

Chemical Solution Deposition of Perovskite Thin Films

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The use of chemical solution deposition for the fabrication of perovskite thin films is reviewed. A variety of approaches including sol–gel, chelate, and metalloorganic decomposition have all been employed with success in the preparation of these materials. For a number of perovskite compounds, thin-film properties that equal those of the bulk materials have been obtained. Various aspects of the solution chemistries for the three different routes are discussed, and the effects of solution precursor properties on the conversion of the as-deposited film to the desired perovskite phase are discussed. The roles that thermodynamic and kinetic factors have on this transformation process are also reviewed. Finally, some of the applications for solution-derived thin films currently under development are reviewed, and the inherent limitations of the deposition technique for device manufacture are considered.

I. Introduction

The development of chemical solution deposition (CSD) processes for perovskite thin films dates to the mid-1980s. Publications by Fukushima and co-workers¹ on MOD (metalloorganic decomposition) and Budd et al.^{2,3} on the sol–gel processing of thin films of lead zirconate titanate (PZT), a widely used ferroelectric material, were some of the first examples that demonstrated it was possible to obtain the desirable properties of bulk perovskite materials in thin-film form. The early work by these investigators and others led to a rapid expansion of research in this area.^{4,5} At about this same time, a number of small companies⁶ interested in the development of nonvolatile memories based on perovskite PZT thin films were started. For some of these companies, because of cost considerations, solution deposition became the fabrication method of choice. While these companies did not commercialize any thin-film products at the time, the work they carried out encouraged the participation of other researchers (and larger corporations) in the field. This led to the evolution of these materials to the point that today they are appearing in a number of devices and continue to be developed for other applications.

Perovskite materials display a wide range of properties that make them attractive for a variety of electrical ceramic applications. The structure is named after the naturally occurring mineral perovskite (CaTiO_3)^{7,8} and is usually depicted in pseudocubic form, as shown in Figure 1. The structure contains two cation sites in the crystal lattice: the larger cation (A) resides on the corners of the unit cell, and the smaller cation (B) is in the center of the unit cell. The oxygen ions (O) are on the centers of the faces, and the structure is formed via a network of corner-linked oxygen octahedra, with the larger cation (A) filling the dodecahedral holes and the smaller cation (B) filling the octahedral sites. Interestingly, and of technological importance, a variety of compositions crystallizes in the perovskite (ABO_3) structure. These are often subdivided into classes depending

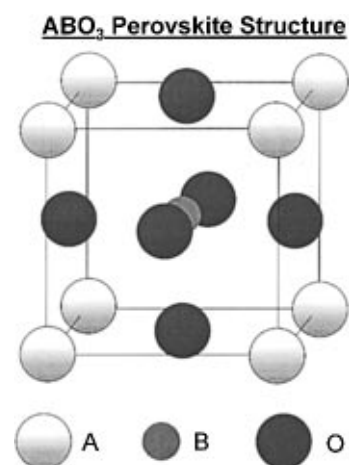


Figure 1. Crystal structure for the ABO_3 perovskite.

on the respective valences of the A- and B-site cations. Examples include PbTiO_3 (PT), $\text{A}^{2+}\text{B}^{4+}\text{O}_3$; NdAlO_3 , $\text{A}^{3+}\text{B}^{3+}\text{O}_3$, and complex perovskites, such as the relaxor ferroelectric, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN).⁹ Other technologically important perovskites include BaTiO_3 (BT), SrTiO_3 (ST), $(\text{Ba,Sr})\text{TiO}_3$ (BST), $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), $\text{Pb}(\text{Sc,Ta})\text{O}_3$ (PST),¹⁰ $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT, a layered perovskite),¹¹ $(\text{La,Sr})\text{CoO}_3$ (LSCO), and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO, a high-temperature superconducting compound). Of these materials, BT, PZT, SBT, and YBCO have received the most attention and will be emphasized in this review.

While the perovskite structure is usually depicted in pseudocubic form, slight distortions from cubic symmetry are responsible for most of the interesting properties of perovskite materials. For example, BT and PZT materials are widely used for their electrooptic, ferroelectric, and piezoelectric properties. For BT, these properties are a direct result of the displacement (~ 0.1 Å) of the B-site species (Ti) from the center of the unit cell, resulting in tetragonal, rhombohedral, or orthorhombic symmetry. In PZT materials, Warren and co-workers have shown that in addition to the Zr and Ti displacements, displacements of the A-site lead species also contribute to ferroelectric behavior.¹² Other im-

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portant properties afforded by these materials are their pyroelectric response, high dielectric constants, and colossal magnetoresistance. Because perovskite materials contain more than one cation species, close control of material composition is required for the preparation of single-phase compounds.¹³

In this paper, solution processing of a number of the materials discussed above will be reviewed. The underlying chemical and physical aspects of the solution deposition of these materials will be discussed, with a focus on understanding the solution preparation, film deposition, and phase transformation (to the crystalline ceramic) processes that occur during film synthesis. In particular, sol-gel, chelate, and MOD fabrication routes will be considered. To understand how to effectively develop chemical routes to the synthesis of perovskites, the roles that the kinetics of different processes and the thermodynamic stability of different phases play in the synthesis process will be discussed.

II. Solution Preparation

The general principle involved in the solution deposition of perovskite films is to prepare a "homogeneous" solution of the necessary cation species that may later be applied to a substrate. The fabrication of thin films by this approach involves four basic steps: (i) synthesis of the precursor solution; (ii) deposition by spin-casting or dip-coating, where drying processes usually begin depending on the solvent; (iii) low-temperature heat treatment for drying, pyrolysis of organic species (typically 300–400 °C), and formation of an amorphous film; (iv) higher temperature heat treatment for densification and crystallization of the coating into the desired oxide phase (600–1100 °C). For most solution deposition approaches, the final three steps are similar despite differences in the characteristics of the precursor solution, and for electronic devices, spin-casting has been used almost exclusively. Depending upon the solution route employed, different deposition and thermal processing conditions may be employed to control film densification and crystallization for the preparation of materials with optimized properties.

Solution preparation of perovskite materials generally involves the use of metalloorganic compounds that are dissolved in a common solvent. The starting reagents are typically metal alkoxide compounds, $M(\text{OR})_x$, where M is a metal and R is an alkyl group, metal carboxylates, $M(\text{OOCR})_x$, and metal β -diketonates, $\text{MO}_x(\text{CH}_3\text{COCHCOCH}_3)_x$. The selection of the starting reagents is dictated by solubility and reactivity considerations and the type of solution precursor species desired. The synthetic strategy used will define solution precursor properties such as equivalent solids content, extent of oligomerization and cation interaction, degree of homogeneity and reactivity, type and number of modifying ligands, and precursor size, structure, and shape. The solution route used will also determine the extent of intermixing of the metal species, whether formation of a network versus formation of individual inorganic phases occurs, the carbon content of the films, the temperature at which pyrolysis of organic species occurs, the weight loss associated with oxide formation, the densification and crystallization behavior of the film, and stress development within the film. As will be discussed below, solution chemistry variations (i.e.,

differences in precursor structure and solvent) can have a significant impact on the processing behavior of the as-deposited film. While some of these effects are now well understood, others are less clear, partly because of the difficulty in characterizing the solution precursor and the resulting amorphous film. In addition to precursor characteristics, film processing behavior, such as substrate wetting, can also play a role in determining the solution chemistry that must be developed. Film properties that can necessitate changes in solution chemistry include poor thickness uniformity (striations), crack formation, crystallization behavior and phase purity, and compositional nonuniformities.^{14,15}

For the production of perovskite thin films, the most frequently used CSD approaches may be grouped into three categories:

- (1) Sol-gel processes that use 2-methoxyethanol as a reactant and solvent.^{2,3,16}
- (2) Chelate processes that use modifying ligands^{17–19} such as acetic acid.
- (3) Metalloorganic decomposition (MOD) routes that use water-insensitive metal carboxylate compounds.^{20–22}

Other approaches that have also been used, but less extensively, include the nitrate²³ method, the citrate route,²⁴ and the Pechini process.²⁵

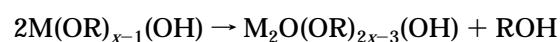
During solution synthesis, the chemical interactions that take place between the starting reagents will depend on both the reactivity of the compound and the solution preparation conditions, such as reflux temperature. In true sol-gel processing routes, the reactivity of the reagents is high, and if alcohol exchange occurs or if modifying ligands are used, the structure of the species in solution can bear little resemblance to the starting compounds. In this case, the species that are generated are frequently oligomeric in nature and can contain more than one type of cation.^{26–29} In contrast, for the long-chain carboxylate compounds that have been historically used in MOD routes,²⁰ such as zirconium 2-ethylhexanoate, reactivity is low and the chemical interactions between the different precursor compounds is minimal.

Sol-Gel Processes. Although other alcohols have also been utilized, the solvent, 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$), is most extensively used in the chemical synthesis of perovskite materials. Processes based on 2-methoxyethanol^{2,3} are most appropriately considered sol-gel processes and the key reactions leading to the formation of the precursor species are hydrolysis and condensation of the alkoxide reagents, in which metal-oxygen-metal (M-O-M) bonds are formed:

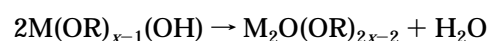
Hydrolysis:



Condensation (alcohol elimination):



Condensation (water elimination):

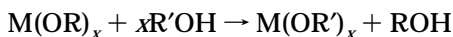


Prehydrolysis of less reactive alkoxides may also be used to improve solution compositional uniformity.

