Homogeneity issues in chemical solution deposition of Pb(Zr,Ti)O$_3$ thin films

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Abstract

Chemical solution deposition (CSD) methods for ferroelectric thin films make higher reliability and lower processing temperatures feasible. Different reactivities of the constituent transition metal alkoxides may decrease the homogeneity on the molecular level in the ceramic precursors during the synthesis and subsequent processing steps: deposition of the film, drying, consolidation and crystallization of the target ferroelectric phase.

In the 2-methoxyethanol based synthesis of Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$, a selective modification of the reactive Zr alkoxide by acetic acid results in a more homogeneous distribution of constituent metal atoms in the sol as compared to the sol prepared from the as-received Zr-propoxide. The improved chemical homogeneity is reflected in the improved functional response of the films.
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1. Introduction

Research on chemical solution deposition (CSD) methods for Pb(Zr,Ti)O$_3$ (PZT) ferroelectric thin films is oriented towards higher reliability and lower processing temperatures.[1–5] Various CSD methods are broadly divided into those involving a reaction leading to a heterometallic precursor, such as (organic) sol–gel, or polymeric precursor routes in water-based media or those based on mixing of non-reactive organic compounds, i.e. metalloorganic decomposition (MOD).[6,7] In the first group, the 2-methoxyethanol based route, originally used by Gurkovich and Blum[8] in case of powders and Budd et al.[9] for thin films is probably the most widely spread. It is based on the reactions of transition metal alkoxides TM(OR)$_4$ (TM = Zr, Ti) with soluble lead compounds, such as acetate, in 2-methoxyethanol resulting in stable polymeric sols. The reaction between an alkoxide and an acetate (Pb(OAc)$_2$, OAc−: CH$_3$COO−) can proceed by either ester elimination and/or addition leading to the formation of oxo or acetate bridges between the metals.[10–13]

From the early days of CSD the problems of local heterogeneities in the films, expressed, for example, as the appearance of the non-ferroelectric surface pyrochlore phase[14–16] or zirconium-rich regions[17] have been recognized. Approaches leading to an improved response of the films preferentially at a lower crystallization temperature have included solution synthesis modifications such as introducing a vacuum distillation[18] or increasing the number of distillations;[19,20] in both cases a more effective removal of acetate groups was achieved. The reactivity of the TM alkoxides towards water has been recognized also as a problem in terms of experimental requirements, as dry atmosphere had to be maintained during solution processing. Therefore, the alkoxides have been modified by substitution or addition of ligands less reactive towards hydrolysis such as chelating acetylacetone (CH$_3$COCH$_2$COCH$_3$), or bidentate, bridging acetic acid (CH$_3$COOH).[21,22] Examples include the use of acetylacetone to stabilize Ti alkoxide in the synthesis of PbTiO$_3$ thin films,[23] or both Zr and Ti alkoxides in the synthesis of PZT thin films.[24–26] This modifier has been also used to increase

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the pyrolysis temperature of the PZT precursor solution and consequentially influence the crystallization of the respective thin film; however, in this case it was added to the already synthesized PZT solution prior the film deposition.[27,28] Acetic acid has also been used in PZT thin film processing in the role of a solvent and modifier.[27,29]

In our previous work, we have observed clustering of zirconium species in the amorphous alkoxide precursors of PZT by extended X-ray absorption fine structure spectroscopy (EXAFS).[30] Sengupta et al.[31] observed M–O–M (M = Ti or Zr) linkages as a result of preferred homocondensation of titanium and/or zirconium species in an EXAFS study of prehydrolyzed amorphous precursors of $PbZrO_3$ (PZ), $PbTiO_3$ (PT) and PZT. Feth et al.[32] found no structural similarities between the amorphous precursor and crystalline PZT. In an EXAFS and XRD study of crystallization of $Ca(Zr,Ti)O_3$ prepared by a variety of solution synthesis routes, Xu et al.[33] noted that the perovskite phase never crystallized directly, transitory calcium-rich and fluorite phases typically formed in the process of annealing.

Zirconium alkoxides are more reactive than titanium alkoxides due to their lower electronegativity and higher coordination number (CN).[22] Therefore, a selective modification of zirconium alkoxide with the aim of decreasing its reactivity relative to titanium alkoxide prior the PZT sol synthesis should improve the homogeneity of the PZT sol and as a consequence influence the thin film evolution and response. This contribution gives an overview of our work in this field.

