-7$. A hybrid MOD Pb—Zr—Ti solution (100 ml) was prepared for the aging study, and separated into 5 ml aliquots. As described below, films prepared from solutions that were aged for 7 days before adding H_2O_2 and then an additional 7 days prior to deposition (7-7) were entirely perovskite and had the best properties. However, waiting for two weeks after solution preparation is inconvenient. Therefore, an accelerated aging scheme was developed: solutions were aged at 60°C for 1 day, then H_2O_2 was added and the solutions aged for an additional day at 60°C (this scheme will hereafter be referred to as 1-1@ 60°C). The solutions were then frozen (-18°C) to limit further effects from aging and then thawed and deposited on an as-needed basis. This method of combating solution aging problems is in the same spirit as Boyle and co-workers' method of removing volatiles from a precursor solution to create a powder that can be made into a solution on demand [15].

To understand the changes in the solution chemistry that accompany the processing and aging of the Pb—Zr—Ti solution, single and dual component solutions were prepared according to the procedure given in Fig. 1 except omitting 1 or 2 of the starting materials. The single component Ti solution was prepared by the same procedure used in the first step of the Pb—Zr—Ti solution preparation. Pb and Zr single component and Pb-Zr dual component solutions were prepared by dissolving the precursor powders in HOAc and H_2O while stirring for 30 min at 100°C . The concentrations of $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zr}(\text{acac})_4$ in the solutions and the ratio of HOAc to H_2O was the same as that in the Pb—Zr—Ti solution. Pb-Ti and Zr-Ti dual component solutions were prepared by combining $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ powder and $\text{Zr}(\text{acac})_4$ powder, respectively, with the Ti solution at room temperature and then stirring at 100°C for 30 min. All solutions (except single component Ti solution) were aged 1 day at 60°C , modified with H_2O_2 and aged an additional day at 60°C (the scheme used to prepare

Pb—Zr—Ti solution). Visual observations of the single and dual component solutions were compared with those made for the Pb—Zr—Ti solution. In addition, FTIR spectroscopy was carried out to investigate the chemical structure of the Pb—Zr—Ti solution, single component, and dual component solutions. FTIR spectroscopy was performed on a Nicolet Magna 750 FTIR for solutions cast on 3 M disposable IR cards containing a microporous polyethylene window. Solutions which did not wet the polyethylene cards, were moisture sensitive or did not contain water were placed between KBr plates.

Thin films of PZT were prepared by spin coating the aged and modified solutions (passed through a $0.2 \mu\text{m}$ syringe filter), onto Pt coated Si substrates (see below) at 4000 rpm for 30 sec. After deposition, the specimens were then placed on a hot plate at 110°C for 10 min and inserted into a preheated oven at 400°C for 10 min. The procedure was repeated to deposit a second layer prior to inserting in a preheated oven at 700°C for 30 min. The above procedure was repeated to prepare a four layer film with a thickness of $0.60 \mu\text{m}$. In addition to Pt, electrode heterostructures contained layers of Ti, TiO_x and SiO_2 (Pt/Ti/ TiO_x / SiO_2 /Si) or Ti, polycrystalline Si, and silicon nitride (Pt/Ti/ TiO_x /poly-Si/ SiN_x /Si).

XRD was used to determine the crystalline phase content of the PZT films. A metastable nonferroelectric phase with a low dielectric constant can be present in amounts below the detection limit of XRD. Based on work on related materials, the metastable phase has either the pyrochlore or fluorite [16] structure; here, this unwanted phase will be referred to as a pyrochlore-type phase. Since the pyrochlore-type phase is characterized by a fine grain size ($\sim 0.01 \mu\text{m}$) in thin films, SEM was also used to aid in phase identification as well as determine PZT film microstructure. Specimens were examined in plan and cross-sectional views.

For electrical property measurements, top gold electrodes were defined by shadow masking and prepared by sputtering. Electrodes were $\sim 0.4 \text{ mm}$ in diameter. Dielectric properties of PZT films were measured at 1 kHz with a HP 4192A LF impedance analyzer. The remnant polarization (P_r) and coercive field (E_c) were measured with a Radiant Technologies RT-66A in the virtual ground mode at peak fields of $\pm 50, 83, 167, 250$ and 333 kV/cm ($\pm 3, 5, 10, 15,$ and 20 V). The determination of dielectric and

Table 1. Summary of observations made during processing of the hybrid MOD Pb-Zr-Ti solution, and single and dual component precursor solutions