Another key reaction in the use of this solvent is the alcohol-exchange reaction that results in a decrease in

the hydrolysis sensitivity of starting reagents such as zirconium *n*-propoxide and titanium isopropoxide used in the production of PZT films:

Alcohol exchange:



where OR is a reactive alkoxy group and OR' is the less reactive methoxyethoxy group. 2-Methoxyethanol has also been found to be beneficial in the dissolution of carboxylate precursors such as lead acetate. In this case, by refluxing the lead acetate precursor in 2-methoxyethanol, one of the acetate groups is replaced, resulting in the formation of the soluble lead precursor, $Pb(OOCCH_3)(OCH_2CH_2OCH_3) \cdot 0.5H_2O$. Lead carboxylate compounds are usually employed due to the instability of lead alkoxides and their limited commercial availability. A typical process involves refluxing lead acetate and the alkoxide compounds in methoxyethanol in separate reaction vessels. This is followed by combining the solutions, further refluxing, distillation, and dilution to the desired volume. Prior to film formation, the stock solution prepared by the above process is then hydrolyzed to promote oligomerization.

The reactions that occur during PZT solution preparation have been extensively studied using spectroscopic techniques.^{16,30} Similar reactions between precursor compounds and 2-methoxyethanol have been also noted in the processing of $Pb(Zn_{1/3}Nb_{2/3})O_3$.³¹ These studies have elucidated certain aspects of the structure of the solution precursors. Some studies have indicated that the precursors formed in the lead zirconate titanate and lead titanate deposition solutions are apparently small, mixed metal oligomers,^{16,30} while others have indicated that the A-site precursor may not be intimately involved in the formation of the gel network.^{32,33} In particular, the results of Sengupta and co-workers³² for EXAFS (extended X-ray absorption fine structure) investigations of PZT gels indicate that separate networks of Ti–O–Ti, Zr–O–Ti, and Pb–O–Pb exist within the gel structure. This would seem to indicate that “intimate” mixing of the starting reagents has not taken place.

In terms of controlling the extent of intermixing and stoichiometry of the precursor species, there have been a number of efforts to synthesize stoichiometric precursors with structures similar to the final crystal structure of the desired perovskite phase. The motivation behind these efforts is that stoichiometric precursors with structures similar to the crystalline phase should undergo crystallization at lower heat treatment temperatures. Most attempts have resulted in mixed metal species with a cation stoichiometry different than that of the perovskite material. Examples in the synthesis of $PbZrO_3$ and $PbTiO_3$ include $[PbZr_2(\mu_4-O)_2(OOCCH_3)_4(OCH_2CH_3)_6]_2$ and $[PbTi_2(\mu_4-O)(OOCCH_3)(OCH_2CH_3)_7]_2$.^{26,27} These results indicate the importance that thermodynamic sinks can play in the synthesis of these materials.³⁴ However, while the stoichiometry of the precursor species may not match that of the crystalline perovskite, this has not inhibited the production of high-quality perovskite films by this processing route.

It has also been demonstrated that through manipulation of the above reactions, i.e., by controlling the reflux, catalysis, and hydrolysis conditions, the nature of the resulting solution precursors and gels may be

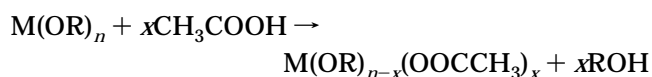
controlled, allowing for control of material properties. The initial interpretation of these effects was based on the more extensive investigations that had taken place for the silica system.³⁵ It was noted that many of the catalyst (acid or base) and hydrolysis effects in perovskite materials paralleled those for silica sol–gel processing using TEOS (tetraethyl orthosilicate). For example, in the production of lead titanate gels, acidic catalysis conditions resulted in gels that seemed more capable of polymeric rearrangement, while gels prepared under basic catalysis conditions exhibited more phase separation and were more highly textured.³⁶ Other physical properties of gel-derived lead titanate powders, namely, surface area and pore characteristics, also indicate a strong similarity in the processing behavior (hydrolysis and catalysis effects) of these materials to silica.³⁷ Solutions prepared with higher levels of hydrolysis resulted in powders with greater surface areas and pore volumes.

Solution processes based on the use of methoxyethanol are perhaps the most widely used of any of the CSD routes, primarily due to the ability of this solvent to solubilize a variety of starting reagents. When properly carried out, sol–gel processes offer excellent control and reproducibility of process chemistry, and nonhydrolyzed solutions exhibit minimal aging effects. Thin films with excellent properties have been prepared by sol–gel for a number of materials including PZT (high dielectric constant and ferroelectric hysteresis),³ $LiNbO_3$ (electrooptic coefficient),^{38,39} $BaTiO_3$ (high dielectric constant),⁴⁰ and YBCO (high critical current capabilities).⁴¹ However, for the nonchemist, the procedures involved in solution synthesis can be rather complex. Thus, while control over precursor characteristics is good, process simplicity is low. In addition, 2-methoxyethanol is a known teratogen, which presents a significant safety concern and inhibits its use in most manufacturing facilities.

Recently, the replacement of methoxyethanol by 1,3-propanediol in this process has been reported.^{42–44} As with the original process, the key reaction that defines the nature of the precursor species is alcohol exchange between propanediol and the original alkoxy groups. Unlike 2-methoxyethanol, which is a bidentate non-bridging ligand, 1,3-propanediol is believed to act as a cross-linking agent in this process, resulting in the production of large oligomeric species. The rather unique properties of 1,3-propanediol also have an effect on film processing behavior, most notably in changing the characteristics of the deposited film. Due to the minimal volatility of this solvent at room temperature, aggregation of the precursor species after spin-casting is inhibited and film instability results. Rapid thermal treatment of the as-deposited layers serves to induce stability, resulting in films with good dielectric and ferroelectric properties.⁴⁵ Another key advantage of the diol sol–gel process is that single depositions result in layers between 0.5 and 1.0 μm , rather than the 0.1 μm thickness typically obtained with other CSD routes. Thicknesses in this range are of interest for manufacturing devices such as decoupling capacitors since these devices utilize perovskite layers that are $\sim 1.0 \mu m$ in thickness, and the films can thus be prepared with one or two deposition and heat treatment cycles.⁴⁶

Chelate Processes. A second class of solution synthesis approaches, i.e., the "hybrid" or "chelate" routes, also utilize alkoxide compounds as starting reagents for the B-site species. Unlike true sol-gel routes, these routes rely heavily on the molecular modification of the alkoxide compounds through reactions with other reagents, namely chelating ligands, such as acetic acid, acetylacetone (acac, 2,4-pentanedione), or amine compounds. Chelate processes share several common attributes with methoxyethanol-based sol-gel deposition, most importantly, the formation of small oligomeric species during solution synthesis. The most commonly used chelate processes are based on the solvent/chelating agent acetic acid, and although several steps are typically required for solution synthesis, solution preparation generally requires less than 1 h.⁴⁷

While hydrolysis and condensation reactions again play a role in chelate routes, the key reaction is chelation of the metal alkoxides, which is illustrated here for acetic acid:



The primary reason for using chelating agents is to reduce the hydrolysis sensitivity of the alkoxide compounds, resulting in solutions that are more easily handled in air. Chelating agents thus serve a similar function to methoxyethanol. Chelation also results in molecular modification of the alkoxide compounds, and chelating reagents thus also dictate the structure and properties of the resulting species. Since ligands such as acetate and acac have different decomposition pathways than do alkoxy ligands, other important changes in precursor properties, such as pyrolysis behavior, also result.

Compared to the 2-methoxyethanol process, chelate processes offer the advantages of relatively simple solution synthesis; involved distillation and refluxing strategies are not required. Representative chelate processes are described by Yi and co-workers¹⁴ and Schwartz et al.¹⁷ In these routes, the addition of the chelating agent to the alkoxides is typically carried out during the initial process stages. Although the process eventually produces solutions that are water-insensitive, the initial phase of the process is usually still carried out under inert atmosphere conditions. As for 2-methoxyethanol processing, in the production of PZT films, lead acetate is used in conjunction with zirconium and titanium alkoxides. Either lead acetate is added to acetic acid for dissolution, followed by addition of the titanium and zirconium alkoxides,¹⁴ or the alkoxides are first chelated by acetic acid, followed by addition of lead acetate.¹⁷ Alcohol and water are then typically added for control of solution viscosity and stability.¹⁴

While chelate processes are simple and rapid, the chemistry involved in solution preparation is quite complex due to the number of reactions that occur. These have been studied in detail using nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy.⁴⁸ Key reactions were found to be chelation, esterification, and hydrolysis and condensation. The complexity of the reactions results in a diminished ability to control precursor structure compared to true sol-gel approaches. The gain in process

simplicity thus comes at a cost. However, precursor properties are still typically acceptable for film formation. Investigations of the nature of the precursor through solid-state ¹³C NMR indicate that for the levels of modifying ligands used, substitution of the original alkoxy groups of the B-site cations is essentially complete and the species formed are oxoacetate in nature. While characterization of the precursor species formed in this process is not as complete as for the methoxyethanol route, studies of crystals generated from the reactions of acetic acid and titanium isopropoxide would tend to indicate that they are small oligomers.^{49,50} Further information regarding the nature of the precursors was obtained through the addition of pyridine to a typical chelate solution.⁵¹ Concentrating this solution resulted in the isolation of lead-pyridine crystals, indicating that as for the methoxyethanol sol-gel process, the lead species remain isolated from the titanium and zirconium. The precursors are thus chemically heterogeneous on an atomic scale.