2. Experimental

PZT sols corresponding to the composition of $PbZr_{0.53}Ti_{0.47}O_3$ with 10 mol% PbO excess were prepared in 100 ml batches by diluting zirconium and titanium *n*-propoxides ($Zr(OPr)_4 \cdot PrOH$, $Ti(OPr)_4$) in 2-methoxyethanol ($CH_3-O-C_2H_4-OH$) and by adding anhydrous lead acetate ($Pb(CH_3COO)_2$) in the required quantity. The metal contents of all compounds were determined gravimetrically. The reaction mixtures were heated to approximately 60 °C to get clear solutions. After 2 h of refluxing and distillation of the by-products, stable 0.5 M sols were obtained. All manipulations were performed in dry nitrogen atmosphere.

Zirconium *n*-propoxide was either used as-received or modified. As modifiers acetic acid (CH_3COOH) or acetylacetone ($CH_3COCH_2COCH_3$) were admixed to Zr alkoxide in the molar ratio of 2 to 1. The unmodified sol is further denoted as PZT and the modified ones as PZT/OAc and PZT/Acac. PZT thin films were deposited on $TiO_2/Pt/TiO_2/SiO_2/Si$ substrates[34] by spin-coating, pyrolyzed at 350 °C for 1 min and annealed at 500–700 °C for 15 min.

Thermal decomposition of the sols, dried at 60 °C, was followed by simultaneous thermal analysis (thermogravimetry and differential thermal analysis TG/DTA, Netzsch STA 409, coupled with a mass spectrometer, Balzers thermostar, for the analysis of evolved gases, heating rate 10 °C/min, flowing air atmosphere, Pt crucibles).

The PZT sols were characterized by EXAFS (Zr K-edge, Pb L3 edge) analysis. Pb and Zr EXAFS spectra were measured in a standard transmission mode at the X1 station of HASYLAB synchrotron facility, DESY (Hamburg, Germany). Experimental details are described in Refs. [35,36].

The films were characterized by a diffractometer with Cu Kα radiation. The thickness of the films determined by Rank Taylor Hobson profilometer was in all cases around 250 nm. After applying Au top electrodes, dielectric constant was determined by an impedance analyzer (HP4192) at 1 kHz and *P–E* hysteresis loops by a FE-tester (Aixacct).

3. Results and discussion

The thermal decompositions of the dried PZT precursors reveal the mass losses of 18, 20 and 22% upon heating to 670 °C for PZT, PZT–OAc and PZT–Acac, respectively (Fig. 1). The increase in mass losses of the three precursors is in accord with the expected increased organic contents. The thermal decompositions occur in three steps: the mass loss of 3–5% from RT to 200 °C for PZT and PZT–OAc and 170 °C for PZT–Acac is accompanied by a broad endothermic peak and is attributed to evaporation of residual solvents and water as confirmed by mass spectrometry of evolved gases (EGA, spectra not shown here). The mass loss of about 12% upon heating to 350 °C is accompanied by a group of strong exothermic peaks and evolution of CO_2 (*m/e* 44) and H_2O (*m/e* 18) attributed to oxidation of organic species, i.e. alkoxide, acetate and/or acetylacetonate groups. Note that in the case of PZT–Acac the evolution of acetone (CH_3COCH_3, *m/e* 58), the decomposition product of acetate groups[37] takes place in two steps with peaks coinciding with the major DTA peaks at 247 and 289 °C. For PZT and PZT–OAc, the acetone peak is observed in a narrower range, between 270 and 350 °C.

In the third step of thermal decomposition, upon heating to 600 °C, the mass loss of 4–7% is again accompanied by a group of exothermic peaks at 470, 500 and 520 °C and evolution of CO_2 and traces of H_2O, therefore predominantly carbonaceous residues are decomposed. A three-step thermal decomposition has been also reported for Pb–Ti acetate–alkoxide precursors.[38,39] At about 650 °C, a weak exothermic peak without any weight loss is observed for PZT, and a strong one for PZT–OAc, while for PZT–Acac it is hardly discernible, and it is attributed to crystallization of the perovskite phase. On the basis of the observed differences in the thermal decomposition pathways of the three precursors we conclude that both Zr alkoxide modifiers, acetic acid and acetylacetone, incorporate into the structure of the original PZT sol.

