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Preparation of multi-coating PZT thick films by sol–gel method onto stainless steel substrates

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Abstract

$PbZr_{0.45}Ti_{0.55}O_3$ ferroelectric films have been prepared by sol–gel method, using alkoxide precursor compounds and multi-layer technique. The gel films were deposited by spin-coating onto stainless steel substrates. In order to obtain crystallization in the perovskite phase, the samples were annealed at 600–700°C for 1 min. The dependence of the electric properties on the heat-treatment temperature is studied, and the coercive electric field as a function of the material thickness is determined. By SEM photography, the microstructure of the films could be shown to be homogeneous.

Keywords: Ferroelectric properties; PZT; Sol–gel process; Substrates; Thick films

1. Introduction

There is a considerable interest in the elaboration of ferroelectric thin films since more than 10 years. Initially driven by the application to non-volatile random access memories, the development has been oriented to ever thinner films; a rather recent tendency is to enhance research activities also on other concepts, like thick films or new substrates. Applications are in micromachines and implementation of ferroelectrics/piezoelectrics/pyroelectrics into intelligent systems, research domains with particular prospective for the upcoming decade.

Classic ferroelectric thin film preparation methods are rf sputtering,[1] metallo-organic chemical vapor deposition (MOCVD),[2] evaporation,[3] and sol–gel deposition.[4] The sol–gel process is appreciated for its advantages like easy and low cost preparation, homogeneity, and purity. Moreover, the stochiometry of the films can be controlled easily. Amongst the different deposition techniques, it is probably the most adapted process for the development of thick ferroelectric films, too.

The present study focuses on the realization of thick $PbZr_{0.45}Ti_{0.55}O_3$ films (hereafter abbreviated as PZT) by multi-layer deposition technique onto metal substrates.

2. Experimental procedure

Sol–gel processing is based on the polymerization of alkoxide compounds producing a gel, which then is crystallized by heat-treatment.[4] Amongst the different existing precursors, n-propoxides and acetates with an acid solvent have been chosen because of the ease and rapidity to obtain the final gel at room atmosphere. Titanium n-propoxide $Ti(C_3H_7O)_4$ has been preferred to the commonly used titanium iso-propoxyde[5] because of its lower toxicity. Zirconium n-propoxide $Zr(C_3H_7O)_4$ and lead acetate $Pb(CH_3CO_2)_2,3H_2O$ with an excess of 19% lead, compensating for the loss of PbO at high annealing temperatures,[6] were used.

The lead acetate is dissolved in acetic acid CH_3COOH in proportions of 1 ml of acid for 1.2 g of acetates. The solution is heated at 110°C for 5 min in order to eliminate the water and is cooled before the addition of the zirconium and the titanium *n*-propoxides. These were mixed at room temperature with a molar ratio of 45/55 and are added to the solution. In order to prevent from film cracking during annealing, ethylene glycol

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(HO–CH_2–CH_2–OH) is added to the basic solution with the role of a cross-linking agent[7] in the proportion of 1 ml to 7.5 g of acetate. Due to hydrolytic reaction of the gel in air atmosphere which causes coagulation, the prepared solution is not very stable and has to be used within several hours.

Prior to the deposition process, and in order to preserve a proper interface between the PZT film and the substrate, the latter is cleaned in an ultra-sonic propanol bath and dried on nitrogen flow. The PZT 45/55 sol–gel is spin-coated at 6000 rpm onto the substrates (stainless steel AISI 304) during 20 s. In order to crystallize the gel film, finally the sample is introduced for 1 min in an open air furnace, pre-heated at the desired temperature ranging from 600 to 700°C. This rather fast heat-treatment permits to use the solution before its coagulation. The thickness of the films was measured with an SEM, the crystalline phase was characterized by X-ray diffraction, and the electric properties were determined with the classic Sawyer–Tower circuit.