Another drawback of chelate processes is that continued reactivity in the precursor solution following synthesis can result in a change in precursor characteristics over time (weeks to months) and thereby a degradation in film properties. This occurs because substituent groups such as acetate, while less susceptible to hydrolysis than alkoxy groups, may still be attacked by water, resulting in a change in molecular structure. This reaction, continued esterification of the solution, and other reactions result in continued oligomerization and realkoxylation of the species, eventually causing precipitation. Using spectroscopic and analytical techniques, Boyle and co-workers have documented the time scale of such processes and their impact on PZT film properties.⁵²

Despite these disadvantages, as with sol-gel processes, thin films with excellent electrical and microstructural properties have been prepared by this approach, and a number of research groups routinely use it as their primary method of film fabrication. These results, together with those for methoxyethanol-based processing, would therefore seem to indicate that complete homogeneity/stoichiometry of the precursor species is not required for the preparation of high-quality materials, provided the interdiffusional distances are sufficiently short.³²

MOD Solution Synthesis. The third solution synthesis approach employed for perovskite film formation, metalloorganic decomposition (MOD), has historically used large carboxylate compounds, such as lead 2-ethylhexanoate, zirconium neodecanoate, and titanium dimethoxy dineodecanoate.²⁰ The basic approach consists of simply dissolving the metalloorganic compounds in a common solvent, usually xylene, and combining the solutions to yield the desired stoichiometry. For solution preparation, investigators have used both commercially available precursors and have synthesized starting reagents in-house.⁵³ Since the starting compounds are water-insensitive, they do not display the oligomerization behavior discussed above, and the precursor species that exist in solution retain a strong resemblance to the starting molecules. This aspect of the process, together with the use of noninteracting solvents, allow us to characterize the solution as a simple mixture of the starting compounds. Solution

synthesis is straightforward, and the approach allows for rapid compositional mapping of material systems. It has been used for a number of ferroelectric materials,^{54–56} for the preparation of perovskite films suitable for magnetoresistive applications,⁵⁷ and for high-temperature superconductors.⁵⁸

While the process is straightforward, it does possess a number of limitations. First, the large organic ligands of the most commonly used starting reagents may cause cracking during thin-film processing due to the large weight loss and shrinkage that can occur. To circumvent this difficulty, proper control of solution concentration and thermal processing is required. Second, while some researchers might justifiably deem this an advantage, most process engineers would consider the minimal reactivity of the starting reagents to be a further limitation. Because the characteristics of the precursor species can exhibit dramatic effects on thin-film properties, the inability to “tailor” the properties of the low-reactivity starting compounds through reactions such as chelation and hydrolysis and condensation restricts process flexibility. Hence, control of structural evolution and thin-film microstructure becomes limited to variations in solvent and solution concentration, and film deposition and heat treatment conditions.

The standard MOD process using large carboxylate compounds is still widely employed, but Haertling has developed an elegant, alternative MOD strategy that minimizes the first problem discussed above.²¹ This route is seeing more widespread use in the fabrication of PZT films, and the concepts involved in its development merit further consideration. In his process, low reactivity starting reagents are again employed, but in this case, short-chain carboxylate (e.g., acetate) and β -diketonate (e.g., acac) compounds are used. The compounds used are both water-insensitive and commercially available, and solution synthesis is straightforward for the nonchemist. The lower organic content of the precursors reduces film shrinkage after deposition, decreasing problems with film cracking. Films with properties comparable to those prepared by sol-gel and chelate processes are obtained. Although the solutions are water-insensitive, the presence of acetate ligands in an alcoholic-based solution still results in esterification. The precursor solutions therefore exhibit aging (and a change in film properties); however, the aging rates are apparently slower than those for chelate processes.⁵⁹

Nitrate, Citrate and Pechini Routes. While sol-gel, chelate, and MOD processes have been used most extensively for perovskite film fabrication, three other processes (Pechini, citrate, and nitrate) have also been studied. In the Pechini process,^{60,61} a liquid mixing technique, metal nitrates are first dissolved in water. Then citric acid [an α -hydroxycarboxylic acid, $\text{HO}(\text{COOH})(\text{CH}_2\text{COOH})_2$] is typically added to chelate the metal cations by forming a polybasic acid. When a polyhydroxyalcohol, most often ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, is then added, the citric acid-metal chelates will react with the ethylene glycol to form organic ester compounds. Heating of the mixture results in polyesterification and the formation of large metal/organic polymers. The process chemistry can be controlled so that a uniform solution, suitable for the deposition of homogeneous thin films, can be produced. An advantage of the Pechini method is that the viscosity and

polymer molecular weight of the solution can be tailored by varying the citric acid/ethylene glycol ratio and the solution synthesis temperature. This allows for control of the thickness of the deposited films, and in the processing of perovskite gas separation membranes on porous supports, minimization of interpenetration of the coating solution into the support.^{62,63}

The citrate process has been used to fabricate a variety of multicomponent electronic ceramic materials. The citrate solution synthesis process is similar to the Pechini process, except that ethylene glycol or other polyhydroxy alcohols are not utilized.²⁴ To produce citrate precursor solutions, stoichiometric amounts of the desired metal nitrates are dissolved in water and citric acid is then added to form citrate species. This process results in solution species that have a lower organic content than in the Pechini process, and consequently, films that display less weight loss during conversion to the ceramic phase. The nitrate method simply involves the dissolution of the desired nitrates in deionized water or alcohol.²³ The approach is thus more straightforward than the Pechini and citrate routes, but dewetting of the substrate may present a problem.

III. Film Deposition

Background. In the processing of thin films by CSD, the goal is to optimize film properties for specific applications. To effectively meet this goal, a fundamental understanding of substrate, solution chemistry, and thermal processing effects on the *structural evolution* of the as-deposited film to the crystalline ceramic state is required. Through the efforts of a number of research groups worldwide, there has been significant progress in understanding the film processing behavior of perovskite materials that has allowed for the preparation of high-quality films. Some of this knowledge has been gained by studying model systems such as titania and zirconia and through detailed analyses of material properties at different processing points. Using this body of work, it is now conceivable that within the next few years it will be possible to truly gain *control* over thin-film microstructure. In the following sections, examples of substrate, solution precursor, and thermal processing effects and their interrelationships with film microstructure will be reviewed to elucidate the mechanisms by which such effects exert an influence on microstructure. Figure 2a illustrates the problem that must be understood. As shown, an oligomeric solution precursor species containing an organic fraction is converted to the desired crystalline ceramic. For this to occur, structural rearrangements on several dimensional scales must take place. For example, for crystallization to occur, $\text{M}-\text{O}-\text{C}$ (or $\text{M}-\text{O}-\text{H}$) bonds must be broken and $\text{M}-\text{O}-\text{M}$ bonds are formed. For the illustrated titanium precursor, the local environment of the titanium species is the same as in the crystalline phase, rutile. However, for most of the oxygen species, the coordination must change to 3-fold, from either nonbridging ($\text{O}-\text{H}$ or $\text{O}-\text{C}$) or 2-fold ($\text{M}-\text{O}-\text{M}$). Rearrangements on other length scales are also required, as shown in Figure 2b for lead titanate.⁶⁴ For most as-deposited films, the film can be considered as an aggregation of oligomeric species, shown here as 2–3 nm clusters in a bulk lead titanate gel. During crystal-

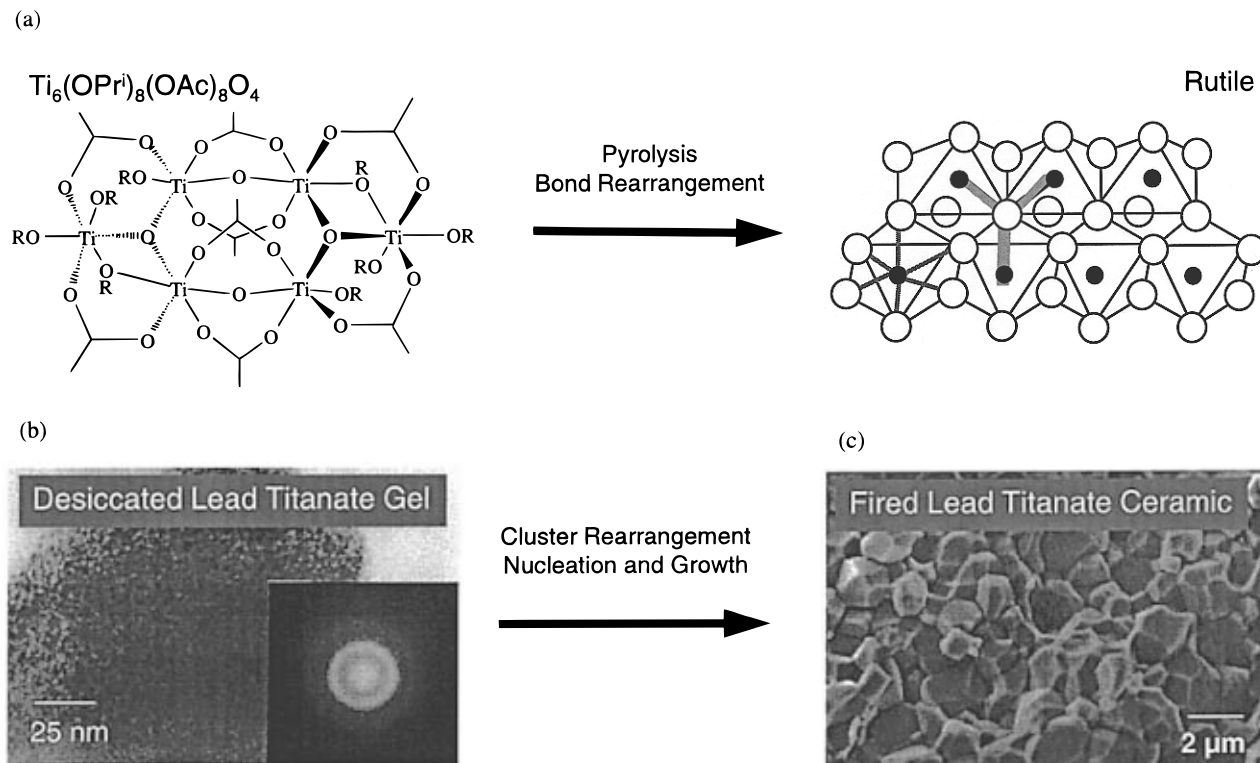


Figure 2. (a) Schematic representation of the transformation of the solution precursor⁴⁹ into the desired crystalline phase for TiO_2 . TEM photomicrographs of (b) a desiccated $PbTiO_3$ gel and (c) the resulting ceramic.⁶⁴

lization, these species rearrange to form an inorganic amorphous film, which then transforms to the ceramic (Figure 2c),⁶⁴ by a nucleation and growth process. Some of the processes involved in the transformation are continued condensation reactions, organic pyrolysis and concomitant M–O–M bond formation, elimination of structural free volume through relaxation (and viscous sintering in some materials), and crystallization. To control the properties of the final ceramic film, an understanding of the thermodynamics and kinetics of the processes that take place during conversion of the solution precursor to the crystalline ceramic is required.

