FERROELECTRIC THIN LAYERS BY SOLUTION CHEMISTRY

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The deposition of ferroelectric thin layers from solution is described. Emphasis is placed on the powder-free ceramic processing method of polymeric sol-gel processing. Materials, include, $PbTiO_3$, $PbZrO_3$, $Pb(Zr,Ti)O_3$, $(Pb,La)TiO_3$, $(Pb,La)(Zr,Ti)O_3$, $BaTiO_3$, $(Ba,Pb)TiO_3$ and other related materials, including $LiNbO_3$. Processing parameters which affect the properties of ferroelectric thin layers are reviewed, including, solution chemistry and heat-treatment conditions. The results are interpreted in terms of the chemistry of precursors and gels, densification and crystallization behaviors, and interfacial reactions with the substrate and with the atmosphere during firing. Properties are reported for each class of materials, and compared with the properties of thin layers prepared by other chemical and physical methods, and with the properties of bulk ceramics and crystals. Of particular importance is the interaction of ferroelectric thin layers with various substrate materials, including semiconductors, for potential electrical and optical devices.

1. INTRODUCTION

For several millennia, the most important ceramic processing route has been powder processing (other than glass forming) where a large amount of material remains in the solid state, even during liquid phase sintering. This feature distinguishes ceramics from metals or plastics, where a significant degree of "melting" occurs, at least once, during processing. On firing powder compacts, structural defects and compositional heterogeneities can occur (due to limited diffusion distances), which leads to poor reproducibility of properties for polycrystalline ceramic materials. This problem has driven ceramic engineers to use the most pure, finely divided powders, economically possible, and to control the innumerable processing parameters, especially for modern engineered ceramics in multi-component systems. However, a new approach is emerging, especially for the formation of thin layers and coatings, in which chemical solutions or gaseous sources are used prior to heat treatment. These modern techniques have enabled molecular-level homogeneity to be achieved prior to deposition, and often lead to reduced processing temperatures for the attainment of dense crystalline structures. Recent demands for high-performance electrical and optical products have spurred intense interest in these alternative processing methods, especially for thin-layer components, where reductions in processing temperatures are especially attractive for the integration of thin-layer elements with semiconducting substrates.[1]

At the present time, integrated ferroelectrics are a major topic of interest in materials science and device engineering. Applications include, non-volatile memories,[2] infrared imaging devices,[3] microactuators,[4] acoustic transducers,[5] DRAM's and decoupling capacitors[6] and electro-optic devices.[7] Solution deposition methods have the distinct advantage of precise compositional control, structural and chemical uniformity, and the use of inexpensive equipment.[8] Such benefits have made wet-chemical routes a leading contender for the preparation of ferroelectric

thin layers. For this to happen, a number of processing parameters are critical for the attainment of reproducible properties. Sequential investigations are necessary, especially with respect to solution chemistry and the evolution of structure, before reliable processing can be established.

In this paper, recent studies on sol-gel processing of ferroelectric thin layers are presented. Although organic ferroelectric materials, e.g., polyvinylidenefluoride (PVDF)[9] are also considered promising candidates for integrated thin-layer devices, the content of this paper is restricted to the polymeric sol-gel processing of metallo-organic or inorganic precursors for metal oxide ceramic ferroelectrics. We review the literature and give selected examples of our own work.

2. SOLUTION PREPARATION

2.1. Sol-gel Processing

Sol-gel processing involves the dissolution of inorganic or metallo-organic precursors in aqueous or organic solvents, followed by hydrolysis and condensation reactions to form -M-O-M- inorganic polymers, where M represents a metallic cation. The most commonly used precursors for thin layer formation are metal alkoxides, $M(OR)_n$, where R represents an alkyl group. An alcoholic solvent, often the parent alcohol of the alkoxide, is used. The reactions from alkoxide to polymer are schematically illustrated below:

Partial hydrolysis

$$RO\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}OR + H_2O \rightarrow RO\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}OH + ROH \quad (1)$$
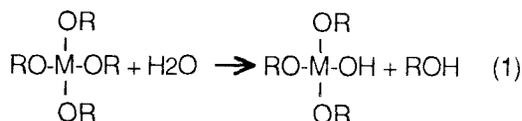
Condensation polymerization

$$RO\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}OH + RO\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}OR$$

$$\rightarrow RO\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}O\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}OR + ROH \quad (2)$$

$$RO\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}OH + HO\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}OR$$

$$\rightarrow RO\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}O\text{-}\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{M}}\text{-}OR + H_2O \quad (3)$$
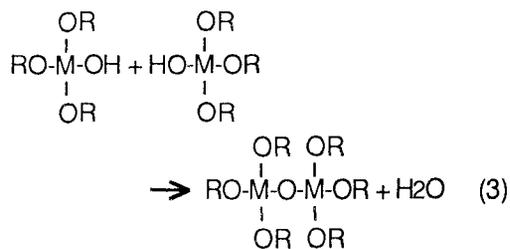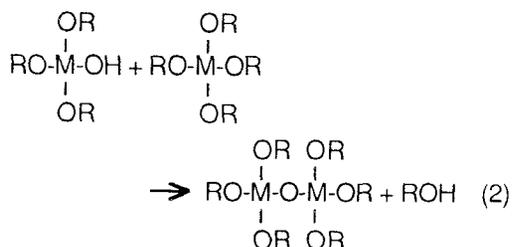
Sequential hydrolysis (1) and dealcoholation (2) or dehydration (3), leads to network formation, oligomers, and eventual gellation. Controlled hydrolysis and condensation can form intermediate species which are often stable. Metallo-organic decomposition (MOD) methods do not include hydrolysis, but involve the deposition of metallo-organic solutions, solvent removal, and pyrolysis of organics with greater shrinkage (compared with polymeric sol-gel) on firing. It is often found, however, that hydrolysis and polymerization reactions can initiate in MOD processing due to atmospheric moisture. For sol-gel processing, reaction rates, polymerization pathways and network configurations, are dependent on experimental conditions, including, the choice of alkoxide ligand, solvent, hydrolysis content, pH, and temperature. Reaction mechanisms for hydrolysis and polymerization are well documented for SiO_2 ceramics derived from silicon alkoxides.[10] However, important ferroelectric materials are multi-component oxide ceramics, and the arrangement of the different cations in the network structure is important for oxide crystallization at low temperatures. In the case of two-component oxides, $MM'O_n$, for example, an ideal inorganic polymeric chain, -M-O-M'-O- could be important. One way to attain this configuration is to use heterometallic alkoxide precursors, or intermediates, with intermolecular cation mixing.

