Thermal Analysis Study of Diol-Based Precursors for Chemical Solution Deposition of
0.7 Pb(Mg_{1/3}Nb_{2/3})O₃-0.3 PbTiO₃ Thin Films

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Abstract

Thermal decompositions of the precursors for chemical solution deposition of 0.7 Pb(Mg_{1/3}Nb_{2/3})O₃-0.3 PbTiO₃ thin films were studied. The precursors were prepared from lead acetate or acetylacetone-modified lead acetate by diol-based route, and dried at 100 °C. Thermal decompositions of the PT, PMN and PMN-PT precursors in air occur stepwise. Between room temperature and approximately 200 °C the weight loss of a few % is due to evaporation of residual solvents. Organic groups decompose in the 200 - 400 °C and 400 -650 °C ranges. The thermal decompositions are affected by the choice of the Pb-compound and chemical composition of the sample.

Keywords: PMN-PT, sol-gel, thin films, precursors, thermal analysis

Introduction

Lead magnesium niobate - lead titanate is a solid solution of relaxor Pb(Mg_{1/3}Nb_{2/3})O₃ and ferroelectric PbTiO₃. Depending on the composition it exhibits interesting dielectric, electrostrictive and piezoelectric properties ¹. In thin film form the materials can be used for applications in microelectromechanical systems (MEMS). The difficulty in Chemical Solution

Deposition (CSD) of PMN-PT thin films is formation of non-ferroelectric pyrochlore phases which could be for example avoided by implementing the principle of solid-state Columbite synthesis ² into the solution synthesis approach. The synthesis of PMN or PMN-PT sols for thin film deposition using a bimetallic Mg-Nb precursor has been reported both for 2-methoxyethanol ^{3,4,5} and diol-based routes ⁶.

In this work the diol-based solutions⁷ for the 0.7 Pb(Mg_{1/3}Nb_{2/3})O₃ – 0.3 PbTiO₃ (0.7PMN-0.3PT) thin films ⁶ were prepared from different Pb-reagents, the lead acetate, which has been commonly used in alkoxide based sol-gel processing of lead-based thin films, including Pb(Zr,Ti)O₃ ⁸ and PMN or PMN-PT ³⁻⁶. In another approach lead acetate trihydrate was prior synthesis reacted with acetylacetone, which is also used as a chelating agent, for example to decrease the reactivity of transition metal alkoxides ⁹. A thermal analysis study of the dried precursors at different steps of the synthesis has been performed to elucidate the influence of solution chemistry on the properties of the precursors which could be further implemented in optimisation of thin film processing.

Experimental

The liquid precursors for 0.7 Pb(Mg_{0.33}Nb_{0.67})O₃ – 0.3 PbTiO₃ (PMN-PT) thin films were prepared by two routes which differed in the lead reagent. In the first, -ac route, lead acetate trihydrate was dissolved in 1,3-propanediol, refluxed and vacuum distilled, while in the second, -acac route, lead acetate trihydrate was first reacted with an equimolar amount of acetylacetone, then refluxed and vacuum distilled. The Mg-Nb precursor was synthesized from a mixture of Mg- and Nb-ethoxides in a 1 / 2 stoichiometric ratio in 1,3-propanediol / acetic acid solvents. The PMN and PT sols were synthesized separately from Pb-acetate or Pb-acetylacetonate precursors, Mg-Nb precursor and Ti diisopropoxide diacetylacetonate in 1,3-propanediol as described in detail in ⁶. A scheme of the syntheses is presented in Fig. 1.

All solutions contained 15 mole % of lead oxide excess. The acetate- and acetylacetonate-PMN and PT sols were mixed in a 70/30 molar ratio.

Figure 1: Scheme of the PMN-PT sol syntheses. (-Et: ethyl, -CH₂CH₃, -iPr: isopropyl, -CH(CH₃)₂, 1,3-PD: 1,3-propanediol, HOCH₂CH₂CH₂OH, Ac-OH: acetic acid, CH₃COOH, AcacH: acetylacetone, CH₃COCH₂COCH₃).

