Homogeneity of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ Thin Films by Chemical Solution Deposition: Extended X-ray
Absorption Fine Structure Spectroscopy Study of Zirconium Local Environment

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Abstract

Sols for $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) thin films were prepared by 2-methoxyethanol route from lead acetate, titanium n-propoxide and zirconium n-propoxide, the latter either unmodified or modified with acetylacetone or acetic acid in a 2/1 molar ratio, and deposited on sapphire (0001). By Zr K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, the structural changes in the Zr local environment, induced by the addition of the two modifiers, were followed from the synthesis of the PZT sol and to the transition to the amorphous film.

In the unmodified PZT sol segregation of Zr species occurs from the original dimers present in the Zr propoxide solution in 2-methoxyethanol. The immediate neighborhood of Zr atoms changes markedly at the transition from the sol to the amorphous film: the local structure around Zr atoms is similar to the one found in tetragonal zirconia particles. The modification of Zr propoxide with acetylacetone in 2-methoxyethanol results in Zr monomers. In PZT sol clustering of Zr species is observed continuing into the amorphous film.

By modification with acetic acid the original dimeric structure of the Zr precursor is retained in the PZT sol and further in the amorphous film. Selective modification of Zr alkoxide with acetic acid therefore results in a more homogeneous distribution of Zr atoms in the PZT sol and amorphous film than in both as-received or acetylacetone-modified Zr propoxide.

Introduction

The research on chemical solution deposition (CSD) methods for $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ferroelectric thin films is oriented towards higher reliability and lower processing temperatures¹⁻⁵. The 2-methoxyethanol based route⁶ is probably the most widely spread of CSD. It is based on reactions of transition metal alkoxides $\text{TM}(\text{OR})_4$ ($\text{TM} = \text{Zr, Ti}$) with soluble lead compounds, such as acetate, in 2-methoxyethanol resulting in stable polymeric sols. From the early days of CSD the problems of local heterogeneities in the films, in the form, for example, of the non-ferroelectric surface pyrochlore phase⁷⁻⁹ or zirconium- rich regions¹⁰ have been recognized. Heterogeneity on the atomic level has been demonstrated in amorphous alkoxide precursors of PZT by Extended X-ray Absorption Fine Structure spectroscopy (EXAFS)¹¹⁻¹³.

The TM alkoxides have been modified by substitution or addition of ligands less reactive towards hydrolysis such as acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$), or acetic acid (CH_3COOH)¹⁴. Examples include the use of acetylacetone to stabilize Ti alkoxide in the synthesis of PbTiO_3 thin films¹⁵, or both Zr and Ti alkoxides in the synthesis of PZT thin films¹⁶⁻¹⁸. This modifier has been also used to increase the pyrolysis temperature of the PZT precursor solution and consequentially influence the crystallization of the respective thin film; however it has been added to the already synthesized PZT solution prior to the film deposition^{19,20}. Acetic acid has also been used in PZT thin film processing in the role of a solvent and modifier^{9,21}.

We have used a selective modification of zirconium alkoxide by acetic acid and by acetylacetone to decrease its reactivity prior to the PZT sol synthesis. We have shown by EXAFS spectroscopy that a selective modification of the Zr alkoxide by acetic acid results in a more homogeneous distribution of constituent metal atoms in the PZT sol as compared to the sols prepared from either as-received or acetylacetone-modified Zr propoxide²².

Structural changes induced by the Zr modifiers are also reflected in the local neighborhood of the Pb-atoms²³. The differences between the three sols in terms of functional group contents could additionally be deduced from the differences in their thermal decomposition pathways. The improved homogeneity of acetic-acid modified PZT films is reflected in its functional response: optimum values of remanent polarization, coercive field and dielectric permittivity are obtained after annealing at 500 °C while the unmodified and acetylacetone-modified PZT films need to be annealed at 600 °C²⁴.