2.2. Precursors for $M^I M^V O_3$

An increasing number of heterometallic alkoxide precursors have been synthesized, and some of their crystal structures are reported.[11] However, heterometallic alkoxides with the desired cationic ratio for the requisite ferroelectric oxide are quite rare at the present time. An important double alkoxide class is $M^I M^V (OR)_6$ (M^I = Li, Na, K; M^V = Nb, Ta),

which are stable and have the correct stoichiometry for polar oxides, $M^IM^VO_3$, including $LiNbO_3$.[12] For example, $LiNb(OR)_6$ (R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9) has been synthesized by the reaction of equimolar quantities of lithium alkoxide and niobium alkoxide in the parent alcohol. Eichorst and co-workers confirmed the formation of $LiNb(OEt)_6$ in solution by NMR spectroscopy,[13] and identified the solid-state structure of isolated crystals by the X-ray Patterson method.[14] In the crystal structure, shown in Figure 1, infinite helical $LiNb(OEt)_6$ polymers are comprised of alternating $Nb(OEt)_6$ octahedra cis linked by tetrahedral Li atoms. The coordination number of O about Nb is 6 in the metallo-organic precursor, the same as in the final oxide $LiNbO_3$ structure. The existence of stable bimetallic alkoxides with maximum cation homogeneity is thought to be necessary for the reduced crystallization temperatures (400-500 °C) reported for stoichiometric thin layers prepared by the solution method — without the formation of additional phases.[15,16] In addition, Hirano and Kato reported that sufficient refluxing of the solution after mixing LiOEt and $Nb(OEt)_5$ was thought to be essential to avoid the formation of mixed phases of $LiNb_3O_8$, $LiNbO_3$ and Li_3NbO_4.[17] The formation of a single phase is a distinct advantage of the sol-gel processing of $LiNbO_3$, since incongruent melting leads to problems in conventional high temperature methods. In fact, Eichorst and Payne demonstrated that stoichiometric $LiNbO_3$ powders could be obtained from initial off-stoichiometric solutions (e.g., Nb/Li = 1.18) if successive crystallizations and filtrations of the bimetallic alkoxide crystals were carried out.[18] The crystal structure of inadvertently hydrolyzed $LiNb(OEt)_6$ was reported by Yanovski et al.[19] The crystal, identified as $[LiNb(OEt)_4(OH)_2]_2$, retains the stoichiometric cation ratio and the same oxygen coordination numbers about the cations as in $LiNb(OEt)_6$. Processing routes which used $LiNb(OCH_2CH_2OCH_3)_6$ in methoxyethanol were reported to hydrolyze in a more controllable manner (than the ethoxide in ethanol), and yield higher-quality oxide thin layers.[15] Hydrolysis content, additions of acid or base, and the choice of alkoxide ligands were reported to influence the epitaxial growth of $LiNbO_3$ on sapphire single crystals.[20,21]
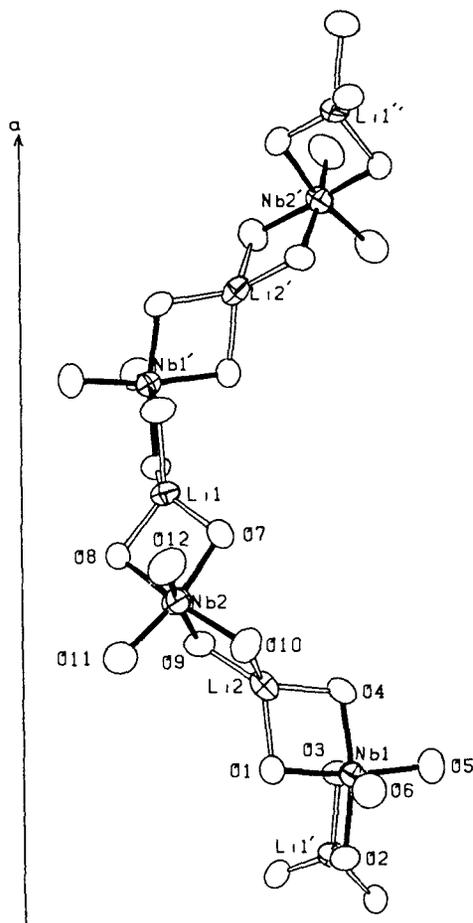
Fig.1 Crystal structure for the double alkoxide, $LiNb(OEt)_6$.