Solution	As-Prepared*	After 1 day @ 60°C	After H ₂ O ₂ addition
Pb-Zr-Ti	golden-yellow	golden-yellow	no precipitate; yellow-orange; gas evolution
Ti	translucent gel	NA	NA
Pb	colorless	colorless	no precipitate; colorless; no gas evolution
Zr	light yellow	light yellow	precipitate; golden-yellow; gas evolution
Pb-Zr	light yellow	light yellow	no precipitate; golden-yellow; gas evolution
Pb-Ti	colorless	colorless	precipitate; golden-yellow; gas evolution
Zr-Ti	golden-yellow	golden-yellow	no precipitate; yellow-orange; no gas evolution

* after stirring 30 min at 100°C.

ferroelectric parameters was performed by direct micro-probe contact with the Au electrodes.

Results and Discussion

Preliminary studies showed that the quality and electrical properties of PZT films prepared by this hybrid MOD route improved with storage of the solution at room temperature or 60°C (accelerated aging scheme). Coincident with this improvement was a change in the solution color, indicating a change in solution chemistry. Below, results of the investigation of the solution chemistry are given followed by results showing the impact of solution aging procedure on the PZT film structure and properties.

Solution Chemistry

The synthesis of the hybrid MOD Pb-Zr-Ti solution begins with the preparation of the Ti precursor solution, followed by the addition Zr acetylacetonate and Pb acetate trihydrate powders and heating at 100°C. The color of the as-prepared solution was golden yellow, but changed to yellow-orange after a day of aging in a closed container at 60°C (or after several days aging at room temperature). After cooling from 60°C and addition of H₂O₂ solution, gas evolved from the solution and its color changed immediately to a deeper yellow-orange. With sonication (30 min.) and further aging at 60°C, the color turned orange-red. These observations indicated changes in the solution chemistry. To gain further insight into the chemical changes in the Pb-Zr-Ti solution, single and dual component solutions were prepared according to the procedure in Fig. 1 except with one or two of the components omitted. A summary of the observations is listed in Table 1 and is

discussed below along with relevant data from FTIR studies.

A single component Ti solution was prepared by the same procedure used in the first step of the Pb-Zr-Ti solution preparation. Acetic acid (HOAc) was added to Ti isopropoxide (TIP) in a molar ratio of ~15, which is 3.7 times the amount necessary to completely replace the isopropoxy ligands with acetate ligands. After ~5 min of stirring under an N₂ atmosphere, water was added and a white precipitate with a stringy, polymeric appearance formed. This precipitate dissolved during sonication (30 min), resulting in a clear solution. Figure 2 gives the FTIR spectrum for this Ti solution, with the spectra for HOAc and TIP included for comparison. The spectrum for the Ti solution does not contain the characteristic sharp band at 1000 cm⁻¹ for the isopropoxy ligands [17], indicating full removal of

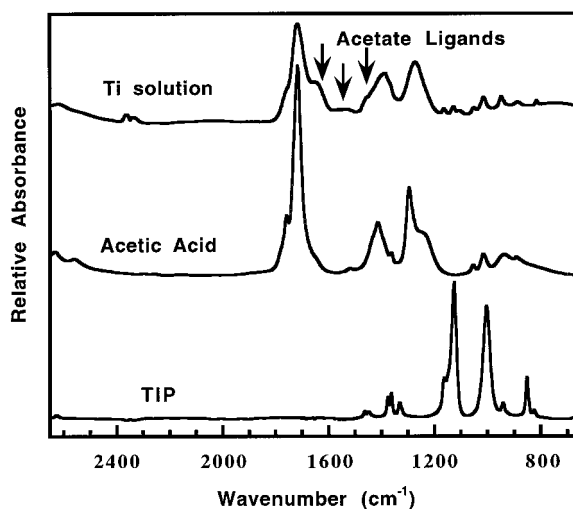


Fig. 2. Transmission FTIR spectra for titanium isopropoxide (TIP), acetic acid and the single component Ti solution.

the original isopropoxide groups, and contains new bands at 1650 and 1460 cm^{-1} . The new peaks correspond to $\nu_{\text{assym}}(\text{COO}^-)$ and $\nu_{\text{symm}}(\text{COO}^-)$ for the acetate ligand, respectively. The frequency separation, $\Delta\nu = 190 \text{ cm}^{-1}$, indicates a bidentate bridging or chelating acetate ligand [18].