Characteristics of As-Deposited Films. After the coating solution has been prepared, thin films are typically formed by spin-casting or dip-coating, and the desired ceramic phase is obtained by heat treatment. At the laboratory scale, deposition is usually achieved by simply depositing a few drops of the solution onto a cleaned, electroded Si wafer using a syringe with a 0.2 μm filter. The wafer is typically flooded during a static dispense, prior to spinning at 1000–8000 rpm. At the industrial scale, deposition is again accomplished by spin-casting, but in this instance, a spin-track system in a clean-room environment may be employed.

An as-deposited film is amorphous and typically retains a significant organic fraction. Its nature at this stage is highly dependent on the characteristics of the solution precursor species and the solvent. The reactivity of the precursors is determined by the starting reagents, the type of modifying ligands used, and the extent of modification. Three general classes of films may be described according to the type of precursor interactions and the film gelation behavior. They are chemical gel films (i.e., significant condensation during or shortly after deposition), physical gel films (i.e., a physical aggregation of precursor species that leads to

film stability), and nongelling films (i.e., minimal precursor interactions due to low precursor reactivity and low solvent volatility). For the production of high-quality films, we have found that either chemical or physical gelation is important. For nongelling films, condensation reactions that lead to film stability and improvements in processing behavior can be induced by a heat-treatment step immediately after deposition. The nature of the as-deposited film, which is defined by the precursor properties and aggregation behavior during deposition, is important since it not only provides insight into the nature of the precursors but also influences film densification during heat treatment.

Titania films serve as a good model system for understanding the processing behavior of perovskite films such as BT, ST, and PZT because the film-processing behavior in these more complex systems is strongly influenced by the behavior of the B-site species (here, Zr and Ti). While numerous processing similarities have been observed between the single component and the perovskite systems, precursor effects have been studied in much greater detail for titania and zirconia; hence, this discussion will focus primarily on these two materials. There is sufficient data to indicate that the processing/property relationships discussed hold for perovskite thin-film processing.

To investigate the effects of precursor properties on aggregation and film consolidation behavior, butanol-based solutions of titanium butoxide with varying amounts of the modifying ligand acac were prepared.⁶⁵ Films were then fabricated by spin-casting at 3000 rpm for 30 s, and immediately following deposition, the variations in film thickness with time (at room temperature) were studied by single-wavelength ellipsometry. Results of this analysis are presented in Figure 3 for the variations in film thickness, shrinkage, and refrac-

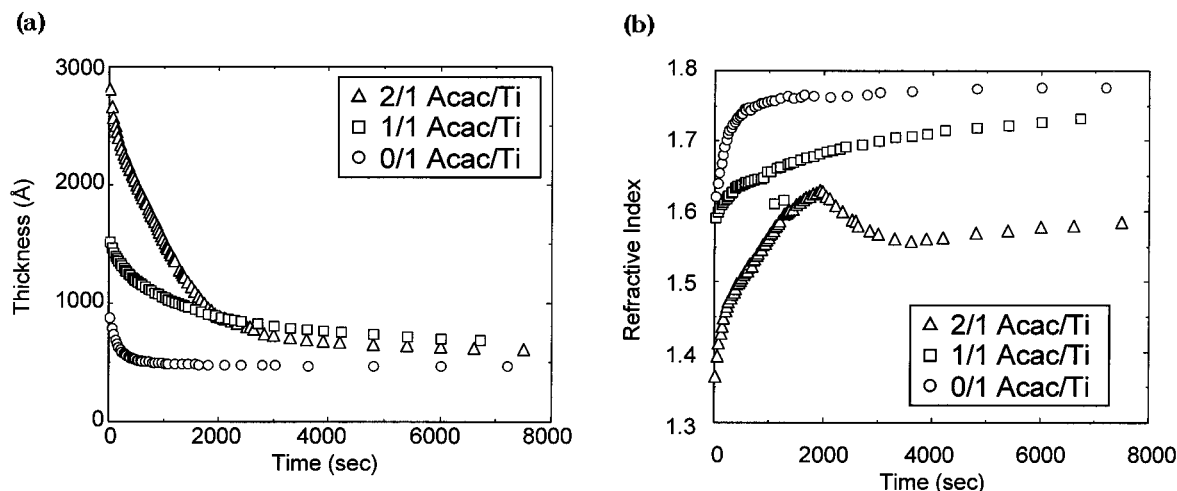


Figure 3. Consolidation behavior of titania thin films at room temperature immediately after deposition. (a) Ellipsometry results for thicknesses and (b) refractive indexes as a function of time. Solution precursors were prepared by reaction of $\text{Ti}(\text{O}i\text{Bu})_4$ and acac; modifying ligand ratio (r) indicated in legend.

tive index. As the level of modification is increased from a molar ratio of 0 to 2 mol of acac/mol of Ti, the initial film thickness increases dramatically, and concurrently, the initial refractive decreases. The observed results may be explained by considering (i) the effect of the acac ligand on precursor nature, (ii) the properties of the modifying ligand compared to the parent groups (butoxy), and (iii) the physical processes that occur during film formation. During the spin-off stage of deposition, as the concentration of the precursor species increases dramatically, they come together and begin to interact. Precursor properties governing this interaction include size, shape (fractal nature), and reactivity.⁶³ Since the viscosities of the solutions are similar, it is believed that the increase in initial film thickness with acac addition is due to a decrease in packing efficiency of the more highly modified precursors during aggregation, most likely as a result of increased precursor/oligomer steric bulk. Another indication of the lower packing efficiency of the more highly substituted precursors is the observed decrease in initial refractive index.

Film consolidation behavior also depends on precursor reactivity. Precursors that are less reactive (toward hydrolysis and condensation) are termed "transparent", since they interpenetrate during aggregation and consolidation; those that tend to react are referred to as "opaque".^{47,65} As greater amounts of acac are used, less reactive, more highly 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,⁶⁶ but being sterically demanding, it can inhibit accessibility to any remaining (reactive) alkoxy species. Films prepared from more highly modified precursors should therefore consolidate to a greater extent than those prepared from more reactive (unmodified) species, because the precursors are more transparent and do not cross-link to as great an extent following deposition. An indication of this behavior may be the fact that even though, initially, the $r = 2$ film is significantly thicker than the $r = 0$ or $r = 1$ films, after drying at 25 °C for about 2 h, the films display similar thicknesses (see Figure 3). In the present case, even more pronounced differences in film consolidation may not have been observed because the butoxy ligand itself is fairly insensitive to hydrolysis and condensation, much less

so than many typically used alkoxy groups, e.g., ethoxy or isopropoxy. It is also worthwhile to note that variations in film consolidation behavior can be induced through the use of different chelating ligands (acetate versus acac, etc.), rather than by changing the reaction stoichiometry as in the present example. These variations can lead to films that are more chemical gel in nature than physical gel.^{65,67}

Film consolidation following deposition is thus strongly related to the nature of the precursor species. Films that are ~ 1000 Å in thickness after crystallization may range in thickness from 2000 to 6000 Å immediately after deposition. Shrinkage during processing is thus extensive, and it occurs at room temperature because of capillary forces, during organic pyrolysis, and through the volume change that accompanies crystallization. Film shrinkage can also generate stresses in the films well in excess of 100 MPa. The magnitude of the stress, and whether film cracking occurs will depend, in part, on the reactivity of the precursors: less reactive precursors do not tend to form "solid" films as rapidly, and hence, the solvent can be removed without producing significant stress.⁶⁸ Consolidation is most pronounced at room temperature and during organic pyrolysis, where the film may shrink in the thickness direction by 50–70%. Since films with thicknesses ranging from 0.5 to 2.0 μm are required for many applications, they are typically fabricated by a multilayering approach, wherein deposition is immediately followed by pyrolysis, and then each layer is crystallized before the next deposition. Alternatively, multiple layers are deposited and pyrolyzed prior to a single crystallization anneal.

In addition to precursor properties, solvent choice is an important consideration. As an example, consider the recent work to develop deposition processes to form thicker layers that is based on the use of 1,3-propanediol.^{42–44,46} It has been demonstrated that films between 0.5 and 1.0 μm /deposition can be prepared by this approach. However, in the preparation of films by this approach, as-deposited films appear liquid and tend to dewet the substrate surface, resulting in nonuniformities and a degradation in film quality. In this instance, the viscosity of the solvent is such that precursor interactions, either physical or chemical, are inhibited. The viscosity of propanediol is ~ 40 cP, while

more commonly used solvents are $\sim 0.5\text{--}1.0$ cP. The extremely low volatility of this solvent at room temperature also plays a role in inhibiting precursor interactions. In contrast, for films deposited from high-volatility solvents, vaporization of the solvent results in film drying, which forces interactions between the precursor species. These interactions are, at minimum, physical in nature and in some instances chemical, as condensation reactions may occur. While chemical gel films are not always desired, some level of aggregation seems critical to the preparation of stable films that will remain uniform throughout subsequent processing. For low volatility solvent systems such as propanediol, film dewetting can also become a problem due to the lack of either chemical or physical gelation during spinning.⁴⁵

IV. Gel to Ceramic Conversion

Single-Step Processing and Film Densification Behavior. Two general approaches have been employed to convert the as-deposited film into the crystalline perovskite phase. In the single-step process, the film is usually heated rapidly to the crystallization temperature, which results in both organic pyrolysis and crystallization. This type of rapid heat treatment may enhance thin-film densification by delaying the onset of crystallization to higher temperatures.^{67,69} This is a significant advantage in the processing of perovskite films for almost all applications, which benefit from high-density materials. Although rapid (>100 °C/s) heating rates are used, cracking in the films is typically not observed. This result is believed to be due to the high compliancy of the film which is retained to higher temperatures; i.e., condensation reactions between the precursor species are delayed, and since the network is more compliant, the film is freer to densify without cracking. Rapid thermal heat treatment also has the potential advantage of being an "isothermal" process, which can alleviate some of the considerations associated with developing a processing route that effectively balances the competing kinetics of the various processes that take place during the transformation to the perovskite phase.