2.3. Precursors for $M^{II}M^{IV}O_3$

Divalent M^{II} and quadravalent M^{IV} cations bonded through oxygen are important members of the perovskite group (ABO_3), which include, $BaTiO_3$, $PbTiO_3$, $PbZrO_3$, $Pb(Zr,Ti)O_3$ (i.e., PZT), etc. However, there are few reports to date of heterometallic alkoxide single crystals with the correct (i.e., required) cation stoichiometry of A:B = 1:1. Kirby investigated the growth of single crystals from a barium-rich $Ba(O^iPr)_6$ + $Ti(O^iPr)_6$ solution, in isopropanol and toluene, and reported an apparent composition of $BaTi(O^iPr)_6$ even though a crystal structure was not determined.[22] Heat-treatment yielded $BaTiO_3$ powder at 800 °C. Yanovski et al. reported the crystal structure of a partially hydrolyzed oxo-alkoxide, $[Ba_4Ti_4O_4(O^iPr)_{16}(^iPrOH)_4][Ba_4Ti_4O_4(O^iPr)_{16}(^iPrOH)_3]$

with the correct Ba:Ti ratio, i.e., 1:1.[23] However, in the proposed structure, Ti has 5-fold coordination and Ba has 7-fold coordination with oxygen, which is different from the perovskite structure. Campion et al. grew heterometallic oxo-alkoxide crystals $Ba_4Ti_{13}O_{18}(OCH_2CH_2OCH_3)_{24}$ from stoichiometric and off-stoichiometric solution compositions (i.e., $BaTi(OCH_2CH_2OCH_3)_6$).[24] The structure indicated Ti in 6-fold coordination and Ba in 12-fold coordination (Figure 2). Heat treatment of gels formed by the addition of excess water (not partial hydrolysis) to solutions of $BaTi(OCH_2CH_2OCH_3)_6$ resulted in the formation of the perovskite structure, $BaTiO_3$, at 400 °C.[25]
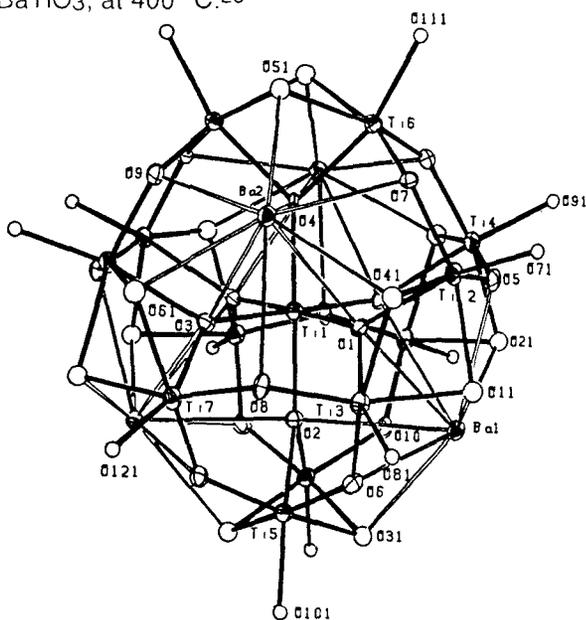
Fig.2 Crystal structure for $Ba_4Ti_{13}O_{18}(OCH_2CH_2OCH_3)_{24}$.

In addition, pyridine solutions of divalent metal α-hydroxycarboxylates, $M^{II}(O_2Me_2OH)_2$ (M^{II} = Pb, Ca, Sr, Ba), have recently been proposed as reactants with alkoxides, $M^{IV}(OR)_4$, to form 1:1 stoichiometric compounds, $M^{II}(O_2Me_2OH)_2M^{IV}(OR)_2$.[26] The use of Ba-acetate has also been proposed as a moisture insensitive precursor which could be used in aqueous solutions.[27] However, high pyrolysis temperatures were needed (>700 °C) to complete decomposition of residual carbonates by the Ba-carboxylates route.[28] $BaTiO_3$ thin layers have also been fabricated by MOD methods. Perhaps the earliest work was reported by Fukushima et al., who prepared 2 μm thick layers from Ba-naphthenate and modified Ti-alkoxide.[29] This was followed by Xu et al. who used Ba-carboxylate with a modified Ti-alkoxide.[30]

2.4. Precursors for Pb-based Perovskite Materials

Substantial effort has been expended in recent years on Pb-containing perovskite material in thin-layer form due to their attractive properties for potential applications. Pb-alkoxides can be synthesized by reaction of anhydrous lead acetate with Na-alkoxides. However, Pb-alkoxides are unstable and insoluble in most alcohols. To avoid this problem, several approaches have been made:
(i) Pb-carboxylates, such as Pb-2-ethylhexanoate, which are soluble in alcohols.
(ii) Pb-acetate, with methoxyethanol as a solvent.
(iii) Pb-acetate, with acetic acid as a solvent.
(iv) Pb-acetate, with additives, such as alkanolamines, which solublize Pb-acetate in most alcohols.

MOD-derived PZT thin layers (i.e., unhydrolyzed, and not strictly polymeric sol-gel) were first reported by Fukushima et al.,[31] who used a solution of Pb-2-ethylhexanoate, Zr-acetylacetonate and $Ti(O^tBu)_4$ in butanol. This was followed by Vest and Xu for La-modified PZT (PLZT).[32] The use of lead acetate with quadravalent alkoxides, using 2-methoxyethanol as a solvent, was proposed by Blum and Gurkovich,[33] and refined and established by Budd and co-workers.[34] In this route, illustrated in Figure 3, inexpensive $Pb(CH_3COO)_2 \cdot 3H_2O$ was dissolved in methoxyethanol and dehydrated by distillation. The Ti/Zr precursor was synthesized by the distillation of $Ti(O^iC_3H_7)_4$ and $Zr(O^nC_3H_7)_4$ in methoxyethanol, and mixed and refluxed with the Pb precursor solution. La was introduced either as $La(CH_3COO)_3 \cdot 1.5H_2O$ with lead acetate, or as $La(O^iC_3H_7)_3$ with Ti- and Zr-propoxides. Low pressure distillation followed by redilution of the mixed precursor solution with methoxyethanol was repeated three times for the complete removal of by-products (e.g., esters). The resultant 1 M solution was found to be stable, with no significant change (over a period of two years) in average molecular