In this work we exploit Zr K-edge EXAFS analysis to follow structural changes in the Zr local environment induced by the addition of the two modifiers, from the Zr precursor, through the synthesis of the PZT sol to the transition from the sol to the amorphous film.

Experimental

PZT sols corresponding to the target composition of $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ with 10 mole % PbO excess were prepared by diluting zirconium n-propoxide (Alfa, 72.49 % in n-PrOH) and titanium n-propoxide (Alfa, 99.84 %) in 2-methoxyethanol (Aldrich, 99.3 %) and by adding lead acetate in the required quantity. Water-free lead acetate was obtained from lead acetate trihydrate (Alfa, ACS) by drying in vacuum at 70 °C for 16 h and in air at 140 °C to constant mass. The metal contents of the starting compounds were determined gravimetrically.

Zirconium n-propoxide was either used as received or modified prior synthesis. As modifiers, acetic acid (CH_3COOH , Aldrich, 100%) or acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$, Alfa, 99%) were used. Acetic acid was admixed to Zr propoxide in the molar ratio of 2 / 1 and diluted to 1 M by 2-methoxyethanol. Acetylacetone diluted by 2-methoxyethanol was added to Zr propoxide solution in 2-methoxyethanol in 2 / 1 molar ratio, the concentration was adjusted to

1 M with respect to Zr. The as-prepared 1M solutions were also used for EXAFS measurements.

The reaction mixtures were heated to approximately 60°C to dissolve lead acetate. After 2 hours of refluxing, distillation of the by-products and after cooling to room temperature addition of formamide (4vol. %, Alfa) stable sols (0.5 M, 100 ml batches) were obtained. All manipulations were performed in dry nitrogen atmosphere. For EXAFS measurements the PZT sols were further concentrated to 1 M solutions in order to increase signal-to-noise ratio.

PZT thin films were prepared from the 0.5 M PZT sols on sapphire (0001) by spin-coating and pyrolyzed at 350°C for 1 minute. The thickness of the films was approximately 200 nm as determined on a Rank Taylor Hobson profilometer.

The unmodified as well as the acetic-acid and acetylacetone modified Zr propoxide sols are denoted as Zr/0, Zr/OAc and Zr/Acac, respectively. For the PZT sols and films analogous notation is used.

Zr K-edge EXAFS spectra of the Zr and PZT sols were measured at the X1 experimental station in HASYLAB at DESY (Hamburg, Germany). A Si(311) double-crystal monochromator was used with 3 eV resolution at 18 keV. Harmonics were effectively eliminated by detuning the monochromator crystal using a stabilization feedback control. The sols were contained in liquid absorption cell with 0.5 mm lucite windows. Sample thickness of about 2 mm provided total absorption thickness of about 2 above Zr K-edge. The empty absorption cell served for reference spectrum measured in identical conditions.

Zr EXAFS spectra of the PZT films were measured in fluorescence detection technique using a 4-channel Ge fluorescence detector. The absorption spectra were obtained as the ratio of the fluorescence detector signal and the signal of the incident photon beam from the ionization cell filled with argon at ambient pressure. The same stepping progression was adopted as in

the case of the sol with an integration time of 4s/step. To improve signal to noise ratio, four consecutive runs were superimposed.

Results

Zr-sols

EXAFS spectra were analyzed by the University of Washington analysis programs using FEFF6 code for ab initio calculation of scattering paths^{25,26}. Fourier transforms of the k^3 weighted spectra of the different Zr sols are shown in Figure 1. Zr neighbors are discerned in two wide shells. Each shell is fitted separately in the k interval from $4 \text{ \AA}^{-1}$ to $14 \text{ \AA}^{-1}$. The R intervals of $[1.3 \text{ .. } 2.1 \text{ \AA}]$ and $[2.7 \text{ .. } 3.6 \text{ \AA}]$ are used for respective shells. The best fit results are collected in Table I.