The samples for thermal analysis were dried at 100 °C in ambient atmosphere. Thermal decompositions of the dried precursors were followed by simultaneous thermogravimetric and differential thermal analysis (TGA/DTA, Netzsch STA 409 C) coupled with evolved gas analysis (EGA, ThermoStar 300, Balzers) in Pt/Rh crucibles with a heating rate of 10 K/min. The final temperature of all analyses was limited to 650 °C in order to avoid possible contamination of the furnace by sublimation of lead oxide. The mass of the samples was between 50 mg and 70 mg for the analyses performed in synthetic air (80%N₂-20%O₂) or Ar and about 20 mg for those in oxygen as more exothermic reactions were expected. Phase

composition of selected samples was determined by X-ray diffraction (X'Pert Pro MPD, Cu K α radiation)

Results

Figure 2 shows the thermal decomposition of the acetylacetonate-modified lead reagent (Pb-acac) as compared to dehydrated lead acetate. The weight loss of Pb-acac upon heating to 500 °C is 26.36 %. The sample loses 1.60 % weight upon heating to 180 °C, which is due to removal of water as confirmed by EGA. The major weight loss of almost 24 % occurs between 180 °C and 460 °C. The weight loss is accompanied by an endo peak at 250 °C and two strong exo peaks at 374 °C and 435 °C. EGA analysis confirms the evolution of CO₂, H₂O and traces of acetone as a consequence of organic groups' decomposition. In contrast, dehydrated lead acetate loses 28.66 % weight between 210 °C and 430 °C with the major exo peak at 399 °C. Thermal decomposition of Pb-acac precursor follows a different course from that of dehydrated Pb-acetate which confirms a reaction between Pb-acetate and acetylacetonate.

Figure 2: TG/DTA curves of Pb-acac precursor and dehydrated Pb-acetate recorded in air. Temperature ranges of evolution of H₂O and CO₂ are marked by arrows.

We further analysed the thermal decomposition of the PMN-PT precursor, prepared by reacting the PMN-ac and PT-ac precursors. The TG/DTA curves of the three precursors, recorded in air, are collected in Figure 3. The PMN-ac precursor loses upon heating to 650 °C 21.58 %. Between room temperature and 200 °C the weight loss of 2.86 % without any major thermal effects is attributed to the loss of residual solvents as confirmed by EGA (spectra not shown here). Between 200 °C and 400 °C the weight loss of 11.50 % is accompanied by a strong exo effect with the main peak at 266.4 °C and between 400 °C and 650 °C a further weight loss of 7.22 % with two exo peaks at 458 °C and 513 °C is detected. The weight loss in 200 °C – 650 °C accompanied by strong exo peaks in air is due to thermal oxidation of organic groups present in the sample, namely acetate, alkoxide and possibly also coordinated solvents. A two-step decomposition of organic groups in air has been previously reported for acetate-alkoxide derived lead-based perovskites¹⁰⁻¹².

The thermal decomposition of PT-ac precursor with the total weight loss of 23.54 % is characterized by two exo effects with the major peaks at 280 °C and at 477 °C. The PMNac-PTac precursor exhibits the total weight loss of 23.54 %, again with two regions of exo effects with the major peaks at 272 °C and 511 °C.

From the comparison of the TG/DTA curves we conclude that the thermal decomposition of the PMN-PT precursor is not a sum of decompositions of its constituent parts. We expect that the PMN-ac and PT-ac components reacted already in solution resulting in a new liquid precursor. We nevertheless observe that all three precursors show similarities especially in the DTA curves.

Figure 3: TG / DTA curves of PMN-ac, PT-ac and PMNac-PTac precursors recorded in air.

We further examined thermal decompositions of the four PMN-PT precursors prepared from either Pb-acac and/or Pb-acetate. The results of TG/DTA/EGA analyses are summarised in Figure 4 which also includes the derivative TG (DTG) curves as insets.

All PMN-PT precursors lose weight gradually upon heating to 650 °C. The total weight losses are between 22 % and 25 %. We can distinguish three main regions of thermal decomposition, similarly as described above for PMNac-PTac. Note that the DTG curves reveal more clearly than the TG curves the similarities between the precursors: for example, the two PMN-PT precursors which contain PMN-ac exhibit a broad DTG peak in the 200 – 340 °C range, a weaker peak at about 400 °C and another strong twin peak in 480-520 °C range.