3. Results and discussion

By varying the spin coating parameters, the maximum obtainable film thickness for a single coating step was determined to be approximately 330 nm, and was limited by cracking of the film during the annealing process. In order to obtain thicker films, therefore multilayer processing has been used, where the samples were annealed after each individual deposition step. A good adhesion of the gel on the substrate could be obtained only when cooling down the substrates to room temperature prior to the consecutive deposition step. By this method, homogeneous PZT films with reproducible ferroelectric properties can be processed. The overall thickness of the ferroelectric film is shown in Fig. 1 as a function of the number of coatings, demonstrating a rather constant thickness of the individual layers. From the SEM cross-section micro-graph of Fig. 2a it can be seen, that a uniform film has been obtained. The roughness of the cross-section is due to the cutting of the sample for the SEM study. From Fig. 2b, we can note that the PZT film has a smooth surface; the grain size is ranging from approximately 100 nm to 1 μm.

Evaporated gold electrodes with a diameter of 0.5 mm were used for the electric characterization of the PZT film. A typical hysteresis loop, established at 50 Hz sinusoidal voltage, is shown in Fig. 3 for a 3.2 μm thick PZT film which was obtained by 10 coating steps and heat-treated at 600°C during 1 min after each deposition, respectively. At an applied electric field of 400 kV/cm, a coercive electric field of approximately 60 kV/cm and a remanent polarization of approximately 23 μC/cm^2 have been obtained. This rather high coercive field is assumed to be caused by a non-suited interface

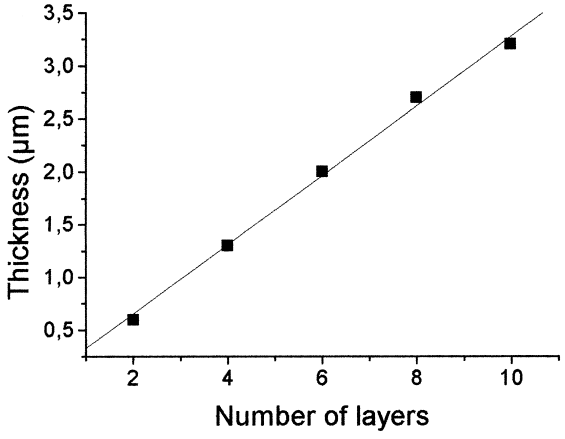
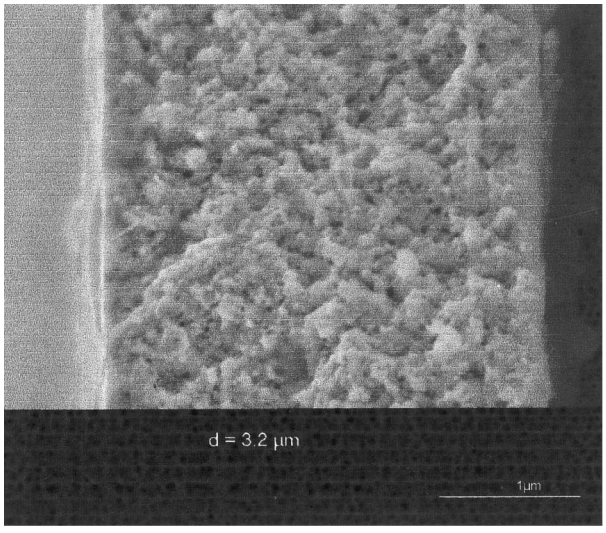
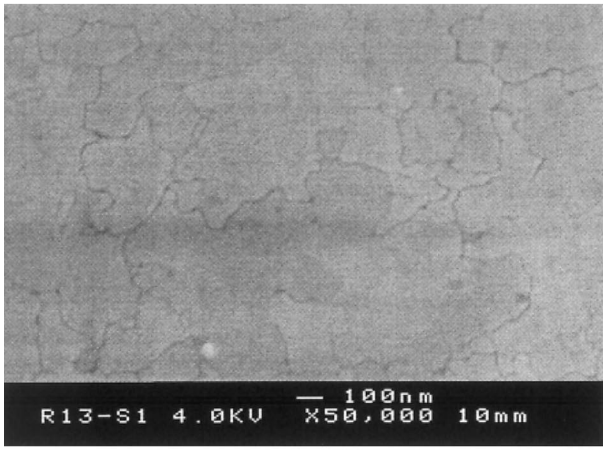


Fig. 1. Overall thickness of a $PbZr_{0.45}Ti_{0.55}O_3$ film as a function of the number of deposition layers on a stainless steel substrate.