These results concur with a study by Sanchez and co-workers [19] in which TIP was reacted with HOAc. Using a $[\text{HOAc}]/[\text{TIP}]$ ratio of 10, they found that a white polymeric precipitate formed after three days and this precipitate could be dissolved in water. Analysis showed that the chemical structure of the precipitate corresponded to $\text{TiO}(\text{OAc})_2$ with a linear structure of oxo ($\text{Ti}-\text{O}-\text{Ti}$) and acetate ($\text{Ti}-\text{OCHCH}_3\text{O}-\text{Ti}$) groups bridging adjacent Ti atoms. For the Ti solution in the present work, FTIR data indicates the formation of a similar oxoacetate structure, although the ratio of $[\text{HOAc}]/[\text{TIP}]$ ratio was 15 and water was added soon after the acetic acid. The formation of a water soluble precipitate was also observed. Based on these results, we conclude that the Ti solution used for the Pb—Zr—Ti synthesis likely contains linear Ti oxoacetate-based oligomers or polymers.

When the single component Ti solution was heated to 100°C with constant stirring (the procedure used in preparing the Pb—Zr—Ti solution), a translucent gel formed in less than 30 min. This observation indicates that heating causes reactions among the Ti oxoacetate-based oligomers which eventually lead to gelation. This single component solution was not processed further.

Pb—Ti and Zr—Ti dual component solutions were prepared by combining $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ powder and $\text{Zr}(\text{acac})_4$ powder, respectively, with the Ti solution at room temperature and then stirring at 100°C for 30 min. For both Pb—Ti and Zr—Ti dual component solutions, no gelation was observed. The Pb—Ti solution was colorless until the H_2O_2 was added when it turned yellow and formed a small amount of precipitate and gas bubbles. The precipitate was dissolved with sonication. The Zr—Ti dual component solution immediately became golden-yellow on addition of $\text{Zr}(\text{acac})_4$; aging 1 day at 60°C and addition of H_2O_2 caused the solution to turn a yellow-orange color. No precipitate formed and no gas evolution was observed. The color sequence and other observations for the Zr—Ti dual component solution was identical to that observed in preparing the Pb—Zr—Ti solution. Pb and Zr single component

and Pb—Zr dual component were also prepared and provided some insight into the changes occurring in the Pb—Zr—Ti solution. Results are summarized in Table 1.

The observation that neither of the dual component solutions (Pb—Ti and Zr—Ti) gelled suggests that Pb acetate trihydrate and the $\text{Zr}(\text{acac})_4$ react with the Ti oxoacetate-based precursor. The reactions likely modify the Ti oxoacetate polymer through the formation of Pb—O—Ti and Zr—O—Ti bonds which eliminate some reactive sites on the Ti oxoacetate-based structure. The dual component Zr—Ti solution underwent color changes similar to those of the Pb—Zr—Ti solution, while the Pb—Ti solution did not. The reaction of the $\text{Zr}(\text{acac})_4$ with the Ti oxoacetate-based precursor was at least partially responsible for the color change which is likely linked to a change in the local environment and coordination of Ti. The hydrogen peroxide addition also instigated a color change. The peroxy ion, O_2^{2-} , is a strong chelating agent and has been shown to cause a change in coordination state and an orange color in Ti(IV) aqueous solutions [20]. Chelation by the peroxy ion could also explain the evolution of gas (H_2). The Zr and Pb—Zr solutions do not exhibit such color changes, reinforcing the role Ti coordination on the color of the solution.

The similarity in the color changes in the Zr—Ti and Pb—Zr—Ti solutions indicates that the reaction between the Zr and Ti precursors may be preferred over the reaction between Pb and Ti precursors. Further evidence for this preference was provided by the formation of a crystalline precipitate in Pb—Zr—Ti solutions aged 2–3 months (room temperature); x-ray characterization determined that the precipitate was lead acetate trihydrate. This result indicates that some or all of the Pb precursor was not bonded to the Ti oxoacetate-based oligomeric structure.

Film Microstructure and Properties

The solution aging procedure and the addition of H_2O_2 affected the quality, microstructure, crystalline phase content and electrical properties of the resulting PZT films. The initial screening of solutions consisted of visual observations of films prepared from the solutions and XRD to determine if perovskite was the sole crystalline phase in the film. In general, the addition of H_2O_2 (1 volume %) reduced streaking in

films and reduced the amount of the pyrochlore-type phase phase at the film surface. Other additives designed to promote wetting of the spin-deposited layer and increase the viscosity (Triton X-100 and glycerol, respectively) were also investigated, but resulted in visually inferior films and/or residual pyrochlore-type phase. Defect-free PZT films were examined by SEM and their electrical properties were determined.