The immediate neighborhood of Zr atoms in the unmodified Zr sol (Zr/0) is populated with six O atoms at two slightly different distances, namely $1.96 \text{ \AA}$ (~ 2 atoms) and $2.17 \text{ \AA}$ (~ 4 atoms). The second shell of neighbors consists of one Zr atom at $3.53 \text{ \AA}$ and of a large number (~ 10) of C atoms, at three distances between 2.96 and $3.69 \text{ \AA}$.

The modification of Zr alkoxide with acetylacetone (Zr/Acac) results in a significant change of coordination namely from ~ 6 to ~ 8 O atoms distributed nonuniformly at three distances: one at $2.01 \text{ \AA}$, three at $2.14 \text{ \AA}$ and four at $2.23 \text{ \AA}$. The second shell of neighbors consists only of six C atoms at two distances. Models including Zr atoms in the second coordination sphere were also tested, but no Zr-Zr correlations were found. A presence of a smaller amount of Zr neighbors (average coordination numbers below detection limit of 0.3) cannot be excluded.

By modification of Zr alkoxide with acetic acid (Zr/OAc) the immediate neighborhood of Zr atoms is populated by six to seven O atoms: one at 1.96 Å and the rest at 2.16 Å. The wide second shell of neighbors consists of one Zr atom at 3.54 Å and a large number (~ 12) of C atoms between 2.97 and 3.69 Å.

Amorphous PZT films on sapphire

The PZT films pyrolysed at 350 °C, are amorphous as determined by XRD²². The comparison of the Zr EXAFS spectra of the PZT sols, recorded in transmission mode, and respective thin films is shown in Figure 2. In spite of the much longer detection time the signal-to-noise ratio of the spectra measured on the films is about one order of magnitude lower. Nevertheless, the local environment of Zr atoms in the PZT films can be reliably deduced in the quantitative EXAFS analysis in the k interval from 4 Å⁻¹ to 11 Å⁻¹.

Figures 3-5 show the k^3 -weighted Fourier transforms of the Zr EXAFS spectra. Two shells of Zr neighbors are discerned in all three spectra. The spectra of the respective PZT sols²² are added for comparison. The complete list of best fit structural parameters is collected in Table II. Relatively high uncertainties in the number of neighbors in individual shells are due to the high correlation of the shell parameters N and σ^2 .

The local neighborhood of Zr atoms in PZT/0 (Figure 3) in the R -range 1.3 to 3.8 Å consists of about four O atoms at 2.14 Å and three O atoms at a much larger distance of 2.67 Å. Three Zr and six O atoms are determined in the second coordination shell. In PZT/Acac film the local Zr neighborhood (Figure 4) strongly differs from the one determined in PZT/0. The first coordination shell consists of about seven O atoms: five at 2.14 Å and two at 2.29 Å. The second shell is composed of about two Zr atoms at 3.39 Å and about seven C atoms at 3.71 Å.

In the PZT/OAc film the local zirconium environment is again different (Figure 5). The first shell of neighbors is comprised of about six O atoms: four at 2.14 Å and two at 2.32 Å. The second shell of neighbors consists of one Zr atom at 3.44 Å and about ten C atoms at three distances between 2.83 and 3.68 Å.

Discussion

Zr-sols

Zr n-propoxide reacts with the solvent 2-methoxyethanol by the transalcoholysis reaction, i.e. by exchange of alkoxide groups ¹⁴, resulting in a less reactive mixed alkoxide (Eq. 1). The extent of the exchange has not been determined within this study; we nevertheless expect that x in Eq. (1) is close to 4 in agreement with ²⁷. In addition, the solvent may coordinatively bond to the alkoxide molecules via the hydroxy and the ether groups ²⁸.

EXAFS analysis of Zr/0 sol reveals a six-fold coordination of O atoms forming a distorted octahedron and one Zr atom at 3.53 Å. A large number of carbon atoms in the second shell of neighbors stems from different organic groups in the solution (Table I).

