PZT FILMS DEPOSITED BY A HYDROTHERMAL METHOD AND CHARACTERIZATIONS

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Abstract

We present a hydrothermal method to deposit PZT films. It uses a single-step hydrothermal process and user-friendly precursors. $Pb(Zr_{0.52},Ti_{0.48})O_3$ polycrystalline films, 5-10 µm thick, were produced in an aqueous basic solution (4M KOH) on titanium substrates in a closed autoclave with a temperature lower than 200°C. In order to have a better understanding of the growth phenomena, a study of the precursor "gel" using X-ray absorption spectroscopy (XAS) has been made. We thus obtained a first insight into its structure. Some actuation testing is also presented.

Introduction

Lead zirconate titanate (PZT), $Pb(Zr_x,Ti_{1-x})O_3$, is a well-known material for acoustic sensors and actuators, in particular in the Micro-ElectroMechanical Systems (MEMS) field. One of the reasons is its high piezoelectric coefficients, which are the highest near the morphotropic phase boundary (MPB) ($x \sim 0.52$). With most of the classical methods of deposition, PZT films thicker than about one micron cannot be obtained. However, thicker films should lead to higher strain/stress needed for some micro-actuators. A few years ago, 15-micron thick PZT films were deposited by a new method: the hydrothermal synthesis [1]. With this technique, thicker PZT films (tens of microns) can be deposited on non-planar substrates, which can allow new types of micro-actuators and micro-sensors. Other advantages are the low temperature processing (less than 200°C) and its low cost. In the following years, several research teams took an interest in this method. Some have reported new types of micro-sensors [2] and micro-actuators [3-5].

We present a new hydrothermal treatment, which is a simplified process of the ones already reported. As far as we know, efforts have focused on applications rather than on the understanding of the phenomena occurring during the hydrothermal growth of PZT films. Believing that better films should be achieved with a better knowledge of these phenomena, we studied the "gel" leading to the hydrothermal PZT films. Results of X-ray absorption spectroscopy (XAS at Zr, Pb and Ti edges), giving an insight into the structure of this "gel", and piezoelectric measurements are presented.

Experimental procedure

The hydrothermal experiments were performed in an autoclave with a Teflon cup of 23 mL. The substrates were metal titanium plates or cantilevers covered with titanium oxide (native oxide or oxide obtained after a short heat-treatment). A hook was machined in the Teflon cover so as to maintain the substrates with Teflon wire. Chosen precursors were $Pb(NO_3)_2$ (1.27g of Carlo Erba 99.5%), $ZrOCl_2.8H_2O$ (0.792g of Fluka 99%) and TiO_2 (0.044g of Fluka 99%) powders. $TiCl_4$, TiS_2 and $Ti[O(CH_2)_3CH_3]_4$ were also tried as precursors for titanium but were rejected as they were more complicated to use and did not lead to better results. Hydroxide potassium (Carlo Erba for Analysis) was used as the mineralizer; its concentration was around 4M. The solution filled the two thirds of the autoclave.

The autoclave was placed in a sand bath leaving its cap in the air. A temperature gradient was thus induced. This gradient creates convection currents promoting ions transport and leading to a regular growing process on the whole substrate surface. The temperature was measured by a thermocouple at a precise place near the bottom of the autoclave. The best temperature was 180°C.

In order to grow films, the hydrothermal treatment lasted 24 to 30 hours. Shorter times were also used to see the growth evolution.

Adding KOH after mixing the precursors of Pb and Zr in water led to a kind of gel that was studied by E.X.A.F.S. (Extended X-ray Absorption Fine Structure). Table 1 summarizes the gels we analyzed: the preparation is always the same, only the quantities of the products change. The experiments were conducted at the Zr K edge (17998 eV), Pb LIII edge (13035 eV) and Ti K edge (4965 eV). We used synchrotron radiation at L.U.R.E. (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique), Orsay, France, on XAS4 in the D44 beamline from DCI. All the XAS data were collected in transmission mode at room temperature using a Si (311) monochromator and a resolution of 2 eV. X.A.N.E.S.