For films that are not pyrolyzed but are heated directly to the crystallization temperature, both precursor chemistry and heating rate (to the crystallization temperature) can affect the densification of the film. Representative results for the effects of different chelating agents on the densification of zirconia thin films are shown in Figure 4. (Again, as with titania films, zirconia films serve as a model system to understand perovskite thin-film processing.) These films were prepared from acetate (acetic acid) or acac-modified zirconium *n*-butoxide. The films were deposited onto Si and heated to 700 °C. Under these heat treatment conditions, X-ray diffraction analysis confirmed that all of the films crystallized into the cubic zirconia phase, independent of heating rate. Relative densities of the films were calculated using a Lorentz–Lorentz analysis⁷⁰ of the refractive indexes of the films; a refractive index of 2.17 for the cubic zirconia phase that was formed was assumed.^{71,72} In general, films prepared from the acac precursor solution densified to a greater extent, particularly at higher heating rates. The highest density obtained for an acac-derived film was $\sim 96\%$ of theoretical, using a ramp rate of 300 °C/min. Under similar

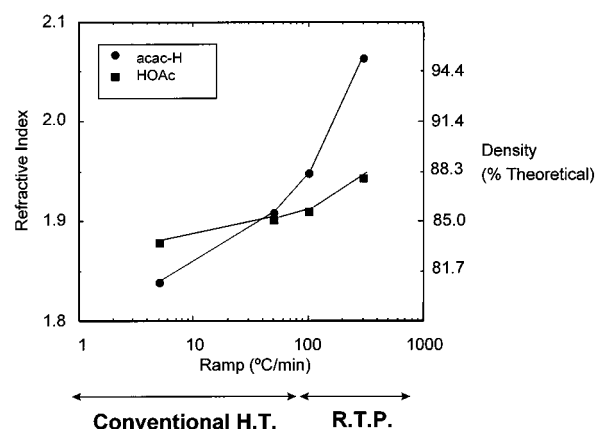


Figure 4. Effects of modifying ligand and heating rate on the densification behavior of zirconia thin films derived from zirconium butoxide: HOAc, acetate-modified precursors; acac-H, acac-modified precursors.⁴⁷ For details of solution preparation see ref 67.

conditions, the highest density obtained for an acetate-derived film was approximately 88%. Thus, in addition to affecting film consolidation behavior, the ability to prepare dense crystalline thin films is determined, in part, by the nature of the precursor species present in solution. Two aspects of precursor nature apparently affect the ability to densify the film: the lower reactivity of the acac precursor, and the fact that the acac precursor crystallizes at higher temperature than the acetate precursor. This allows for film densification by structural relaxation and viscous flow, rather than solid-state sintering as would be required by a crystallized film.^{69,73} Since solid-state sintering is energetically less favorable than structural relaxation and viscous flow, it is more difficult to densify crystalline films. Therefore, to obtain the highest density, it is important to densify the film prior to crystallization.

It is also important to note the significant effect of heating rate on densification that is apparent in Figure 4. Faster ramp rates, typically attainable only through rapid thermal processing, result in higher density materials for both precursor systems, although the effect is much more pronounced for the acac films. It has been reported that this is due to the fact that, with faster heating rates, a lower viscosity structure is retained to higher temperatures.⁷³ By heating the film more rapidly, fewer M–O–M cross-links are introduced into the structure at lower temperature, and the material is therefore capable of more extensive consolidation. The use of faster heating rates also delays the onset of crystallization to higher temperatures, which allows for further densification of the film. Since the retention of carbon in the film can also inhibit crystallization, this may in part be due to the fact that pyrolysis of organic species is also delayed to higher temperatures (when the heating rate employed is faster than the kinetic rate of the pyrolysis processes).

Two-Step Processing. The second, more commonly used approach to convert the as-deposited film into the ceramic is the two-step process. In this method, the as-deposited film is first subjected to a separate pyrolysis step prior to the crystallization anneal. The film is typically placed on a hot plate held at 200–400 °C for burnout of the organic species. While it might be expected that this type of rapid heat treatment would cause cracking, in reality, it appears that this is often

the best approach. It has been proposed that this procedure allows for the removal of the organic constituents prior to the collapse of the amorphous network, which minimizes cracking and blistering. Lakeman et al.³³ have studied the rearrangements that occur within the film during pyrolysis and the development of the amorphous structure. As-deposited coatings were found to be amorphous but possessed short-range order. Following pyrolysis, the development of medium-range order was observed, and chemical heterogeneity at the nanometer length scale was evident. The degree of heterogeneity was observed to decrease with higher heat-treatment temperatures.³³ Films that have been pyrolyzed may also still contain small amounts of residual organic and hydroxyl species. Pyrolyzed films are subsequently heated to higher temperatures (500–700 °C) for crystallization, at heating rates that have ranged from 5 to 7500 °C/min. These latter rates have been obtained using rapid thermal annealing furnaces.^{74,75}

Film Crystallization Behavior. The substrate, solution chemistry, material chemistry [for example, BaTiO₃ versus Pb(Zr,Ti)O₃], transformation pathway, and thermal processing conditions can all have a significant effect on thin-film microstructure and orientation. While different microstructures and film orientations are required for different applications, it is imperative that in the processing of perovskite films no residual intermediary phases such as pyrochlore remain, since the presence of this phase can dramatically degrade the performance of the films. In this section, some of the underlying kinetic and thermodynamic aspects of the processes that affect thin-film microstructure will be discussed. These processes include condensation reactions, pyrolysis, structural rearrangement, densification, precursor volatilization (for some perovskites), and nucleation and growth. While a detailed review of all of these processes is not possible within the scope of this paper, the thermodynamic principles will be reviewed, and examples will be presented to demonstrate the importance of thermodynamic and kinetic effects.

Since pyrolyzed films are typically amorphous, film crystallization in solution-derived thin films occurs by a nucleation-and-growth process. The theoretical description for nucleation and growth in solution-derived films is analogous to that used extensively to describe crystallization in traditional glasses. The characteristics of the nucleation-and-growth process will serve to define the resulting microstructure; films that display microstructures where only interface nucleation takes place are frequently columnar in nature, while those where nucleation occurs throughout the film are typically polycrystalline with equiaxed grains. From a thermodynamic perspective, it has been demonstrated that the driving forces that govern the transformation from the amorphous (pyrolyzed) film to the crystalline ceramic can play a significant role in defining the active nucleation events and, thereby, film microstructure.¹⁵ The diagram shown in Figure 5 that was originally proposed by Roy⁷⁶ demonstrates the difference in free energy between the solution-derived amorphous film and the crystalline ceramic phase. While this diagram does not necessarily provide insight into the transformation pathway the film undergoes, it is very useful in

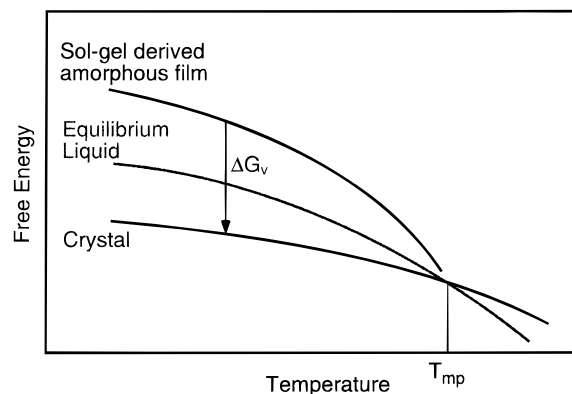


Figure 5. Schematic diagram of the free energies of a solution derived amorphous film, the ideal supercooled liquid, and the crystalline perovskite phase. ΔG_v is the thermodynamic driving force for crystallization. After ref 76.

understanding the role that driving force (ΔG_v , the energy difference between the amorphous and crystalline states) can have on the transformation process and the final ceramic microstructure. Consideration of driving force is important since it influences the barriers for nucleation of the crystalline phase at different locations (substrate interface, surface, bulk) within the film. A comparison of the thermal energy available (via heat treatment during the crystallization anneal) to surmount these different nucleation barriers will define which nucleation events take place and, thus, the resulting film microstructure.

Examination of the figure indicates that crystallization driving force is determined by the free energy of the two material states and the temperature below the melting point at which crystallization occurs. The free energy of the amorphous phase is greater than the supercooled equilibrium liquid due to surface area, residual hydroxyl, and excess free volume contributions to free energy.⁷⁷ The free energy of the crystal is determined in part by the thermodynamic stability (lattice energy) of the material. From standard nucleation and growth theory, the energy barriers for homogeneous and heterogeneous nucleation, and their dependence on driving force, are described by

$$\Delta G_{\text{homo}}^* = 16\pi\gamma^3/3(\Delta G_v)^2 \quad (1)$$

$$\Delta G_{\text{hetero}}^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} f(\theta) \quad (2)$$

where γ is the interfacial energy, ΔG_v is the driving force for crystallization, i.e., the free energy difference per unit volume for the amorphous film–crystalline film transformation, and $f(\theta)$ is a function related to the contact angle, θ , according to eq 3. For a hemispherical nucleus:

$$f(\theta) = (2 - 3 \cos \theta + \cos^3 \theta)/4 \quad (3)$$

The difference in barrier heights for nucleation events such as interface, surface and bulk nucleation is therefore defined by the surface energy term, the driving force for crystallization, and the contact angle with the substrate.