Our results indicate oligomeric Zr units, most probably dimeric, in agreement with the model of Peter et al. ²⁹ who examined the structure of Zr n-propoxide in a n-propanol solution, and found six O atoms evenly distributed at three distances, one Zr atom at 3.52 Å and proposed dimeric units with two terminal, two bridging and two ROH-coordinated Zr-O bonds. We

found a simpler distribution of bond distances in our case: two shorter and four longer Zr-O bonds. Such distribution of Zr-O bond distances has been observed also in a mixed Zr-Ti n-propoxide in n-propanol ³⁰.

The reaction of Zr alkoxide with acetylacetone in a 1 / 2 molar ratio in should result in the exchange of the functional groups ¹⁴ (Eq. 2) with an increase of coordination number of zirconium as a consequence of chelate-bonding of the acetylacetonate groups. Note that the equation does not include any coordinative bonding of the solvent.

The absence of Zr-Zr correlations in the Zr/Acac sol, established by EXAFS (Table I) indicates monomers. The eightfold coordination of O atoms is strongly asymmetric which confirms that different groups – chelating acetylacetonate, 2-methoxyethoxide and/or propoxide - are bonded to Zr atoms, in agreement with stoichiometric considerations. We cannot exclude coordinative bonding of the solvent molecules. This leads to the conclusion that the original Zr dimers disintegrate into monomers upon reaction of acetylacetone with Zr alkoxide.

In contrast, Peter et al. ³¹ observed that upon addition of acetylacetone to Zr butoxide in a strongly diluted (0.03 molal) n-butanol solution, dimers were obtained with two moles and monomers with four moles of acetylectone. The difference could arise from the dilution, and the choice of the solvent, 2-methoxyethanol in our case, and consequently, its exchange reaction with the original Zr propoxide.

Zr alkoxide reacts with acetic acid in a 1 / 2 molar ratio to yield a mixed Zr alkoxide acetate (Eq. 3).

In Zr/OAc sol the local neighborhood of Zr atoms is populated with six to seven O atoms, and about one Zr atom at 3.53 Å (Table I). Note that both coordination numbers 6 and 7 are common for zirconium species. The result again indicates dimeric Zr units as in the case of the unmodified Zr precursor. The Zr-O and Zr-Zr distances remain unchanged, however the distribution and possibly the number of O neighbors in the nearest coordination shell are altered in comparison to unmodified Zr sol. We ascribe this change to the reaction of acetic acid with the Zr alkoxide. In agreement with stoichiometric considerations each Zr atom is coordinated by two acetate and at most four alkoxide groups, depending on the type of reaction.

This result is in agreement with similar findings for Zr n-propoxide or n-butoxide modified with 2 moles of acetic acid in a 0.03 molal parent alcohol solution, where FTIR and EXAFS spectroscopy demonstrated that acetate groups substitute terminal alkoxide groups and that the dimeric Zr-Zr units are preserved³¹.

PZT sols

Upon the synthesis of PZT sol the heterometallic precursor should be formed by a reaction between individual transition-metal (TM = Zr, Ti) alkoxide and lead acetate^{6,28}. The reaction can proceed by ester elimination and/or addition leading to the formation of oxo viz. acetate bridges between the two metal atoms. (Eq. 4, 5). (The schematic reactions below are for one functional group per reactant.) In reality both reactions occur, leading to a product containing oxo, alkoxo and acetate groups (Eq. 6)³²⁻³⁴.

The three Zr sols have been used in the synthesis of the PZT sols and the local neighborhoods of Zr in the PZT sols have been examined ^{22,24}. These results are briefly summarized here. In all cases the local environment of Zr atoms consists of two broad shells of neighbors. The first shell is composed of six to eight O atoms at two slightly different distances, 2.10-2.14 Å and 2.20-2.28 Å. In PZT/0 and PZT/Acac sols the coordination is close to eight while the lower octahedral coordination is more probable for the PZT/OAc sol. The second shell of Zr neighbors is composed of Zr and C atoms. The number of Zr neighbors located at 3.44-3.49 Å is about three for PZT/0 and PZT/Acac sols and only about one for PZT/OAc sol.