Figure 3 gives XRD data for PZT films prepared using solutions with two different aging conditions. For both the optimized room temperature aging (7-7) and the accelerated aging at 60°C (1-1@60°C), the data indicate the presence of the perovskite phase only. The XRD data for films prepared from solutions aged with 3-3 and 5-5 conditions were similar (i.e., only perovskite detected), while some thin films prepared from solutions aged for lesser amounts of time showed a peak for the pyrochlore-type phase.

Figure 4 shows SEM micrographs of $\sim 0.6 \mu\text{m}$ thick PZT thin films prepared from several solutions. The PZT prepared from solutions aged with 7-7 and 1-1@60°C conditions show a dense perovskite microstructure with an average grain size of $\sim 0.1 \mu\text{m}$. By contrast, the films prepared from solutions aged with 3-3 and 5-5 conditions show a dense perovskite phase, with the a fine grained ($\sim 0.01 \mu\text{m}$) pyrochlore-type phase on the surface. For solution deposited films, the sequence of phase formation includes the initial crystallization of a pyrochlore-type phase followed by transformation to perovskite; the perovskite phase most likely nucleates from a pyrochlore-type matrix at the PZT/Pt interface

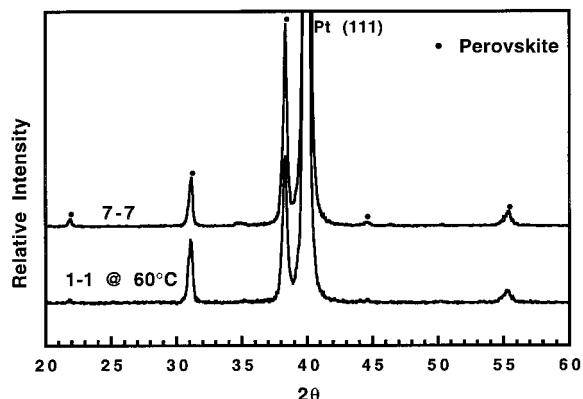


Fig. 3. X-ray diffraction data for PZT thin films prepared using solutions aged under two different conditions, 7-7 and 1-1@60°C (see text for explanation of notation).

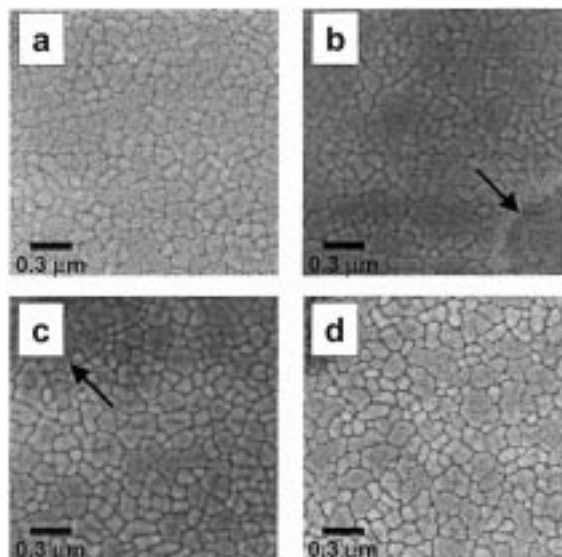


Fig. 4. SEM micrographs showing the surface structure of PZT thin films prepared using solutions aged for conditions (a) 7-7, (b) 5-3, (c) 3-3 and (d) 1-1@60°C. (see text for explanation of notation). The arrows point to regions of fine-grained microstructure associated with the pyrochlore-type phase phase.

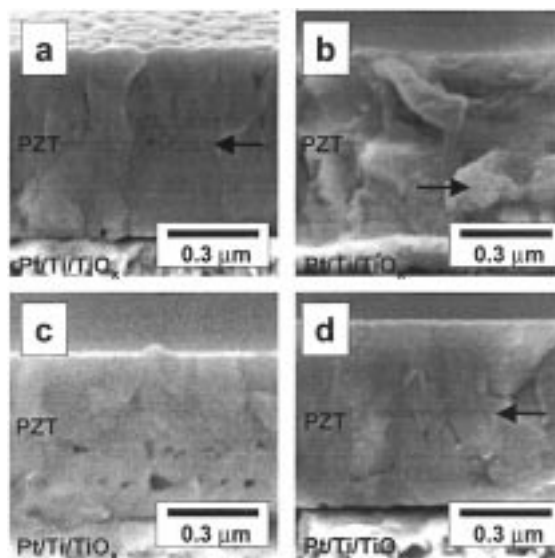


Fig. 5. SEM micrographs showing the cross-sections of PZT thin films prepared using solutions aged for conditions (a) 7-7, (b) 5-3, (c) 3-3 and (d) 1-1@60°C. (see text for explanation of notation and arrows).