Here, we summarize and discuss the results of EXAFS spectroscopy studies of the local neighborhoods of
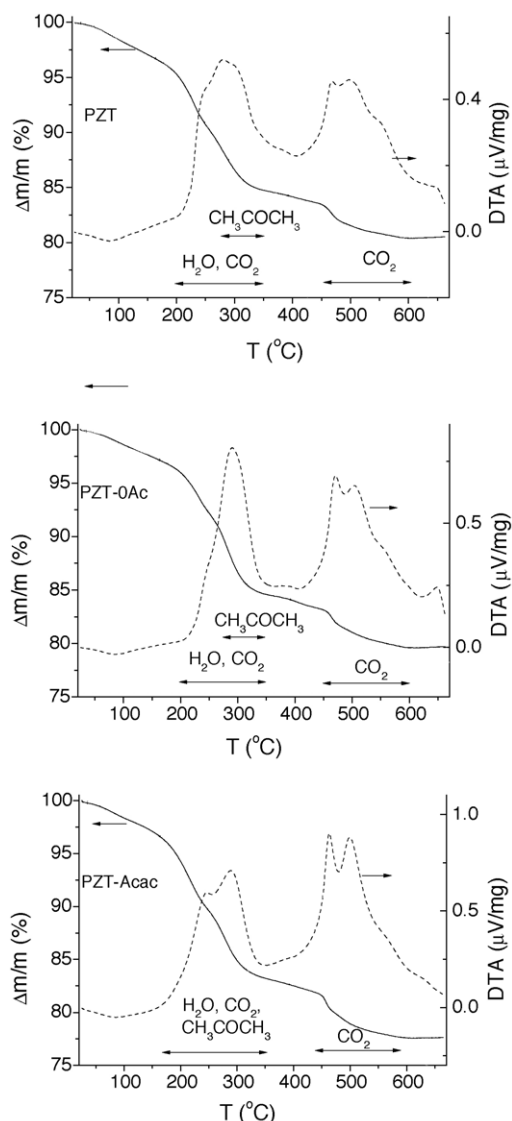
Fig. 1. TG/DTA curves of the PZT, PZT/OAc and PZT/Acac precursors, dried at 60 °C. The regions of evolution of CO_2, H_2O and CH_3COCH_3 are marked with arrows.

zirconium[35] and lead[36] atoms in unmodified and modified PZT sols up to 3.7 and 4.0 Å, respectively (Fig. 2, Table 1). The local environment of zirconium atoms consists of two broad shells of neighbors. The first shell is composed of six to eight oxygen atoms at two slightly different distances. The lower, octahedral coordination is more probable for the acetic acid modified PZT while in unmodified and Acac-modified PZT the coordination is close to 8. The coordination number of zirconium exceeding 6 in amorphous zirconate precursors has been also proposed by Xu et al.[33,40] while Sengupta et al.[31] reports the CN 6 for amorphous PZT precursor, dried at 425 °C. We also observed distorted octahedral coordination of oxygens in concentrated PZT sols[41] and in the amorphous PZT precursors prepared in aliphatic alcohol.[30] These differences may arise from the different synthetic routes and thermal budgets.

The second shell of zirconium neighbors is composed of zirconium and carbon atoms, the latter stemming from the functional groups. No heterometallic correlations could be determined in the examined zirconium neighborhood. The existence of Zr–O–Zr linkages is important from the viewpoint of homogeneity: a large number of Zr–O–Zr linkages points to the segregation of zirconium species[30] and can thus be used as a measure of homogeneity of the PZT sol. The tendency for homocondensation of zirconium species in sol–gel derived precursors has been observed in a number of EXAFS analyses of amorphous precursors of PZT,[30,31] $Ca(Zr,Ti)O_3$[33] and $ZrTiO_4$.[40] Compositional heterogeneity in sol–gel derived PZT has been detected by neutron scattering studies and attributed to segregation taking place upon early stages of processing.[42]

In acetic acid-modified PZT sol the number of Zr-neighbors is 0.8, noticeably less than 2.9 and 2.5 for unmodified and Acac-modified PZT, respectively. For the acetic acid-modified PZT sol, the dimeric zirconium units with bridging alkoxide groups are assumed in agreement with the structure proposed by Peter et al.[43] for the Zr-propoxide in parent alcohol solution.