weight, viscosity, and time to gellation upon hydrolysis. Equal volumes of a methoxyethanol solution of water containing acid or base additions, and the stock precursor solution, were mixed. The resulting partially-hydrolyzed solution was spin-cast on a substrate. Hydrolysis conditions are known to affect the polymerization process, and the derived microstructures, of gels. Budd concluded that highly cross-linked and coarse-textured PbTiO3 gels were produced under basic conditions, whereas acidic gels were more linear and capable of extensive polymeric rearrangement on heat treatment, resulting in lower crystallization enthalpies.[35] This process is compatible with many commercially available alkoxides, and has been adopted by many researchers, who have made modifications for the preparation of Pb-based ferroelectric thin layers. The importance of the vacuum distillation step was emphasized by Lakeman and Payne, who characterized the process through use of NMR and FTIR analysis of solutions, and X-ray diffraction and electron microscopy analysis of PZT gels and microstructures.[36] They concluded that the retention of residual ester, which may not be completely eliminated in the distillation process, may result in inhomogeneous stock solutions and, lead to problems with single phase perovskite development on heat treatment. Aging of properly processed solutions could also lead to phase separation.[37] Several other experimental factors have been reported to give the so-called "rosette structure" on PZT thin layers, where larger-sized (μm) perovskite grains are surrounded by a matrix of finer-sized (nm) "pyrochlore-type" grains.[38] The formation of a non-ferroelectric pyrochlore phase has been a problem for Pb-based thin layer preparation, regardless of the precursor/solvent systems used. Yi et al. developed an acetic acid-based method, in which $Zr(O^nC_3H_7)_4$ and $Ti(O^iC_3H_7)_4$ were added sequentially to Pb-acetate solutions in glacial acetic acid.[39] Schwartz et al. followed Yi's method and reported the extensive formation of ester by the reaction of acetic acid with alkoxy ligands, and observed the formation of a pyrochlore phase.[40] Use of Pb-2-ethylhexanoate with acetic acid as an additive was reported to cause phase separation in PZT thin layers.[41] The "pyrochlore-type" matrix was Pb-deficient

and Zr-rich, compared with the desired perovskite stoichiometry.[42] Tuttle et al. proposed that phase separation occurred as hydrolysis and condensation reactions proceeded to form the gel.[43]
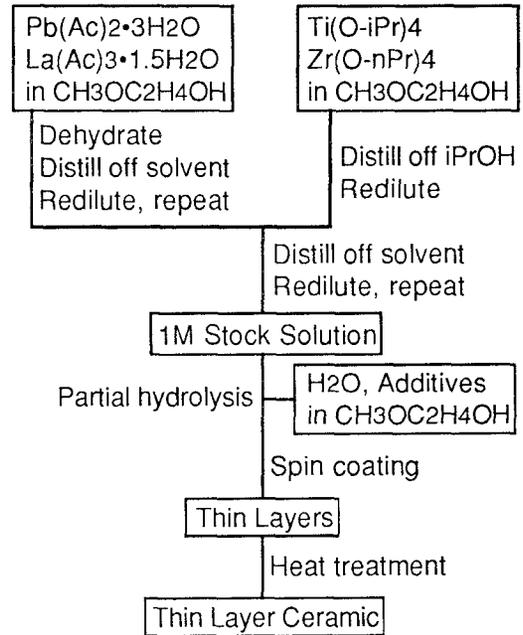
Fig.3 Flow diagram for the sol-gel processing of PLZT thin layers.

For Pb-based systems, significant effort has been made to identify the structures of mixed alkoxides, and partially hydrolyzed oxo-alkoxide intermediates, both in solution and in formed gels, by a variety of methods, including, FTIR, NMR, ESR, Raman spectroscopy, mass spectrometry, and X-ray analysis. Dekleva et al.[44] and Ramamurthi and Payne[45] probed the structural nature of PbTiO3 precursors prepared by Gurkovich's[33] and Budd's methods,[34] respectively. The former suggested the existence of a bimetallic, oligomeric structure, Ti(OR)OPbOAc, in the precursor solution before hydrolysis, which was supported by Li and co-workers.[46] The latter proposed a more polymeric structure including -Ti-OR-Ti- and -Ti-OR-Pb- bonds. Single crystals, isolated from the reaction products of Pb-acetate and Ti- or Zr-alkoxides under partial hydrolysis, are reported to have an oxoacetoalkoxide structure with Pb:Ti (or Zr) = 1:2, or 1:3.[47,48,49] This change in stoichiometry

could be associated with the eventual phase separation observed in the final microstructures, with the development of a Pb-deficient pyrochlore phase, especially from aged solutions.

An alkanolamine-alkoxide system, proposed by Takahashi et al.,[50] is reported to be resistant to hydrolysis, and Pb-acetate can be used without dehydration. However, X-ray diffraction after heat treatment identified Pb (at 300 °C) and PbO (at 400 °C) in PZT material, which may also suggest phase separation in solution. Precursors with Pb:Ti = 1:1 were recently reported with the empirical formula, $Pb_4Ti_4O_3(O^iPr)_{18}$.[51] A possible crystal structure for this compound contains a central $Pb_4O_3(O^iPr)_2$ core.

In other systems, Pb-Zn (1:1) acetoalkoxide,[52] and Pb-Nb (6:4) oxoalkoxide,[53] have been synthesized and the crystal structures determined. These heterometallic species were suggested as possible precursors for relaxor ferroelectrics in thin-layer form. A(B,B')O_3-type relaxors, including lead magnesium niobate (PMN), lead zinc niobate (PZN), and lead scandium tantalate (PST), are reported to be more vulnerable to additional phase formation (i.e., "pyrochlore") than PZT.[54] To overcome this problem, mixing of B-site cation alkoxides was carried out by refluxing prior to combination with the Pb-precursor solution,[55,56,57] similar to the "Columbite Method" used in conventional powder processing of PMN ceramics.