(X-ray Absorption Near Edge Structure) experiments were also performed on some of the gels to determine which crystalline reference compounds to use in the EXAFS spectra treatment.

Gel	$Pb(NO_3)_2$	$ZrOCl_2.8H_2O$	KOH	TiO_2
PZ1	1	1	1/4	0
PZ4	1	1	1	0
PZ8	1	1	2	0
PZT4	1	1	1	1
PZT8	1	1	2	1
PZTX4	1	1	1	4
P2Z4	2	1	1	0
ZK4	0	1	1	0
ZKT4	0	1	1	1
PTX4	1	0	1	4

Table 1: Signification of the names the gels. The numbers are to be multiplied by the usual quantities.

The actuation testing was performed with the Optical Heterodyne Interferometer BMI SH-130 designed by Royer et al. [6]. Piezoelectric coefficient "d_{33}" was determined with the thickness motion of a plate and "d_{31}" with the flexion of unimorph and bimorph cantilevers (150 to 500 µm thick with a length varying from 6 to 12 mm). Bimorph samples could also be used as unimorph cantilevers with driving only one film. When not using the titanium metal, electrodes were deposited by evaporation and consisted of 500Å Ti and 3500 Å Au. Contacts with wires were made with conducting epoxy. The samples were tested without any post-polarization treatment.

Results and discussion

Generality

With a temperature of 180°C, we obtained films made of a pure polycrystalline phase of PZT near the MPB as shown with XRD (cf. Fig. 1). They consisted of a homogenous distribution of regular cubes with edges about 1 µm (cf. Fig. 2). The thickness of the films, measured by cross-section SEM and with a profilometer, was between 5 and 10 µm after 24 hours of deposition. A study of films with the hydrothermal treatment stopped at earlier times revealed that a thin intermediate layer, containing lead and zirconium atoms, formed before the nucleation and then growth of the PZT cubes.

Only a small amount of TiO_2 was needed since most of the titanium of the PZT probably came from the substrate, at least at the beginning of the process. Using more titanium or an oven instead of the sand bath showed that there was a competition between growth of $PbTiO_3$ (or Ti-rich PZT) and PZT: choosing the good parameters insure that PZT growth is favored with no trace of $PbTiO_3$.