The important point to consider in the use of nucleation theory to understand transformation in solution-

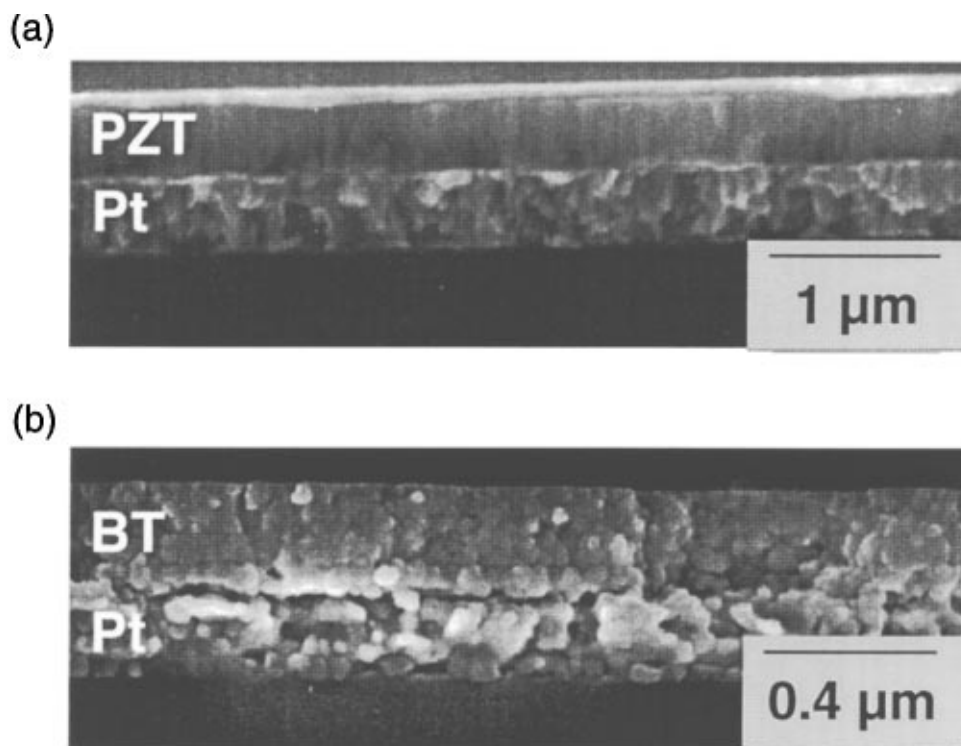


Figure 6. SEM photomicrographs of typical thin film microstructures for PZT and BT films prepared by a chelate process. (a) The PZT film displays only nucleation at the lower electrode interface (white surface layer is upper Pt electrode); (b) the BT film displays both interface nucleation and nucleation within the bulk of the film.

deposited perovskite thin films is how the terms in eqs 1 and 2 define the barrier heights, and the difference in barrier heights, for the possible nucleation events. Although more detailed analyses are possible, only a few concepts need to be kept in mind to use the diagram in Figure 6 to interpret film crystallization behavior:

(1) As the crystallization driving force is increased, bulk nucleation becomes (essentially) as probable as interface nucleation. Although the $f(\theta)$ term still results in a lower energy barrier for interface nucleation, when crystallization driving force is high, i.e., in typical heat treatment scenarios, there is more than sufficient energy to surmount the energy barriers for all (including less energetically favorable) nucleation events.

(2) The effects of crystallization temperature on driving force and nucleation must also be considered: crystallization at higher temperatures results in lower driving forces, and due to the $f(\theta)$ term, lower energy heterogeneous nucleation events become more important. The importance of processing solution-derived films at temperatures significantly below the melting point of the material have been discussed by Wilkinson and co-workers.⁷⁸

(3) Unless rapid thermal processing techniques are used, film crystallization usually begins during heating to the anneal temperature. Therefore, as the temperature of the sample increases, more energy becomes available to surmount the barriers for nucleation events in addition to the energetically most favorable nucleation event. This can lead to film microstructures defined by nucleation and growth processes associated with more than one nucleation event.

(4) The transformation pathway (from the amorphous film to the final crystalline ceramic) has a major effect on nucleation and growth behavior. Speck and co-workers have shown that for perovskite materials that

transform via an intermediate metastable phase, e.g., PZT via a fluorite phase, the crystallization driving force is reduced by the formation of this metastable phase, resulting in films that display only heterogeneous nucleation at the substrate interface.⁷⁹

A few examples will serve to illustrate the role that driving forces may play in the crystallization of perovskite thin films. First, compare the microstructures of typical PZT and BT thin films shown in Figure 6. Although these films were prepared in our laboratory, they are representative of those typically prepared at other research institutions.^{4,5,55,75,80,81} Most chemically derived PZT films crystallize with a columnar microstructure with nucleation only occurring at the substrate interface. Grain growth from these nuclei proceeds toward the surface of the film through the consumption of an intermediate fluorite (or pyrochlore phase). Because of this type of nucleation and growth behavior, PZT films are usually only a single grain thick. In contrast, BT films are typically polycrystalline in nature. This indicates that "homogeneous" nucleation [$f(\theta) \sim 1.0$] within the bulk of the film has occurred in addition to nucleation at the interface [$f(\theta) < 1.0$]. Although this nucleation event is less favorable than interface nucleation due to the contact angle term, $f(\theta)$, in this instance it serves to define thin-film microstructure, and in terms of the overall transformation process is equally important.

Two contributing factors to these microstructural differences may be the difference in crystallization driving force for the PZT versus the BT transformation and the different transformation pathways displayed by these materials. To fully consider thermodynamic driving force effects, we need to know the free energies of the amorphous states, the free energies of the crystalline states, the crystallization temperatures, and the trans-

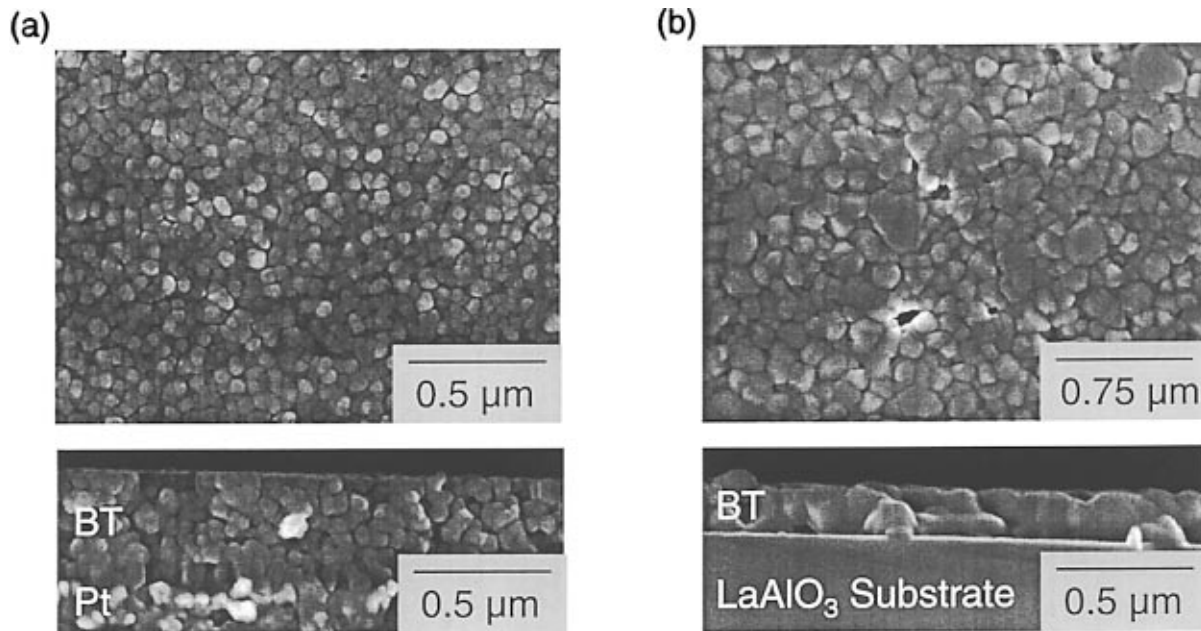


Figure 7. SEM photomicrographs of BT films prepared by a chelate process. (a) BT film deposited on Pt coated silicon and heat treated at 750 °C; (b) BT film deposited on LaAlO₃ and heat treated at 1100 °C.

formation pathways. First, consider the free energies of the amorphous and perovskite phases and the transformation temperatures for the two materials. Unfortunately, two of these factors are difficult to estimate. While it is difficult to assess the free energy of sol-gel derived amorphous materials, since the materials were prepared by similar chemical preparation routes, for this analysis, it is assumed that the free energies of the BT and PZT films are similar in the amorphous state. While the free energies of BT and PZT are not well-known, recent calculations of lattice energies (~free energy) for the two materials indicate that they are similar in nature.⁸² Therefore, in Figure 5, it is expected that the positions of the curves for the BT and PZT crystalline phases are similar. To consider driving force effects, it is also important to know the temperature at which the films crystallize. To compare materials, a homologous temperature should be used, and therefore, we should know $T_{\text{cryst}}/T_{\text{melting}}$.⁷⁸ PZT crystallization takes place at ~550 °C, or at ~0.49 of the melting point while BT crystallization takes place at ~700 °C, or at ~0.51 of the melting point. Therefore, a large difference in crystallization driving force is not expected from the standpoint of crystallization temperature. Analysis of the factors that define driving force therefore seem to indicate that the different transformation pathways these materials display are responsible for the differences in microstructure. PZT films transform from the amorphous phase to the perovskite phase via a fluorite (pyrochlore) phase,⁸³ unlike BT films, in which fluorite phases are not stable. The formation of the fluorite phase reduces the driving force associated with the nucleation of the perovskite phase.⁷⁹ This reduction in driving force separates the energy barrier heights for different nucleation events and makes interface nucleation in PZT much more preferred than bulk nucleation, as discussed above. The result is a film microstructure defined solely by nucleation at the substrate interface. Other differences in transformation pathways that may contribute to the different microstructures are further discussed below.