2.5. Inorganic Precursors

An alternative to metallo-organic systems is the use of inorganic precursors in aqueous solution. Yoshimura et al. developed a hydrothermal-electrochemical method for the preparation of titanate thin layers[58]. $BaTiO_3$ was formed on a positively-biased Ti metal substrate by reaction with $Ba(OH)_2$ at 100 - 200 °C under saturated vapor pressure. Direct current was not necessary for the initial formation of $BaTiO_3$, but electrically-driven species were necessary for the growth of the layer. Venigalla et al. used a similar method with Ba-acetate and prepared 0.7 μm-thick $BaTiO_3$ layers on Ti at temperatures as low as 55 °C.[59] Low-temperature hydrothermal processing enabled the formation of $BaTiO_3$ and $SrTiO_3$ thin layers, even on flexible polymer substrates coated with a Ti layer.[60] While these low temperature synthesis routes produced cubic $BaTiO_3$, the tetragonal-phase was formed hydrothermally at 400 - 800 °C.[61] The use of nitrates (e.g., $Pb(NO_3)_2$, $Bi(NO_3)_3$) with $(NH_4)_2TiF_6$ in aqueous solution was proposed by Abe and co-workers.[62] Heat-treatment at 500 °C crystallized $PbTiO_3$ and $Bi_4Ti_3O_{12}$ layers on Ti/glass and Ti metal substrates, respectively.

2.6. Coatings on Substrates

With the exception of the hydrothermal methods just described, the deposition of thin layers is usually carried out by either dip-coating or spin-casting processes. Important processing parameters, including, the concentration and viscosity of the solution, affect the thickness and the quality of the deposited layer.[63]

Substrate materials must be chemically and physically stable at the heat-treatment temperatures necessary for the densification and crystallization of the deposited material. In addition to acting as a physical support, substrates can play an important role on the development of microstructure and properties of the supported layers. Specifically, chemical effects, in which interfacial energy between the substrate and the thin layer controls heterogeneous nucleation at the substrate-coating interface, and hence affects crystallization behavior and texture development, can be significant.[64] Lattice-matched crystal structures for the substrate and the crystallizing layer can serve as a "template" for epitaxial nucleation and growth.[65,66] Interdiffusion between a substrate and a deposited material, on the other hand, may retard crystallization and deteriorate the properties of the layer.[67,68] Physical effects, such as residual stresses arising from thermal mismatch between a substrate and a thin layer, may influence polarization reversal and phase transformation behavior, as well as the static properties of the ferroelectric material.[69,70] Noble metals are commonly used as electrodes deposited on the substrate material. The use of oxide electrodes, with ohmic contact, has recently been suggested as means of developing interfaces which are resistant to fatigue on switching.[71]

A number of successful results have been reported for the preparation of ferroelectric thin layers by combining a variety of precursors, solvents, and additives. Subsequent phase development, and microstructures, reflect the chemical nature of the heterometallic precursors in solution. Thus, careful control of solution chemistry is thought necessary for the establishment of industrial-level processing conditions for the attainment of devices with reproducible properties.

3. HEAT TREATMENT

3.1. Atmosphere

After the deposition of thin layers, thermal processing removes entrapped solvent, pyrolyzes residual organics, and densifies the coating usually with later stage crystallization. Decomposition and densification are often competing processes, and incomplete decomposition can cause porous structures, and/or residual carbon, which are deleterious to the dielectric properties. The effect of atmosphere is important for complete decomposition at low temperatures. Hirano et al. reported the use of water vapor with oxygen during decomposition enhanced the crystallinity of PZT thin layers, and produced highly oriented (100) perovskite structures on (100) MgO.[72] They suggested that water vapor effectively removed carbonates, promoted condensation reactions, and crystallized the perovskite phase. Warren et al. detected residual carbon radicals by ESR in PZT thin layers when fired at 650 °C in a low oxygen partial pressure (0.1 % O_2) but not when the layers were fired in air.[73] Atomosphere also affects the formation of defects. Kwok and Desu reported, however, that sol-gel derived PZT layers on Pt-coated Si have a Pb and O depletion depth up to 5 nm from the surface, even when fired in air or oxygen at 650°C for 15 min.[74] Oxygen tracer diffusion measurements revealed that as much as 65 % of the oxygen in a PZT thin layer was exchanged with the ambient by heat treatment at 600 °C for 30 min.[75] It was suggested that thermal dissociation from the lattice was the mechanism for oxygen exchange, and that diffusion was sensitive to the microstructure in PZT layers. Thus, interactions at two major interfaces, between the coating and the substrate, and the coating and the atmosphere, can affect the properties of ferroelectric thin layers.

3.2. Crystallization of Pb-based Perovskite Materials

Pb-based perovskite layers crystallize from either the amorphous state or transform from the aforementioned pyrochlore structure, depending upon thermal processing conditions. It is important to minimize the presence of the pyrochlore phase to optimize the ferroelectric and dielectric properties associated with the perovskite structure. The pyrochlore structure is more stable than the perovskite structure at low temperatures for large B-site cations under Pb-deficient conditions.[76] Besides careful control of solution chemistry, four processing techniques have been proposed to reduce the pyrochlore problem:
(i) Additions of excess Pb in solution.
(ii) Seeding for perovskite crystallization.
(iii) Rapid thermal processing (RTP).
(iv) PbO coverage.