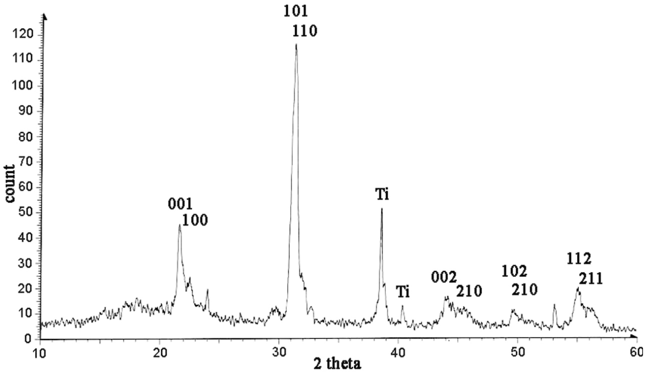

Figure 1: XRD of the hydrothermal PZT films

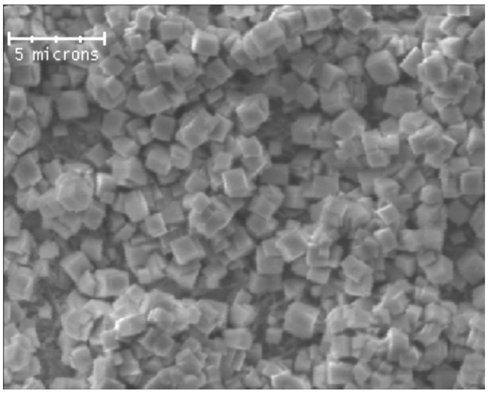

Figure 2: SEM picture of the hydrothermal PZT films

The heat treatment of the titanium substrate was used in order to help the growth of PZT, since Ti is oxidized in PZT, and to increase the adherence of the PZT films, precursors reacting with the thin titanium oxide film. However, a very well crystallized titanium oxide film (rutile form after a heat treatment above 700°C) slowed the hydrothermal growth of PZT. The best results were obtained with thin amorphous TiO_2 films, probably because the formation of titanium hydroxide on the surface of the substrate, which is supposed to be the true precursor of titanium, is facilitated by the amorphous phase, which is more reactive. Native oxide can also be used, but pollution in that layer and oxygen vacancies can lead to a PZT film of lesser quality.

We also noticed that the order and the way to put the precursors and the mineralizer into the solution greatly influenced the quality of the films. Some changes were directly visible to the naked eye. Adding KOH to a solution of $Pb(NO_3)_2$ and then adding $ZrOCl_2.8H_2O$ led to the partial precipitation of the lead. On the contrary, a gel was formed when adding KOH to a solution of $Pb(NO_3)_2$ + $ZrOCl_2.8H_2O$. The best results were obtained when forming the gel: a mix of phases (usually $PbTiO_3$ and PZT) is often obtained otherwise.

X-ray Absorption Spectroscopy

EXAFS data analyses were carried out with A. Michalowicz's software "EXAFS pour le MAC" [7]. k^3 weighting and a Kaiser window (τ = 2.5) were used for the Fourier transform. No signal was obtained at the titanium edge, which means that the titanium was hardly part of the gel even if, as we will see, it has an influence. Also no titanium was detected in the second spheres at Zr and Pb edge, except for gel PTX4. We used ZrO_2 for the sphere-interactions Zr-O and Zr-Zr; $PbZrO_3$ for Zr-Pb; and massicot PbO for Pb-O as crystalline reference compounds for the fits because their XANES spectra were similar to the gels' ones, which indicates that the atoms' environments of these references are similar to the gel ones.

For all the gels, Zr-O distance is around 2.15 Å, the same as in ZrO_2. Although a bit higher (8), the number of oxygen atoms is also similar to ZrO_2 one (7). The differences are within the error margin. Concerning the second sphere at Zr edge, Zr-Zr and Zr-Pb distances are once again equivalent to Zr-Zr one in ZrO_2 (3.45 Å). The structure of the gels is thus near ZrO_2 one, with some Pb atoms replacing Zr ones.

The only difference between the gels is the number of atoms in the second sphere (cf. Table 2). The more KOH that was used, the more metallic atoms there is. Adding TiO_2 tends to decrease the number of Pb neighbors, although using four times more of it leads to no visible change. Using twice more lead increased as predicted the number of Pb.

Gel	N (Zr-Zr) ± 20%	N (Zr-Pb) ± 20%
PZ1	4.0	2.7
PZ4	5.0	3.4
PZ8	6.0	4.3
PZT4	5.1	2.7
PZT8	5.7	3.5
PZTX4	5.3	3.1
P2Z4	5.1	4.1
ZK4	3.9	
ZKT4	4.0	

Table 2: Second sphere of Zr edge

Concerning the study at Pb edge, the distance Pb-O of all the gels is the same as in massicot PbO (2.36 Å). Contrary to the study at Zr edge, the number of oxygen atoms varies with the gels. Gels PZ1, PZ4 and PZT4 (5 O) are near the oxygen configuration of PbO (4 O). Gels PZ8 and P2Z4 have more oxygen atoms (6 O) but it is still far lower than with $PbZrO_3$ (8O). Gel PTX4 has a completly different structure, which is near $PbTiO_3$ one (8O).