Other indications of driving force effects in the crystallization of barium titanate films are given in Figure 7. The two films were prepared from identical solutions, but with different substrates and different crystallization temperatures. The film shown in Figure 7a was deposited on a Pt-coated Si substrate and was crystallized at 750 °C. The film of Figure 7b was deposited on single-crystal LaAlO₃ and was crystallized at 1100 °C. The film on LaAlO₃ is characterized by a larger grain size and a microstructure that is essentially a single grain thick. In contrast, the film deposited on Pt/Si is characterized by the bulk nucleation observed above. While higher grain growth rates at the higher crystallization temperature may contribute to the larger grain size, crystallization driving forces may again play a role in the observed microstructural differences. The use of substrates with a higher level of lattice matching and of the same crystallographic structure as the perovskite film would be expected to decrease the value of $f(\theta)$. This would lower the energy barrier for nucleation at the substrate interface compared to nucleation within the bulk of the film. In addition, crystallization at higher temperatures reduces the driving force associated with the transformation. This also makes heterogeneous nucleation at the interface preferred to other nucleation events. It is believed that both of these factors may contribute to the observed film characteristics, where the microstructure is defined by nucleation at the substrate interface.

Fabrication of Highly Oriented Films. Control of nucleation at the interface has also been used for the preparation of epitaxial and highly oriented (textured) films. For films that are subjected to rapid thermal processing, or are processed at higher temperatures, material chemistry, lattice matching with the substrate, and thermal processing parameters are key factors in the preparation of textured or epitaxial films;^{84–89} solution chemistry becomes potentially less important in defining film orientation under rapid thermal or high-temperature processing. One reason rapid thermal processing may be beneficial in preparing oriented films

is that nucleation is delayed to higher temperatures. When using fast heating rates, the physical processes leading to densification and crystallization of the film are delayed to higher temperatures. This causes nucleation to occur at a higher temperature than with conventional heating. Considering the diagram of Figure 5, nucleation at higher temperatures implies that the crystallization process occurs with a lower driving force, which causes heterogeneous nucleation at the substrate to become more important in defining film microstructure. This may also favor the production of films with a higher degree of orientation.

Crystal chemistry may also play a role in the preparation of oriented films. For substrates that have a higher degree of lattice matching with the film, $f(\theta)$ is expected to decrease, which can cause heterogeneous nucleation at the substrate to become more preferred than other nucleation events (see eqs 1 and 2). This again results in more highly oriented films. To obtain highly oriented or epitaxial films, the film must be processed so that (at the conclusion of processing) the heterogeneous nucleation event at the interface dictates the microstructure. For the case where only nucleation at the substrate interface occurs, crystallographic growth along fast growth directions (such as in PZT and LiNbO_3) can result in highly oriented films; the transformation from the amorphous state to the crystalline state is completely associated with the grains nucleated at the substrate. For other materials, epitaxial films may also be prepared when nucleation occurs at both the substrate and within the bulk of the film. For example, in the processing of yttrium-stabilized cubic zirconia, while epitaxial grains were formed at $\sim 400^\circ\text{C}$, higher heat treatment temperatures were used to densify the film and permit the epitaxial grains to grow and consume the other misoriented grains in the initial polycrystalline film.⁸⁴

The use of solution deposition in the preparation of epitaxial films has been described by Lange and co-workers^{84,85} to proceed according to three different phenomena, depending on lattice matching and structural differences between the film and substrate. The different phenomena are as follows:

(1) *Epitaxial grain growth*: For materials that display good lattice matching (difference in lattice constants less than a few percent), the development of epitaxial films involves the growth of small, nanometer sized grains at the substrate/film interface. The grains eventually grow along the interface and then through the film to consume randomly oriented grains.^{84,85} The method has been used for the preparation of epitaxial ZrO_2 ,⁸⁷ PbTiO_3 ,⁸⁵ and LiNbO_3 .⁹⁰

(2) *Two-step processing*: For the situation where the film and substrate have different structures or large mismatches, the fabrication of epitaxial films is still possible. In this case, epitaxy is achieved through a two step process where a polycrystalline film is first deposited, and then heated to cause it to break up into isolated grains (seeds) that possess a low interfacial energy. Subsequently, a thicker layer is deposited onto this surface; the isolated islands act as nucleation sites (seeds) for the growth of a highly oriented film.⁸⁶ It should be noted that seed layers have been employed by several investigators for the preparation of highly oriented perovskite films;^{91–94} however, in these inves-

tigations, it is unclear whether islands are formed in the seed "layer" or if the increase in lattice matching between the seed and the film improves the contact angle and makes nucleation at the seed layer preferred to other nucleation events. Seed layers can also be used to generate a gradient in lattice matching.

(3) *Liquid-phase processing*: When higher processing temperatures are employed, epitaxial films may also form via a liquid phase.⁹⁵

For materials that are processed at lower temperatures or using conventional heating rates, substrate properties (e.g., roughness⁹⁶ and lattice matching), thermal processing conditions and solution chemistry variations have been demonstrated to affect film orientation. Chen and co-workers⁹⁷ studied the degree of orientation of PbTiO_3 (PT) films derived from 2-methoxyethanol solutions that were deposited onto (100) MgO substrates. Although the films were crystallized under identical heat treatment conditions, they found that films prepared from solutions with low hydrolysis ratios ($r = 2$; where $r = \text{mol of H}_2\text{O/mol of metal alkoxides}$) demonstrated a greater degree of (100) orientation than those prepared from solutions with high hydrolysis ratios ($r = 6$). These results are in agreement with those of Nashimoto and Nakamura,⁹⁸ who determined that highly (001) oriented PZT 52/48 thin films could be prepared from nonhydrolyzed precursor solutions on MgO . Effects of thermal processing variations and film thickness on film orientation have also been noted by a number of investigators.^{54,99–103} In PZT thin-film processing, these effects have been attributed to such diverse phenomena as the formation of intermetallic phases (Pt_{5-7}Pb) at the electrode,^{101,102} the development of an in situ reducing atmosphere for high organic content films,⁹⁹ the diffusion of the underlying titanium adhesion layer to the film/electrode interface resulting in the formation of a Pt_3Ti phase which influences orientation,¹⁰² and nucleation versus growth control of microstructure.¹⁰³

Kinetic Effects. The kinetics of competing reactions can also affect microstructural development in perovskite films. In the solution processing of PZT thin films, excess lead precursor is typically added to compensate for lead oxide volatilization during heat treatment. The excess lead added must balance the lead loss to generate single phase perovskite PZT films.⁷⁹ Since the rate of lead loss varies for the amorphous, fluorite, and perovskite phases, the amount of excess lead needed is dependent upon the heat treatment schedule and the rate of crystallization of the perovskite phase. For PZT compositions near the morphotropic phase boundary (PZT 53/47; $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$), 5–10 mol % excess lead is added to the solution batch. As illustrated in Figure 8a, single-phase perovskite films with uniform microstructures may be prepared from these solutions. However, for the preparation of high zirconium content PZT materials, such as PZT 95/5, the simple incorporation of excess lead in the solution batch, even in amounts up to 20 or 25 mol %, is not effective in generating single-phase films, as shown in Figure 8b. For these compositions, the crystallization rate of the perovskite film is slower than for higher Ti compositions, and it is difficult to balance the lead loss and crystallization processes. This dictates the use of other strategies, such as that proposed by Tani and Payne,¹⁰⁴ where a PbO

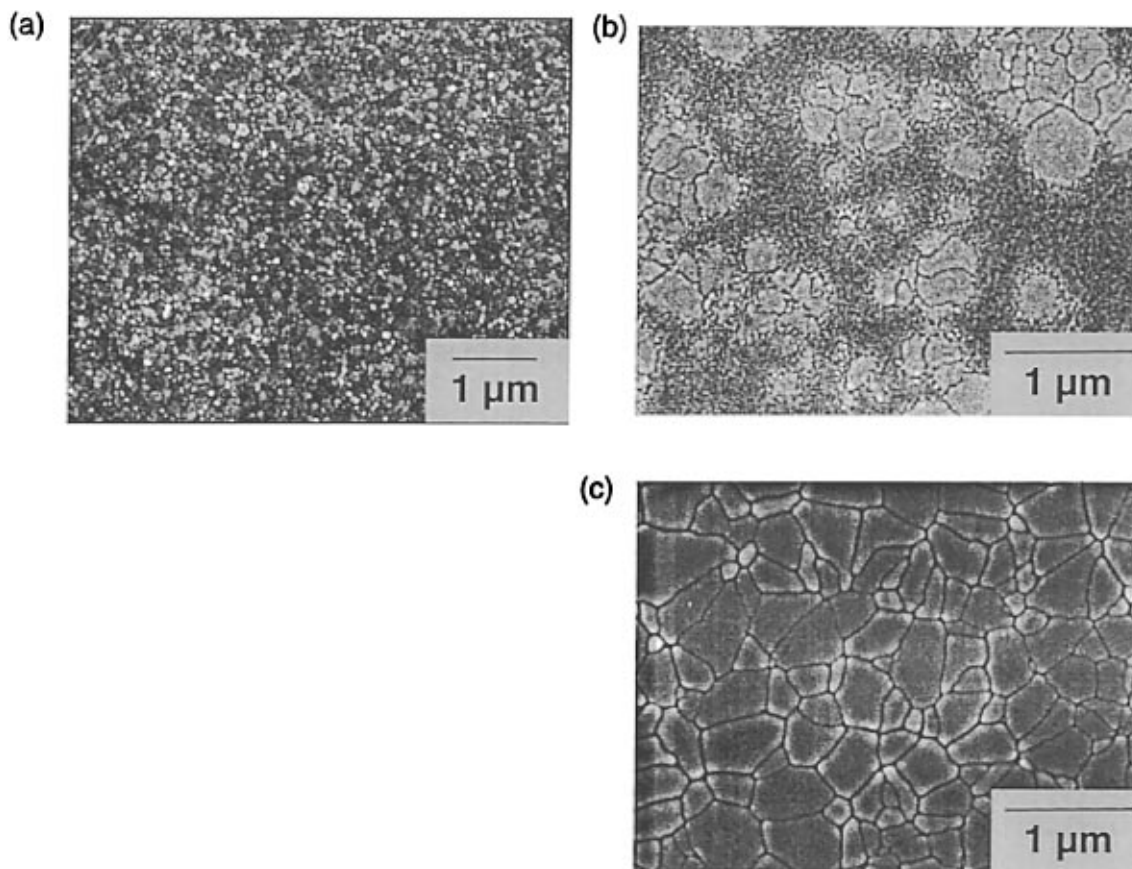


Figure 8. SEM photomicrographs of PZT thin films prepared by a chelate method: (a) PZT 40/60 prepared with 10 mol % excess lead and heat treated at 650 °C; (b) PZT 95/5 prepared by standard chelate process, 15 mol % excess lead and heat treated at 675 °C (nanocrystalline surface fluorite phase is observable); (c) PZT 95/5 film prepared by standard chelate route with lead precursor overcoat.

overcoat is used to suppress lead volatility. Using this approach, it has been possible to prepare single-phase, high zirconium content perovskite films (Figure 8c) that display excellent dielectric, ferroelectric, and electrooptic properties. The effective processing of thin films thus requires a knowledge of the different processes that occur during the gel-to-ceramic transformation and also the kinetics of those processes.