In the PZT/0 sol we observe a major change in the local Zr environment ²² in relation to the Zr/0 sol. In the first shell of neighbors not only the number of O atoms increases from six to about eight, but also the distribution of distances changes (Figure 6a). The short Zr-O distance at 1.96 Å attributed to two terminal alkoxide groups (in addition to the four Zr-O bonds at 2.14 Å from bridging and/or coordinated groups) in Zr/0 is not present in the PZT/0 sol; instead there are almost eight O atoms equally distributed at 2.13 and 2.25 Å. In the second shell of neighbors the number of Zr atoms increases from ~ 1 for Zr/0 to ~ 3 for PZT/0 sol. In

addition the number and the distribution of C atom neighbors are changed: in the PZT/0 sol there are less C atoms, located at larger distances, than in the Zr/0.

The increase of the number of Zr-O bonds and bond distances leads to the conclusion that the degree of cross-linking of Zr species in PZT/0 sol is increased; the short bond-distances stem namely from the terminal groups ²⁹. In addition, the increased number of Zr- Zr correlations also supports increased cross-linking. Segregation of Zr species has been quite commonly observed in various amorphous Zr containing alkoxide precursors (dried or heat treated at a few 100 °C) ^{11-13,35-37}.

Our EXAFS results therefore show, that for Zr species the major reaction during the PZT/0 sol synthesis is the formation of larger oligomeric units. A possible reaction yielding such species could take place during refluxing, and distillation i.e. at temperatures close to the boiling point of the PZT sol. Namely, at such temperatures, polynuclear oxo-alkoxides may form by the ether elimination-reaction (Eq. 7) as reported for TM-alkoxides including Zr such as Zr₃O(OiPr)₁₀ or for the reaction between Ba and Ti alkoxides ²⁸.

The summary reaction between Pb-acetate and TM-alkoxides in 2-methoxyethanol proceeds to some extent as confirmed by the formation of esters – these are by-products of the ester-elimination reaction (Eq. 4) - and also by Pb-EXAFS that showed the existence of a Pb-Ti correlation ²³. We also cannot exclude the possibility of heterometallic bonding below the sensitivity of the EXAFS method.

In the PZT/Acac sol the local environment of Zr atoms is composed of about eight O atoms in the first shell distributed at 2.13 and 2.25 Å in a 2 to 1 ratio and of two to three Zr atoms in

the second shell ²² (Figure 6b). Similarly as in the unmodified PZT sol the EXAFS results point to the segregation of Zr species.

Note however that the distribution of O neighbors in PZT/Acac sol is different from the one in PZT/0 sol, indicating that the chemical compositions – the type and amount of functional groups bonded to metal atoms in the two PZT sols - are different as confirmed by thermal analysis of the respective as-dried sols²⁴. Further, clustering of Zr species, possibly via the formation of oxo-alkoxides²⁸, is not hindered by the presence of acetylacetonate groups.

In PZT/OAc sol Zr atoms are octahedrally coordinated with O atoms distributed in a 4 to 2 ratio at 2.14 and 2.25 Å. The second shell is composed of about one Zr atom at 3.44 Å and of about ten C atoms at two distances ²². The comparison of Zr atom environments in Zr/OAc and PZT/OAc sols reveals that the octahedral coordination of Zr is retained upon the synthesis of PZT sol, however, the distribution of Zr-O distances is changed. Namely, the short Zr-O distance of 1.96 Å in the original Zr/OAc is not present in the PZT/OAc. The Zr-Zr distance in PZT/OAc is smaller than in Zr/OAc, 3.44 Å instead of 3.54 Å (Figure 6c). Similarly, a decrease in the Zr-Zr distance upon modification with acetic acid has been observed by Peter et al. ³¹. By modification with acetic acid the original dimeric structure of the Zr/OAc precursor is still retained in the PZT/OAc sol, which is not the case in PZT and PZT/Acac.