It is well known that excess PbO is added to powders in conventional processing to compensate for lead-loss on heat treatment.[77,78] This technique is also used in sputtering methods at reduced pressures.[79] In sol-gel processing, it is claimed that excess PbO leads to crystallization of dense perovskite microstructures at reduced temperatures[80]. Tuttle et al. reported an optimum amount of 5 mol% PbO content for PZT (53/47) thin layers,[81] while Francis and Payne found that 15 mol% gave the best properties for lead magnesium niobate (PMN) based compositions.[82] Crystallization at reduced temperatures was also promoted through the use of seeded layers. Swartz et al. deposited PLZT precursor solutions on a PbTiO3 interlayer and obtained perovskite PLZT.[83] Hirano et al. reported on the preparation of perovskite PMN-PT layers over a seeded PZT base layer.[84] In addition, RTP has been used to maximize the perovskite content by avoiding extended time in the temperature range in which the pyrochlore phase is stable.[85] This kinetic approach has been successful for a variety of compositions and substrate materials. RTP has a role of also minimizing both PbO loss due to evaporation, and interdiffusion between the substrate and the layer.[86]

(a)

(b)

200 nm
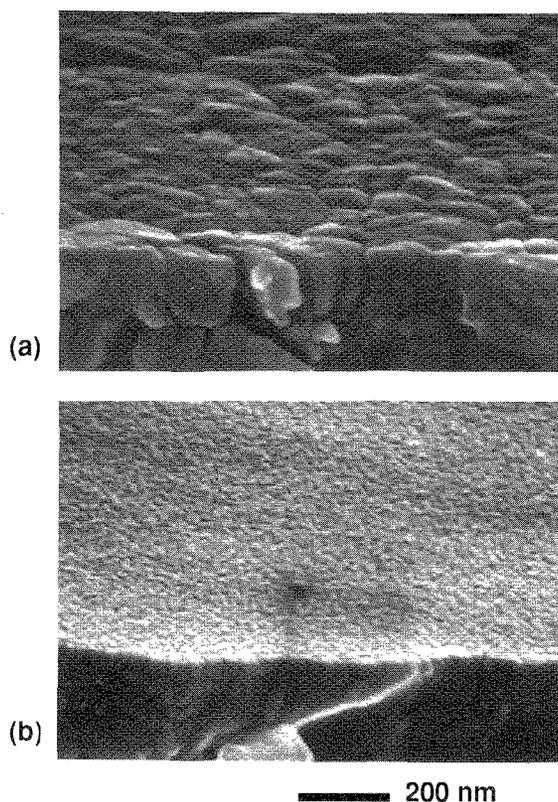
Fig.4 SEM photomicrographs of 7.5/70/30 PLZT thin layers fired at 700 °C for 5 min (a) with and (b) without a PbO-precursor cover coat.

Another approach to reduce Pb loss on firing has recently been demonstrated by Tani and Payne, who deposited a Pb-precursor solution before (i.e., under coat) and/or after (i.e., cover coat) deposition of PLZT layers.[87] It was found that PbO coatings enhanced crystallization into the perovskite structure. For example, after 1 min at 650 °C single phase perovskite material was formed. There was no evidence of a pyrochlore phase. Figure 4 gives the surface morphology of a PLZT coating which had been heat treated at 700 °C for 5 min. PbO-covered PLZT layers had a grain size between 0.1 and 0.2 μm, whereas specimens without a PbO cover coat had a nanocrystalline surface layer.[87] Any remaining PbO particles on coated surfaces could be removed after firing. PbO-covered PLZT layers had a higher dielectric constant (K = 615) when compared with uncovered layers (K = 239) for PLZT (7.5/70/30). Figure 5 illustrates the ferroelectric properties for these layers. The PbO-covered PLZT exhibited slim-loop behavior with polarization saturation, whereas uncovered layers had lossy characteristics. Thus, the deposition of a PbO-precursor solution over the top surface of a PLZT layer is an effective method for the reproducible preparation of single phase perovskite material. In addition, PZT thin layers processed with a PbO cover coat have better dielectric and piezoelectric properties than uncoated PZT layers.[88] This method is applicable to other Pb-containing materials, and can be extended to other systems containing volatile species such as alkali cations.

We have reviewed some of the problems and strategies in the heat treatment of PZT thin layers and related materials. Most of the problems are common to other ferroelectric materials. Therefore, the strategies may also be common, i.e.,

(i) Removal of organics and gas evolution from layers at low temperatures.

(ii) High rates of heating to the final crystallization temperature.

(iii) Control of atmosphere to prevent loss of volatile species (including oxygen).

The processing should be compatible with integrated technologies for future device applications. Post-heat treatment techniques, such as chemically assisted ion-beam or plasma etching, are also under investigation.[89]
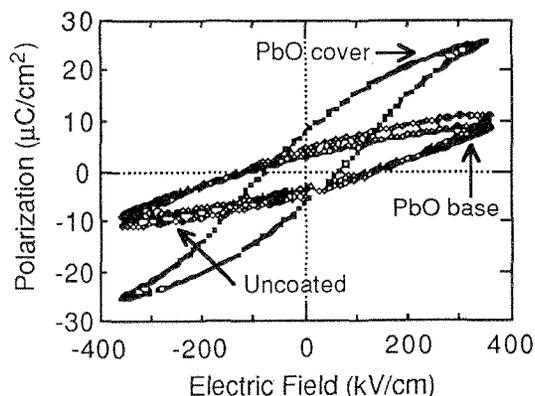
Fig.5 Ferroelectric hysteresis for 7.5/70/30 PLZT thin layers heat treated at 700 °C for 5min.