In PZT sol, the first shell of Pb neighbors consists of two oxygen atoms at slightly different distances, and the second shell of one carbon and 0.5 titanium atoms, but the model with two carbon atoms also fits the data.[36] In the Acac-modified sol, the local Pb neighborhood consists of two oxygen atoms in the first shell and only carbon atoms in the second shell of neighbors. The acetic acid-modified PZT sol has a quite different local lead environment: two oxygen atoms in the first shell and an increased numbers of both carbon and titanium atoms in the second shell. The increase in the number of carbon atom neighbors could be tentatively explained by a higher degree of polycondensation. No Pb–Zr correlations could be determined in the samples.

The choice of the starting zirconium compound therefore influences the local lead environment. Similarly, we have observed that different lead sources, namely oxide and acetate, have a major impact on the local zirconium environment while they only weakly influence the local lead environment.[41] Although the EXAFS study elucidates only the close neighborhoods of Zr and Pb atoms of the three liquid precursors, it definitely confirms the structural differences induced by the addition of the modifiers, acetylacetone and acetic acid.

While the two modifiers do not influence significantly the microstructure and the crystallization of PZT films deposited on platinized silicon substrate: the films consisting of 100 nm columnar grains are perovskite at 500 °C; their orientation strongly depends on the choice of the sol.[35] For example, at 500 °C the PZT–OAc is predominantly (1 0 0), the PZT–Acac predominantly (1 1 1) and the unmodified PZT is (1 0 0)/(1 1 1) oriented with traces of a pyrochlore-type phase, at 550 and 600 °C both modified PZT films are predominantly (1 0 0) and the unmodified PZT is (1 1 1) oriented. These results are rather surprising in view of the fact that the substrate
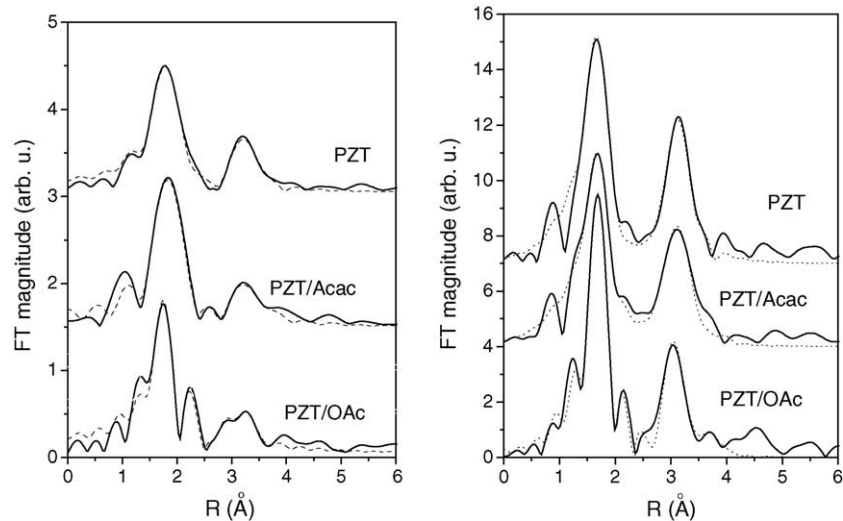
Fig. 2. The k^3 weighted Fourier transforms of Pb L_3 EXAFS spectra (left, after Ref. [36]) and of zirconium EXAFS spectra of PZT sols (right, after Ref. [35]). Solid line, experiment; dotted line, model.

contains a 2 nm thin TiO_2 layer that should act as a nucleation site for the (1 1 1) orientation.[34] In fact, the unmodified PZT film is (1 1 1) oriented at 600 °C. We speculate that these differences stem from a more homogeneous arrangement of metal atoms in the case of acetic acid modified PZT sol that is closer to the stoichiometry of the perovskite phase. Note that the bulk compositions contain 10 mol% lead oxide excess. Based on the EXAFS results, we assume that the PZT–OAc sol should exhibit a high level of homogeneity. It is possible that the perovskite phase from this sol crystallizes without the typically encountered losses of PbO, that is reaction with the Si-substrate and/or evaporation from the surface.[15,44] Therefore, the film contains a secondary, lead-oxide rich phase that can cover or react with the TiO_2 nucleation layer yielding a nucleation site for (1 0 0) orientation in concordance with earlier studies on nucleation of (1 0 0) PZT.[45,46] To verify this assumption, we deposited a film from the stoichiometric

acetic acid modified PZT sol; the XRD pattern of the film annealed at 550 °C reveals predominantly (1 1 1) texture for the stoichiometric PZT in relation to the film with PbO-excess (Fig. 3).