Amorphous PZT films

The local neighborhood of Zr atoms in the amorphous PZT/0 film consists of about four O atoms at 2.14 Å and about three O atoms at a much larger distance of 2.67 Å. Three Zr and six O atoms are determined in the second shell of neighbors, at 3.43 and 4.19 Å (Table II) ³⁸. The arrangement of O atoms around Zr atoms in the film is significantly altered from that in the PZT/0 sol: the distribution of O atoms in the first shell of neighbors is changed, the three O

atoms in the film are located at a much larger distance than in the sol, 2.67 Å as compared to 2.20 Å. The second shell consists of Zr and O atoms only, no C atoms could be determined as in the sol (Figure 7a). We attribute this difference to the decomposition of the organic groups, which occurs, according to thermal analysis of the respective sol ²⁴, between 250 and 350 °C. The local structure around Zr atoms is similar to Zr neighborhood in tetragonal zirconia particles ³⁹.

In PZT/Acac film the Zr neighborhood consists of about five O atoms at 2.14 and about two O atoms at 2.29 Å. The second shell of neighbors consists of about two Zr atoms at 3.39 Å and about ten C atoms at two distances. The difference between PZT/Acac sol and film is not as significant as in the previous case: in the first shell of neighbors the total number of O atoms is decreased. In the second shell the main difference is in the number of Zr neighbors and the distances between them: both are lower in the film. In both cases C atoms are non-equally distributed at two distances (Figure 7b).

In PZT/OAc film the Zr local neighborhood remains almost unchanged as compared to the PZT/OAc sol: the first shell of neighbors is composed of about four O atoms at 2.14 and two O atoms at 2.32 Å, in the form of a distorted octahedron. The Zr-O distances in the sol and in the film are the same within experimental errors. The second shell of neighbors consists of one Zr atom at 3.44 Å, the distance is again the same as in the sol (Figure 7c). The number and distribution of C atoms in the sol and in the film are similar. Acetic acid therefore successfully contributes to the retention of small oligomeric Zr units in the transition from the sol to the amorphous film.

Summary

The sols for $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) thin films were prepared by 2-methoxyethanol-route from lead acetate, titanium n-propoxide and zirconium n-propoxide, the latter either unmodified or modified with acetylacetone or acetic acid in a 2/1 molar ratio, and deposited on sapphire (0001). Structural changes in the Zr local environment, induced by the addition of the two modifiers, from the synthesis of the PZT sol and upon transition from the sol to the amorphous film were traced by Zr K-edge EXAFS analysis in transmission and fluorescence mode, respectively. To our knowledge this is the first EXAFS study of amorphous PZT thin films.

In Zr propoxide dissolved in 2-methoxyethanol Zr atoms form small oligomeric units, most probably dimers, which are retained also upon modification with acetic acid. Upon addition of acetylacetone, Zr monomers are formed.

In the unmodified PZT sol the segregation of Zr species resulting in larger oligomeric units is confirmed by EXAFS. The immediate neighborhood of Zr atoms changes markedly upon transition from the sol to the amorphous film: the local structure around Zr atoms is similar to the one found in tetragonal ZrO_2 particles. In acetylacetone-modified PZT sol, clustering of Zr species is observed continuing into the amorphous film. By modification with acetic acid the original dimeric units from the Zr sol remain in the PZT sol as well as in the amorphous film. The changes in the Zr local environment in the transition from the sol to the film are schematically depicted in Figure 8.