4. MATERIALS AND PROPERTIES

4.1. Barium Titanate

Sol-gel processed BaTiO3, crystallized on Pt/Ti/SiO2/Si, had a fine-grain nanostructure (25 nm) when heat-treated at 750 °C.[90] The integrated layer was 200 nm thick and had some unusual features:[91]
(i) A cubic structure with linear P-E characteristics (Figure 6).
(ii) A room temperature dielectric constant of 230 with no dielectric anomaly between -85 and 200 °C (Figure 7).
(iii) High dielectric strength (1 MV/cm dc) with high electrical insulation.
The overall properties, especially, a low temperature coefficient of capacitance, makes this material a potential candidate for integrated applications, including stable decoupling capacitors.
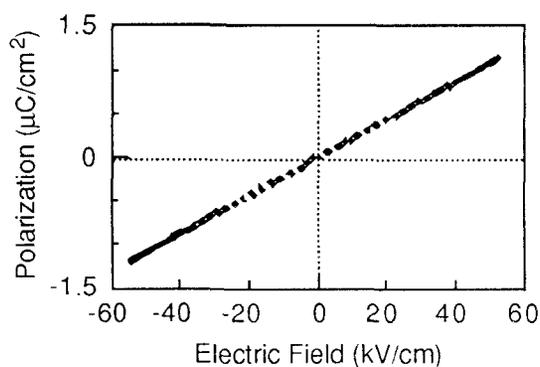
Fig.6 Linear P-E behavior for a nanocrystalline BaTiO3 thin-layer capacitor.
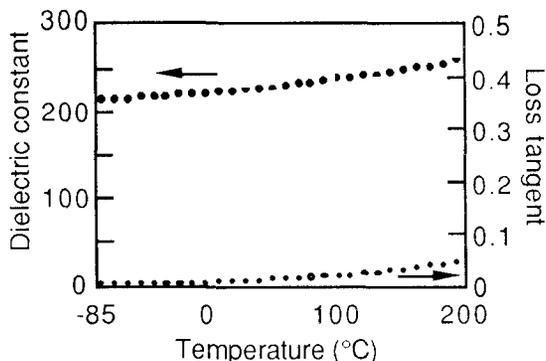
Fig.7 Temperature dependence of dielectric constant for a nanocrystalline BaTiO3 thin-layer capacitor.

Partial substitution of Ba by Pb was found to increase the grain size and dielectric constant, and decrease the thermal expansion mismatch with the substrate material.[92] Crystalline solutions with SrTiO3, e.g., (Ba,Sr)TiO3 (with Ba/Sr = 70/30) are reported to have a higher values of K (e.g., 500).[93] Heat treatment on oxide electrodes at higher temperatures produced larger grain sizes with ferroelectric properties. Kuwabara et al. reported a grain size of 0.1 μm for BaTiO3 thin layers on BaPbO3 ceramics by heat treatment at 800 °C, and observed a slanted and saturated hysteresis loop.[94] Xu et al. reported a 0.2 μm grain size for a BaTiO3 thin layer heated to 1200 °C on a MOD-derived ITO layer on Pt.[30] This material was reported to have a dielectric constant of 1000 at room temperature, with a Curie temperature (Tc) of 136 °C, and demonstrate ferroelectric behavior (PR = 3.1 μC/cm2).

4.2. Lead Titanate, PZT and PLZT

PbTiO3 oriented along the c axis has a high pyroelectric coefficient (Π), a relatively low dielectric constant (K), and a small temperature coefficient of Π, making it an ideal candidate material for infrared sensing elements. By doping with La, the Tc is decreased and Π is increased. Sputter-deposited 10 %La-doped PbTiO3 (PLT) thin layers on Pt/MgO have been reported for linear array infrared sensors.[95] Sol-gel processed PbTiO3 has also been reported to have high value of Π (10^{-7} C/cm2·K) for thin layers deposited on polycrystalline Si.[96] Efforts continue for the development of 2-dimensional sensor arrays.[97]

Substitution of 28 mol% La for Pb stabilizes the cubic paraelectric phase of PLT at room temperature.[98] Sol-gel derived PLT (28 mol % La) exhibited linear polarization (P)-field (E) behavior with high values of K (1400 up to 40 kV/cm) and low leakage current density (0.5 μA/cm2 at 200 kV/cm). It was suggested for use in DRAM's and decoupling capacitor applications. Slim-loop ferroelectric PLZT (9/65/35) was also proposed for DRAM applications because of the high charge storage density (36 μC/cm2 at 5V).[99]

PZT thin layers are also under investigation for applications in non-volatile ferroelectric memories, microactuators and motors, and piezosensors. Most of the studies have

focused on compositions near the morphotropic phase boundary (MPB) between the rhombohedral and tetragonal phases, e.g., Zr/Ti = 53/47 (i.e., PZT 53/47).[100] The first reports for solution-derived PZT (50/50) thin layers by Fukushima et al. indicated values for P_R (31 $\mu C/cm^2$) and E_C (45 kV/cm) which were comparable with bulk ceramics.[31] Tuttle et al. reported the highest P_R value of 61 $\mu C/cm^2$ for sol-gel derived c-axis oriented PZT (40/60) by controlled epitaxy off (100) Pt || (100) MgO substrates.[70] This value exceeded values for P_R in PZT thin layers prepared by RF sputtering (46 $\mu C/cm^2$ for PZT 90/10),[95] ion-beam sputtering (36 $\mu C/cm^2$), and laser ablation (40 $\mu C/cm^2$ for PZT 52/48),[101] and is comparable with MOCVD (60 $\mu C/cm^2$ for PZT30/70).[102] However, degradation of P_R with switching has been a common problem for PZT thin layers deposited on Pt electrodes regardless of the processing method. Resistance to fatigue was improved by addition of dopants,[103] and the use of oxide electrodes.[104] Reported size effects with layer thickness may be attributed to various factors, including, the co-existence of a non-perovskite surface phase, space charge polarization, mechanical stresses and grain size effects.[105] Udayakumar et al. reported higher K values ~ 1300, lower $\tan\delta$ ~ 0.03, higher P_R > 35 $\mu C/cm^2$ and breakdown strength > 1 MV/cm when the thickness exceeded 300 nm for PZT.[106]

Piezoelectric sol-gel derived PZT thin layers may find applications in micromotors,[107] microsensors,[108] and the other electromechanical transducer devices.[109] Piezoelectric coefficients have been determined by interferometric techniques for sol-gel derived PZT thin layers.[4,110] Reported d_{33} values are comparable with bulk ceramics.[100]