We assume to an extent a similar reasoning for PZT–Acac although the EXAFS results do not support it; nevertheless, we should keep in mind that we lack insight into more distant surroundings of the Pb and Zr atoms.

The unmodified, Acac- and OAc-modified PZT films on platinized silicon substrates annealed at 600 °C exhibit the values of remanent polarization (P_r) 17, 21 and 22 $\mu C/cm^2$, coercive field (E_c) 73, 66 and 52 kV/cm, and dielectric permittivity (ε) 1088, 1145 and 1444, respectively.[35] Note however, that the PZT–OAc films annealed at as low as 500 °C reach almost the same values as at 600 °C while the response of unmodified PZT is noticeably reduced (Table 2). Only after annealing at a higher temperature, and therefore, promoted diffusion and homogenization, this film exhibits the response comparable to that of acetic acid modified PZT, annealed at 500 °C, taking into account to an extent the differences due to the different orientations of the two films.[47,48]

Table 1

Neighbors of lead (after Ref. [36]) and zirconium (after Ref. [35]) atoms in PZT sols: atomic species, average number N and distance R

	PZT		PZT–Acac		PZT–OAc	
	N	R (Å)	N	R (Å)	N	R (Å)
Pb neighbor						
O	1.1 (2)	2.23 (2)	1.5 (4)	2.30 (1)	1.5 (3)	2.23 (1)
O	0.8 (2)	2.37 (2)	–	–	0.9 (3)	2.42 (1)
C	–	–	1.2 (3)	3.25 (2)	–	–
C	0.9 (3)	3.40 (6)	2.0 (3)	3.48 (2)	3.9 (7)	3.42 (1)
C	–	–	2.0 (3)	3.80 (2)	–	–
Ti	0.5 (1)	3.82 (3)	–	–	1.6 (3)	3.81 (1)
Zr neighbor						
O	4.2 (5)	2.10 (4)	5.8 (9)	2.13 (4)	4.0 (4)	2.14 (1)
O	3.6 (5)	2.20 (4)	3.2 (9)	2.25 (4)	2.2 (4)	2.28 (2)
C	2.2 (4)	3.25 (1)	2.7 (9)	3.29 (4)	3.8 (7)	3.30 (4)
Zr	2.9 (5)	3.49 (2)	2.5 (9)	3.47 (2)	0.8 (4)	3.44 (4)
C	4.2 (7)	3.62 (5)	4.8 (9)	3.65 (5)	6.5 (8)	3.68 (4)

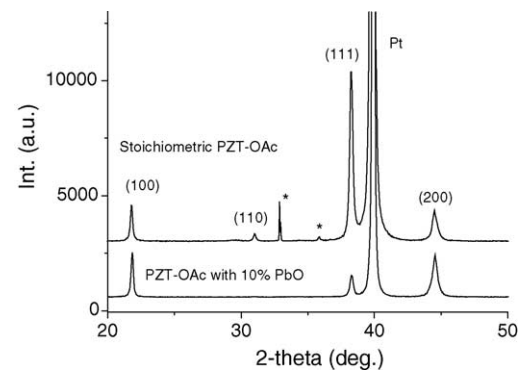Uncertainty of the last digit is given in parentheses.

Fig. 3. XRD patterns of PZT–OAc films with and without 10 mol% PbO excess annealed at 500 °C for 15 min.

Table 2
The values of remanent polarization (P_r), coercive field (E_c), dielectric permittivity (ε) of PZT and PZT–OAc films annealed at 500 and 600 °C

	PZT		PZT–OAc	
	500 °C	600 °C	500 °C	600 °C
P_r (μC/cm^2)	17	17	20	22
E_c (kV/cm)	137	73	68	52
ε	448	1088	998	1444

4. Summary

In the 2-methoxyethanol-based chemical solution deposition of Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ thin films, a selective modification of the reactive Zr alkoxide by acetic acid results in a homogeneous distribution of constituent metal atoms in the sol. The improved chemical homogeneity is reflected in the improved functional response of the films.

Acknowledgements

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