Both modifiers, acetic acid and, to a lesser extent, acetylacetone suppress the changes in the local Zr atom environment upon transition from the PZT sol to the amorphous film. However, while acetic acid is successful in retaining the original dimeric Zr units, the clustering of Zr species occurs when acetylacetone is used. It is possible that in the case of the two modifiers the retention of the Zr local environment upon transition from the sol to the amorphous film is the consequence of different processes taking place during the pyrolysis step at 350 °C. Both

modifiers induce the higher weight losses of the as-dried sols and they influence, each in a specific way, the thermal decomposition pathways of the sols ²⁴. The crystallization of the perovskite phase on sapphire is enhanced in the acetic-acid modified PZT and to a lesser extent for acetylacetone modified in relation to unmodified PZT films. Homogeneous microstructure is characteristic for the acetic acid modified PZT films ⁴⁰. The improved chemical homogeneity of the PZT films achieved by acetic acid modification is reflected in their improved functional response even after low annealing temperatures. The unmodified, acetylacetone and acetic-acid modified PZT films on platinized silicon substrates annealed at 600 °C exhibit the values of remanent polarization, coercive field, dielectric permittivity 17, 21 and 22 $\mu\text{C}/\text{cm}^2$, 73, 66 and 52 kV/cm and 1088, 1145 and 1444, respectively ²². The acetic-acid modified PZT 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 ²⁴.

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Table I: Parameters of the nearest coordination shells around Zr atoms in different Zr sols: atomic species, average number N, distance R and Debye-Waller factor σ^2 . Uncertainty of the last digit is given in parentheses.

	Zr/0			Zr/Acac			Zr/OAc		
Zr neighbor	N	R (Å)	σ^2	N	R (Å)	σ^2	N	R (Å)	σ^2
O	1.7(5)	1.96(1)	0.003(1)	1.0(3)	2.01(1)	0.002(1)	1.2(4)	1.96(1)	0.002(1)
O	4.5(5)	2.17(1)	0.007(1)	3.1(5)	2.14(1)	0.002(1)	5.7(4)	2.16(1)	0.006(1)
O	-	-	-	3.9(5)	2.23(1)	0.005(1)	-	-	-
C	2.1(6)	2.96(2)	0.002(1)				2.4(6)	2.97(2)	0.003(1)
C	3.5(8)	3.09(3)	0.002(1)	0.8(5)	3.19(3)	0.002(1)	3.4(8)	3.11(3)	0.003(1)
Zr	0.9(2)	3.53(2)	0.004(1)	-	-	-	1.0(2)	3.54(2)	0.004(1)
C	4.2(9)	3.69(5)	0.002(1)	4.5(9)	3.67(1)	0.003(1)	6(2)	3.69(5)	0.002(1)

TABLE II: Parameters of the nearest coordination shells around zirconium atom in PZT thin films: atomic species, average number N, distance R and Debye-Waller factor σ^2 . Uncertainty of the last digit is given in parentheses.

	PZT/0 film ^{a)}			PZT/Acac film			PZT/OAc film		
Zr neighbor	N	R (Å)	σ^2	N	R (Å)	σ^2	N	R (Å)	σ^2
O	4.0(7)	2.14(4)	0.003(1)	5.0(8)	2.14(2)	0.004(2)	4.4(4)	2.14(1)	0.0010(5)
O	2.8(7)	2.67(4)	0.002(1)	2.0(4)	2.29(2)	0.004(2)	2.0(4)	2.32(2)	0.007(5)
C							1.5(7)	2.83(4)	0.001(1)
C				3.3(5)	3.36(3)	0.003(1)	2.0(7)	3.32(4)	0.001(1)
Zr	3(1)	3.43(2)	0.006(2)	1.6(4)	3.39(2)	0.004(2)	1.0(4)	3.44(4)	0.004(2)
C				7.0(9)	3.71(3)	0.003(1)	6.5(8)	3.68(4)	0.001(1)
O	6(1)	4.19(5)	0.007(3)						

^{a)} The data for PZT/0 film are from Ref. 38.

Figure Captions

Figure 1: The k^3 weighted Fourier transforms of zirconium EXAFS spectra of Zr sols. Solid line- experiment, dotted line - model.

Figure 2: Zr K-edge EXAFS spectra of PZT sols (solid line) and amorphous thin films on (0001) sapphire (dots). The spectra of PZT/0 sol and film are from Ref. 38.