Reaction kinetics in material systems where (refractory) carbonate phases are formed can also affect microstructural evolution. Consider the different transformation pathways by which PZT and BT transform into the perovskite phase. In PZT materials, the transformation from the amorphous phase to the perovskite phase occurs via an intermediate fluorite phase. In contrast, in BT and high-temperature superconductors such as YBCO, the formation of carbonate phases plays an important role. In BT processing, during heat treatment, the as-deposited film first converts to BaCO_3 and TiO_2 , then to an oxycarbonate phase, $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$, and as higher heat treatment temperatures (700–800 °C) are used, BaTiO_3 forms with the evolution of CO_2 .^{105,106} Although BaTiO_3 is the stable phase at ~410 °C,¹⁰⁷ significantly higher temperatures are required for complete conversion to the perovskite phase due to the slow decomposition kinetics of the carbonate and oxycarbonate phases. The formation of TiO_2 throughout the bulk of the film and the kinetics of carbonate decomposition may contribute to the polycrystalline, equiaxed grain microstructure shown in Figure 6b, and may be more important in defining the microstructure

of these materials than some of the thermodynamic nucleation factors discussed.

The formation of barium carbonate in YBCO thin-film preparation has also presented difficulties. This phase, which is only decomposed above 800 °C, is believed to result in the poor electrical properties of the YBCO films because the high temperatures required for carbonate decomposition promote interactions between the substrate and the film.¹⁰⁸ To avoid carbonate formation and prepare films with improved properties, trifluoroacetic acid precursors have been used in the fabrication of YBCO films. The precursors decompose to oxyfluorides (not carbonates) and heat treatment at higher temperatures in wet oxygen results in the formation of the YBCO perovskite phase.^{108,109} The route also appears to hold promise for the fabrication of perovskite films used for dielectric applications.

V. Applications

Potential applications for a number of perovskite thin films are shown in Table 1. The technological importance of these materials, particularly in thin-film form, has resulted in a global effort aimed at the development of electronic devices based on these materials. A number of products based on these devices are currently commercially available, and the product market continues to grow rapidly. It is also evident that over the past few years, corporate participation in the field has increased dramatically. Due to the requirements of coating conformality and other integration issues dic-

Table 1. Applications and Key Material Properties for a Number of Devices Based on Perovskite Thin Films

material	property	device
BT, ST	high dielectric constant voltage dependence of dielectric constant	DRAMs (dynamic random memories) communication filters, ^a resonators, phase shifters
SBT, PZT	ferroelectric response	FRAMs (ferroelectric (nonvolatile) random access memories) ^a
PZT, BST	high dielectric constant	decoupling capacitors ^a
PZT, SBT	ferroelectric response	NDRO memories (nondestructive readout) RF ID tags ^a smart cards ^a
PZT, PST	pyroelectric response	infrared imaging arrays ^a
PZT	piezoelectric response	micromotors, ^a actuators ^a
BT, ST	lattice matching, chemical compatibility	buffer layers ^a for YBCO integrated on Ni (high T_c films, wires)
YBCO	high-temp superconductivity	films, ^a wires, ^a transformers

^a Applications where fabrication of the perovskite layer by chemical solution deposition may be feasible.

tated by the underlying Si and electrode structure, CSD is not a suitable fabrication approach for some of the devices in Table 1. For example, for the fabrication of DRAMs (dynamic random access memories), the underlying topography on which the perovskite coating will be deposited is extreme, and the coating must be both thin (~ 200 Å) and conformal. In recent years, these more stringent requirements have led away from an emphasis on solution deposition technologies to vapor phase deposition techniques, such as chemical vapor deposition (CVD).¹¹⁰ This process allows for deposition and perovskite film integration at lower temperatures than solution routes, and there has also been a significant amount of work carried out on the synthesis of suitable precursors for these multicomponent materials.¹¹¹ Perhaps more importantly, CVD seems to be a technique with which computer memory manufacturers are comfortable. And since products such as DRAMs are manufactured on such a large scale, they tend to set the technological direction of the field as a whole, which has resulted in an increased emphasis on CVD and a decreased emphasis on CSD.

Irrespective of this change in emphasis, CSD remains an attractive fabrication approach for two main reasons. First, it is a technique that may be rapidly developed for the evaluation of new material systems,¹¹² or material systems not previously studied in thin-film form. Second, the low cost of establishing a perovskite film fabrication capability based on wet chemical techniques is particularly attractive. Specific applications for which solution deposition may be a commercially viable fabrication approach include superconducting wires and films, chemical microsensors, piezoelectric micromotors, uncooled pyroelectric infrared detectors, and decoupling capacitors. While the technique may not meet the more stringent processing needs of DRAMs, CSD is a technique that is amenable with standard semiconductor manufacturing methods that offers a high throughput rate. Because of these considerations, in the long run, CSD may be more attractive for thicker (~ 1 μm and above) film applications, while CVD may be more appropriate for thinner (20–500 nm) film applications. Device density will also undoubtedly play a role in determining the deposition technique selected. As device density increases, step coverage becomes more of an issue, and vapor deposition becomes more attractive than solution deposition.

Two devices for which CSD techniques are currently being evaluated are decoupling capacitors⁴⁶ and pyroelectric imaging arrays.¹¹³ For decoupling capacitors, diol-based chemistries are being used to prepare ~ 1 μm PZT-based films in a one to two coating process suitable

for scale-up to manufacturing. For pyroelectric imaging arrays, CSD techniques may greatly simplify the manufacturing process. For example, historically, pyroelectric detectors were prepared from bulk ceramics by a manufacturing-intensive process involving pressing of oxide powders, lapping, polishing and laser reticulation of the resulting ceramic, and solder bump bonding for integration with the electronic components of the detector.¹⁰ Using CSD techniques, a silica aerogel layer (used for thermal isolation) and the perovskite pyroelectric layer may be both processed from solution and directly integrated with the underlying CMOS circuitry.¹¹³ The use of an aerogel layer also results in a simplified isolation strategy compared to microbridge technologies that have been previously developed,¹⁰ improving device yield. CSD may thus allow a higher level of integration in a much simplified manufacturing process, and the overall cost of detector manufacturing is dramatically reduced.

Two key aspects for device development are optimization of perovskite processing conditions and process integration. The number of processing variables that must be controlled in a standard CSD fabrication approach is extensive, and can be both an asset and a detriment. If the inherent processing-property interrelationships are well understood, CSD is a flexible process that can be used for robust manufacturing of films. One approach that has been employed to optimize solution preparation variables is statistically designed experimentation.^{114,115} This approach should also be useful for optimization of integration conditions, namely, deposition, heat treatment, patterning and other processing conditions.

For the successful integration of perovskite thin films into higher density architectures such as pyroelectric and memory devices, two additional issues that must be solved are oxidation of underlying contacts (TiW or TiN) and patterning. To increase device density, it is desirable to deposit the perovskite layer directly on top of the underlying transistor circuitry. Since the perovskite layer is an oxide phase, it can act as a source of oxygen during heat treatment. While TiW and TiN are refractory electrodes, they are porous to oxygen, and if oxidized, the device architecture is ruined. This problem may be reduced by developing solution deposition strategies that generate films that transform to the perovskite phase at lower temperature. In addition, barrier metals, such as Ir, to prevent oxygen diffusion from the perovskite layer into the TiW (TiN) plug are being investigated.

An increase in device density, which is always a driving force due to the continuing trend of component

miniaturization, also requires improved patterning processes. While perovskite films have typically been patterned by wet etching,¹¹⁶ a large (~10 μm) etch bias, which limits device density, is typically necessary due to undercutting of the photoresist. Recently, other patterning approaches, including stamping with self-assembled monolayers,¹¹⁷ e-beam,¹¹⁸ ultraviolet,¹¹⁹ and ion etching¹²⁰ have been studied. The ability to prepare true high-density devices from solution deposited films may, however, require the development of plasma etching.¹²¹

VI. Summary

Over the past 10–12 years, the development of perovskite thin films for electronic ceramic devices has progressed remarkably. Much of the growth of this field is directly attributable to the ability of researchers to use solution deposition to prepare device-quality thin films that could be tested under application conditions. Initially, films with only average properties were obtained, and the yield of acceptable test devices was poor. However, since the early work on CSD routes by Budd et al.² and Fukushima et al.,¹ as well as others,^{10,22–24} the development of solution-based processing routes has progressed to the extent that high-quality perovskite materials are routinely prepared by a variety of routes.^{25–27} For PZT materials, films with properties comparable to those of single crystal have been obtained. The improvement in film quality is at least partially due to the effort that was invested in understanding the pathways by which solution chemistry and thermal processing variations affect thin film microstructure. The further growth of technologies based on perovskite thin films owes a lot to the efforts of researchers who worked to develop effective solution deposition technologies for the preparation of these films.

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