Because the spectra at Pb edge were noisy at the end and because of the amorphous character of the gels, the disorder leading to a rapid decrease in the EXAFS signal, the useful signal was limited. Thus, we were not able to extract and fit the second spheres at Pb edge, although we were able to see the shape of the EXAFS curves of the second spheres and do some qualitative discussion. There is no visible Pb in PZ4 second sphere and only a little in PZT4. There is a mix of Pb and Zr for the gels P2Z4 and PZ8 and mostly Pb for PZ1. As predicted, there is a mix of Pb and Ti for the gel PTX4.

Either with EXAFS experiments at Zr edge or Pb edge, we now have evidence of Zr-O-Pb hetero-condensation. Through oxygen links, zirconium and lead atoms associate themselves in a structure roughly based on ZrO_2, with Pb replacing Zr atoms. On the contrary, titanium is not part of the gel even when its concentration is roughly equal to the Zr one (gel PZTX4). Zr and Ti do not act the same way. This is corroborated by the fact that the structure of the gel PTX4 is completely different.

By increasing the concentration of the mineralizer KOH, we can obtain more metallic atoms around Zr ones. Thus it favors Zr-O-Pb hetero-condensation. Nonetheless, as we may have competition between $PbTiO_3$ and PZT, too many links Zr-O-Pb may favor $PbZrO_3$ instead of PZT. The fact that, in gel PZ8, the O-sphere has one more O atom and is nearer the $PbZrO_3$ structure; and the fact that, in gels PZ1 and PZ8, Pb atoms are no longer mainly surrounded by zirconium atoms lead us to think that KOH concentration must be precisely adjusted.

The concentration of TiO_2 seems less important, although we have seen that, even if it is not visibly part of the gel, its mere presence decreases the number of Zr-O-Pb links and change the environment of lead atoms.

An increase in $Pb(NO_3)_2$ concentration logically increases the number of lead atoms around zirconium and lead ones. This effect should be studied more, but the less lead we use, the better it is from an ecological point of view.

3- Actuation testing

We found a piezoelectric coefficient d_{31} of a few pm/V. This result was rather low for non-doped PZT. This might come from the structure of the film: the heaping up of PZT cubes led to an apparent PZT Young modulus lower than the theoretical PZT Young modulus. Filling the holes with some dielectric may enhance greatly the d_{31} coefficient. Kandal et al. [8] advised to grow larger crystals in order to reduce the gaps. The fact that Morita et al. [9] obtained 25 pm/V let us think that we can greatly improve our films concerning d_{31}.

On the contrary, measuring the thickness displacement of a plate covered with PZT film, we found a d_{33} of 120 pm/V. Although lower than the d_{33} of non-doped PZT ceramics (223 pm/V [10]), this result is better than most d_{33} of non-doped PZT thin films which are usually under 100 pm/V. The fact that d_{33} was far bigger than $2*d_{31}$ was once again attributed to the structure of the film. Concerning d_{33}, lateral strains might be easier, which should lead to bigger thickness-strains.

Conclusion

We have reported a new hydrothermal treatment to grow PZT films on titanium substrates. It has been observed that the way of putting the precursors and the mineralizer into solution was very important for the grown film quality. The films consisted of a homogenous distribution of regular PZT cubes, near the MPB, with edges about 1 micron. Films' thicknesses were between 5 to 10 microns.

A study by EXAFS at the Zr, Pb and Ti edges has shown the structure of gel leading to the films. Number of links Zr-O-Pb depended strongly on the concentration of KOH, which therefore must be optimized. It was noted that Zr and Ti do not act the same way.

Actuation testing confirmed the piezoelectric activity without poling the PZT films. A d_{33} piezoelectric coefficient of 120 pm/V was measured.

The quality of our PZT films depended drastically on the Zr-based gel. It is noteworthy that, since there is no such gel, the growth of $PbTiO_3$ is different. For instance, using an oven instead of a sand bath is better.

Acknowledgement

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