Figure 3: The k^3 weighted Fourier transforms of zirconium EXAFS spectra of PZT/0 sol and the respective amorphous thin film on (0001) sapphire, calculated in the k range of $4 - 11 \text{ \AA}^{-1}$: (Solid line – experiment, dashed line - model). (The data are from Ref. 38.

Figure 4: The k^3 weighted Fourier transforms of zirconium EXAFS spectra of PZT/Acac sol (from Ref. 22) and the respective amorphous thin film on (0001) sapphire, calculated in the k range of $4 - 11 \text{ \AA}^{-1}$: (Solid line – experiment, dashed line - model).

Figure 5: The k^3 weighted Fourier transforms of zirconium EXAFS spectra of PZT/OAc sol (from ref. ²²) and the respective amorphous thin film on (0001) sapphire, calculated in the k range of $4 - 11 \text{ \AA}^{-1}$: (Solid line – experiment, dashed line - model).

Figure 6: Number of Zr neighbors (N) at interatomic distances (R) for a)Zr/0 and PZT/0, b)Zr/Acac and PZT/Acac and c)Zr/OAc and PZT/OAc sols deduced from the EXAFS results. Note that only Zr-O and Zr-Zr correlations are included, the Zr-C correlations are not shown here. Error bars represent the uncertainty of the results.

Figure 7: Number of Zr neighbors (N) at interatomic distances (R) for a) PZT/0, b) PZT/Acac and c) PZT/OAc sols and amorphous thin films deduced from the EXAFS results. Note that

only Zr-O and Zr-Zr correlations are included, the Zr-C correlations are not shown here. Error bars represent the uncertainty of the results.

Figure 8: The scheme illustrates the changes in Zr local environment in the process of PZT thin film formation depending on the choice of the modifier that can be deduced from the EXAFS results.

Figure 1: The k^3 weighted Fourier transforms of zirconium EXAFS spectra of Zr sols. Solid line- experiment, dotted line - model.

Figure 2: Zr K-edge EXAFS spectra of PZT sols (solid line) and amorphous thin films on (0001) sapphire (dots). The spectra of PZT/0 sol and film are from ref. ³⁸.

Figure 3: The k^3 weighted Fourier transforms of zirconium EXAFS spectra of PZT/0 sol and the respective amorphous thin film on (0001) sapphire, calculated in the k range of $4 - 11 \text{ \AA}^{-1}$. (Solid line – experiment, dashed line - model). (From ref. ³⁸)

Figure 4: The k^3 weighted Fourier transforms of zirconium EXAFS spectra of PZT/Acac sol (from ref. ²²) and the respective amorphous thin film on (0001) sapphire, calculated in the k range of $4 - 11 \text{ \AA}^{-1}$: (Solid line – experiment, dashed line - model).

Figure 5: The k^3 weighted Fourier transforms of zirconium EXAFS spectra of PZT/OAc sol (from ref. ²²) and the respective amorphous thin film on (0001) sapphire, calculated in the k range of $4 - 11 \text{ \AA}^{-1}$: (Solid line – experiment, dashed line - model).

Figure 6: Number of Zr neighbors (N) at interatomic distances (R) for a)Zr/0 and PZT/0, b)Zr/Acac and PZT/Acac and c)Zr/OAc and PZT/OAc sols deduced from the EXAFS results. Note that only Zr-O and Zr-Zr correlations are included, the Zr-C correlations are not shown here. Error bars represent the uncertainty of the results.

Figure 7: Number of Zr neighbors (N) at interatomic distances (R) for a) PZT/0, b) PZT/Acac and c) PZT/OAc sols and amorphous thin films deduced from the EXAFS results. Note that only Zr-O and Zr-Zr correlations are included, the Zr-C correlations are not shown here. Error bars represent the uncertainty of the results.

Figure 8: The scheme illustrates the changes in Zr local environment in the process of PZT thin film formation depending on the choice of the modifier that can be deduced from the EXAFS results.