Electro-optic properties have also been a focus of interest for PZT and PLZT thin layers. Budd and Payne reported an electro-optic valve effect for a sol-gel derived waveguide.[111] Yi et al. observed a quadratic dependence of Δn on E (R = 10^{-18} m^2/V^2) for an unpoled layer, and a linear effect (r_c = 24 pm/V) for a poled sol-gel derived PZT (60/40) thin layer. Higher quadratic coefficients (R = 50×10^{-18} m^2/V^2) were reported for MOD-derived PLZT (8/65/35) thin layers by Vest and Xu.[112] This value is comparable with sputter-deposited (9/65/35) PLZT (R = 100×10^{-18} m^2/V^2).[113]

4.3. Lead Zirconate and Antiferroelectrics

Antiferroelectric (AFE)-ferroelectric (FE) phase transformations attract attention for large-strain actuators and precise positioners.[114,115] Figure 8 gives a typical double hysteresis loop for a sol-gel derived $PbZrO_3$ (PZ) thin layer. As much as 0.7 % linear strain was measured at the phase transformation by interferometry.[116] Electro-optic responses have also been detected for $PbZrO_3$ thin layers and possible applications to optical memories have been suggested.[117] An effective way of reducing the switching field is by tin (Sn) substitution. For example, antiferroelectric PZST has a switching field of 80 kV/cm,[118] compared with 200-250 kV/cm for PZ, and may be suitable for practical applications.[115,116]
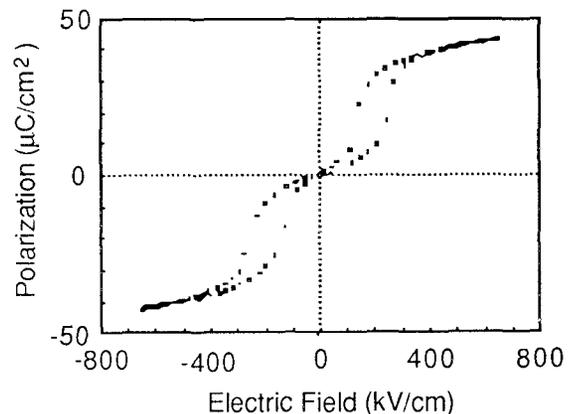
Fig.8 Field enforced antiferroelectric-ferroelectric switching for sol-gel derived $PbZrO_3$.

4.4. Lead-Based Relaxor Ferroelectrics

Values of dielectric constant for PMN-PT[119] and PST[120] thin layer relaxors have been reported to be 6000 and 9000, respectively. These could find applications in integrated capacitors. PST is also a candidate for infrared imaging arrays, and PMN for microactuator elements (with a d_{33} value of 265 pC/N and with minimal hysteresis).

4.5. Other Perovskite-Type Materials

$KNbO_3$,[121] $KTaO_3$,[122] and their crystalline solutions in thin layer form[123] have been prepared by sol-gel methods. Epitaxial layers were deposited on MgO and $SrTiO_3$ substrates. Their properties have yet to be reported.

4.6. Lithium Niobate Group

$LiNbO_3$ and $LiTaO_3$ have received attention for infrared sensors, surface acoustic wave (SAW) devices, and electro-optic applications. Epitaxial thin layers were deposited on sapphire substrates.[124,125] Ti doping changed the optical properties (Figure 9), which may find applications in graded refractive index devices.[126]
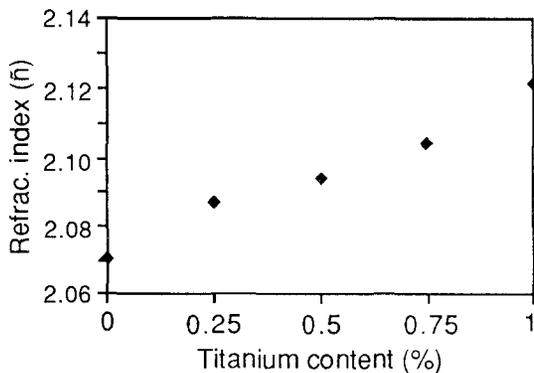
Fig.9 Refractive index as a function of Ti content for $LiNbO_3$ thin layers.

4.7. Tungsten Bronze Structure

Xu et al. deposited $Sr_{0.6}Ba_{0.4}Nb_2O_6$ thin layers on various substrate materials by sol-gel processing and reported ferroelectric, pyroelectric, and electro-optic properties.[127] The pyroelectric coefficient (2×10^{-8} C/cm^2K), determined at room temperature for an Au/SBN/Si structure, was similar to single crystal SBN.[128] The reported linear electro-optic coefficient was 30 pm/V, which was an order of magnitude less than single crystal SBN. The difference was attributed to dielectric and optical anisotropies.[129] Highly oriented $Sr_{0.5}Ba_{0.5}Nb_2O_6$ thin layers were deposited on MgO single crystals, but no property measurements were reported.[130] Significant second harmonic signal generation has been observed for sol-gel derived barium sodium niobate (BNN) layers.[131]

4.8. Bismuth Titanate and Other Materials

Stoichiometric $Bi_4Ti_3O_{12}$ thin layers have been prepared with a square hysteresis properties ($P_R = 4$ $\mu C/cm^2$) and with a low coercive field ($E_C = 1.8$ kV/cm) by sol-gel processing.[132] Reported values of dielectric constant and tan ∂ were 120 and 0.5 %, respectively. Various polar materials in thin layer form, including BaB_2O_4,[133] $La_2Ti_2O_7$,[134] and $KTiOPO_4$[135] have recently been deposited by sol-gel techniques.

5. SUMMARY

The deposition of ferroelectric thin layers from solution was reviewed, with emphasis on polymeric sol-gel processing. The solution method appears to be an attractive approach for the control of purity, stoichiometry, homogeneity, and with enhanced reactivity for low temperature densification. The properties of integrated ferroelectrics on substrate materials indicate the potential for future electrical and optical applications. Device integration will come about through a thorough knowledge of materials chemistry in ceramic processing.

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