Between RT and approximately 200 °C all samples lose a few % of weight, accompanied by weak, broad endothermic peaks. Mass spectrometry of evolved gases confirmed evolution of H₂O and in a lesser extent of CO₂ which we attribute to evaporation of residual solvents.

Between 200 °C and 400 °C the major weight loss of about 10 % is accompanied by strong exo peaks. These coincide with the DTG and the EGA peaks of H₂O (m/e 18) and CO₂ (m/e 44). The simultaneous evolution of H₂O and CO₂ confirms oxidation of organic – acetate, acetylacetonate and various alkoxide - groups upon heating. A weak peak of acetone (m/e 58)

is a by-product of decomposition of both acetate and acetylacetonate groups and it is more pronounced in the –acac based samples, in agreement with ¹¹.

The weight loss of about 5 % between 400 °C and 650 °C is accompanied by at least two overlapping exo peaks which coincide with two EGA (CO₂) peaks, while the EGA signal of H₂O is noticeably lower and it decreases. We attribute this weight loss mainly to thermal oxidation of predominantly carbonaceous residues which could not be completely decomposed at lower temperatures in air.

The PMN-ac and the PMN-acac containing samples can be distinguished by characteristic sequences of DTA, EGA, and as mentioned above, also DTG peaks, which could be used as their 'fingerprint' patterns.

The precursors after the thermal analysis (=heating to 650 °C with 10K/min in air) consisted of both pyrochlore and perovskite (P) phases. It should be noted that this temperature was selected to follow the thermal decomposition of the precursors and not to crystallize the perovskite phase. The choice of the Pb-reagent did not have a major influence on the phase composition of the precursors.

Figure 4: TG, DTA and EGA curves of PMN-PT precursors prepared from Pb-acac reagent and/or Pb-acetate recorded in air. Inset in the TG graphs: derivative TG (DTG). The EGA curves include the mass peaks (m/e) 18: H₂O, (m/e) 44: CO₂, (m/e) 58: CH₃COCH₃ (acetone).

We followed the influence of the atmosphere on the course of thermal decompositions of the PMN, PT and PMN-PT precursors. We show in Figure 5 the results for the PMN-ac precursor, and, as expected, the trends were quite similar for all examined samples. All samples lose a few % of weight upon heating to 200 °C notwithstanding the atmosphere. Thermal decomposition of organic groups in oxygen in the 200 – 400 °C range is more exothermic and

results in a larger weight loss than in air. Consequently the next step of the decomposition in the 400 – 650 °C temperature range is more pronounced in air than in oxygen. Namely, the weight losses of PMN-ac sample in oxygen are 13.22 % and 5.04 % as compared to 11.42 % and 7.24 % for the 200 – 400 °C and 400-650 °C ranges, respectively, while the DTA curves reveal the strongest exo peaks at 250 °C and 345 °C for the sample heated in oxygen and at 266 °C and 513 °C for the sample heated in air.

Thermal decomposition of the PMN-ac sample in Ar occurs without major DTA effects. We detected metallic lead in the samples after the thermal analysis by XRD which was due to strongly reducing conditions in the thermal analyser upon decomposition of organic groups.

Figure 5: TG/DTA curves of the PMN-ac precursor recorded in synthetic air, oxygen and argon.

Summary

Thermal decompositions of the precursors for chemical solution deposition of 0.7 Pb(Mg_{1/3}Nb_{2/3})O₃-0.3 PbTiO₃ thin films were studied. The precursors were prepared from the

PMN and PT diol-based sols using either lead acetate or acetylacetone-modified lead acetate, which were reacted in a stoichiometric ratio, and dried at 100 °C. The PMN, PT and PMN-PT precursors prepared from both lead reagents underwent similar courses of thermal decomposition in air: in the first step, up to 200 °C residual solvents evaporated, while in the next two steps, in the 200 – 400 °C and 400 – 650 °C ranges thermal oxidation of different organic groups occurred. The PMN-ac and the PMN-acac containing PMN-PT precursors could be distinguished by characteristic sequences of DTG, DTA, and EGA peaks, which could be used as their 'fingerprint' patterns.

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