[21]. Formation of this pyrochlore-type phase has been linked to Pb deficiencies from PbO loss. Since pyrochlore can tolerate Pb deficiency while the

Table 2. Electrical properties of PZT thin film capacitors prepared from hybrid MOD solutions aged under different conditions

Solution Aging	K	$\tan \delta$	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
3-3	835	0.040	24.13	54.94
5-5	726	0.048	21.32	61.24
7-7	898	0.048	27.96	57.40
1-1@60	959	0.039	21.39	40.78
1-1@60; 7 days*	948	0.049	27.18	38.09
1-1@60; 14 days*	1145	0.045	29.93	38.28
1-1@60; 33 days*	1039	0.056	26.88	39.61

* days frozen.

perovskite structure can not, the inability of the Pb deficient pyrochlore phase to transform to perovskite results in the pyrochlore-type phase at the surface. Figure 5 shows SEM micrographs of these PZT thin films, in cross-section. Figure 5(a) shows the columnar microstructure of the PZT film, and a boundary in the middle of the cross-section due to an interface formed by intermediate heat treatments and subsequent solution deposition. These features indicate nucleation of perovskite at the Pt/PZT interface. The arrow in Fig. 5(b) points to a region consisting of the pyrochlore-type phase in the interior of the film (identified by the grain size). This interior pyrochlore-type phase may have resulted from residual surface pyrochlore after the first 700°C heat treatment. Figure 5(c) shows porosity in the interior of a film prepared from a solution which was not aged properly.

The electrical properties of the films (K , $\tan \delta$, P_r , E_c , d_{33}) were measured to determine the device worthiness of PZT thin films prepared from the hybrid MOD solution route. Table 2 lists the electrical properties (K , $\tan \delta$, P_r , E_c) of representative films prepared from solutions with different aging conditions. Electrical properties reflect changes in the microstructure and phase content. Films prepared from solutions aged for longer times at room temperature (i.e., 7-7) resulted in a higher K , and P_r , and a lower E_c . Porosity (see Fig. 5(c), pyrochlore-type phase on the surface of the film (see Figs. 4(b) and 4(c) or in the interior of the film (see Fig. 5(d)) are likely the causes of the poorer properties. The presence of the pyrochlore-type phase will affect the electrical properties, as it is not ferroelectric and has a dielectric constant of ~ 50 .

Solution chemistry studies indicate a link between the changes in solution and the resulting PZT film quality and properties. The observations discussed in the previous section show that reactions among the

precursors in solution continue during storage at room temperature. Since the Zr—Ti solution color changes were identical to those in the Pb—Zr—Ti solution, there is some evidence that a reaction between Zr and Ti precursors occurred over time as the solution ages. The reactions occurring during the aging period may improve the homogeneity of the solution and make the formation of perovskite more favorable. For example, Zr-rich PZT compositions form the pyrochlore-type phase more easily and require higher temperatures to transform to perovskite. Achieving a uniform distribution of Zr and Ti at the 53/47 composition would favor perovskite formation. In addition, the nature of the bonding of the Pb-containing species in the metalorganic structure should be important as it may influence PbO loss from the pyrochlore-type phase. The electrical properties of thin films prepared from solutions that were frozen and thawed were somewhat better than others in the study, indicating that these procedures may also have an effect on solution chemistry. While the reactions that go on at room temperature are certainly slowed by reducing the temperature other changes, including inhomogeneous freezing and phase separation, may occur on freezing and thawing and therefore influence the chemical structure and resulting film properties.

Conclusions

A hybrid MOD solution route for PZT thin films was developed and the effects of solution processing on the structure and properties of PZT films determined. The preparation of single and dual component precursor solutions provided insight into the key interactions of the hybrid MOD Pb—Zr—Ti solution route. The formation of a Ti oxoacetate polymeric precursor and subsequent reaction with Pb and Zr

precursors appeared to provide the necessary molecular level mixing when the solution was aged under the appropriate conditions. Improper aging (either too much or too little) resulted in retention of varying degrees of the pyrochlore-type phase on the surface degrading electrical properties. The aging was accelerated by storage at 60°C and then halted by freezing the solution. The convenience of accelerating the process and freezing individual at vials of solution makes the use of this route ideal for use by a large group of researchers.

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