(a)



(b)

Fig. 2. SEM micro-graph of a $PbZr_{0.45}Ti_{0.55}O_3$ film of 10 layers deposited on stainless steel and annealed at 600°C for 1 min, showing (a) a cross-section and (b) the surface of the film.

between the ferroelectric film and the metal substrate. Other metal substrates, for example with less iron, showed better hysteresis loop properties.[8] Stress due to the thermal treatment and a small crystallite size might be equally responsible for the rather high value of E_c.[9]

The X-ray diffraction patterns for different annealing temperatures of the ferroelectric films are shown in Fig. 4. At temperatures below 600°C, the pyrochlore phase (○) appears to be dominant. The PZT phase (■) appears at a temperature between 550 and 575°C; at 600°C and at higher temperatures the PZT films are well crystallized and no pyrochlore peak is visible anymore. The peaks from the stainless steel (S) are also shown in the figure.

The development of the remanent polarization and the coercive electric field of the PZT films is shown in Fig. 5a and b as a function of the applied electric field and for three different annealing temperatures, respectively. Highest values for P_r but also for E_c were obtained at 700°C. This might be explained by a higher degree of crystallinity when increasing the annealing temperature, which results in a higher polarization. The less significant variation of the coercive electric field might be also due to the different crystalline structure.

The dependence of the coercive electric field on the overall film thickness is shown in Fig. 6 for an annealing temperature of 600°C and for an applied electric field of approximately 400 kV/cm. With decreasing film thickness, E_c is increasing, a dependency which has been reported also for ferroelectric thin film deposition on Si-wafers.[10]

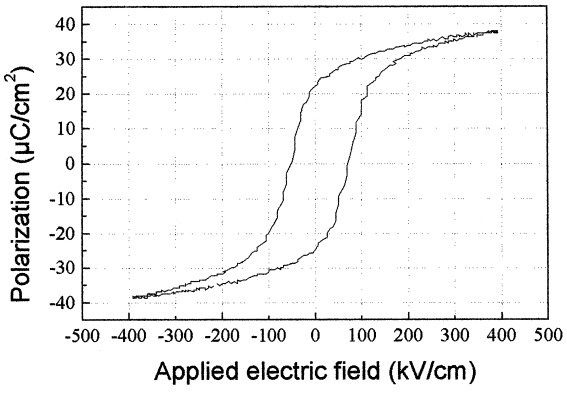


Fig. 3. Hysteresis curve of a 3.2 μm thick $PbZr_{0.45}Ti_{0.55}O_3$ film deposed on stainless steel and annealed at 600°C for 1 min.

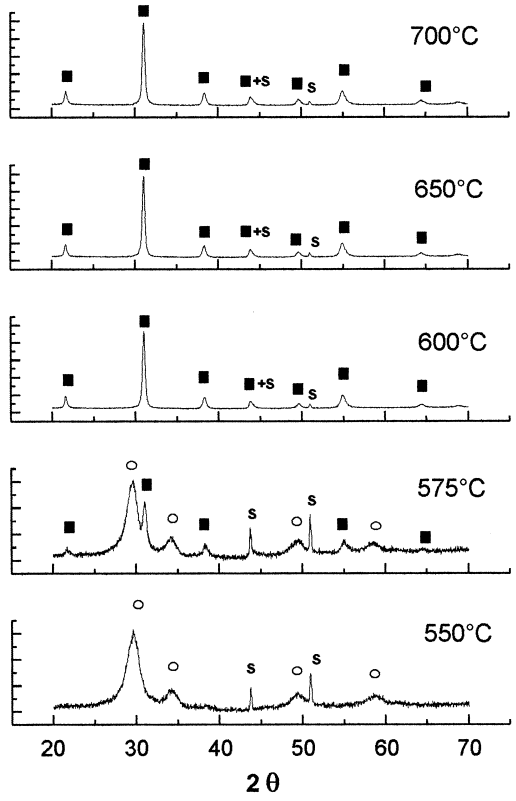


Fig. 4. X-ray diffraction patterns of the $PbZr_{0.45}Ti_{0.55}O_3$ films annealed during 1 min. at different temperatures as indicated (S = stainless steel, ○ = pyrochlore phase, ■ = perovskite phase).

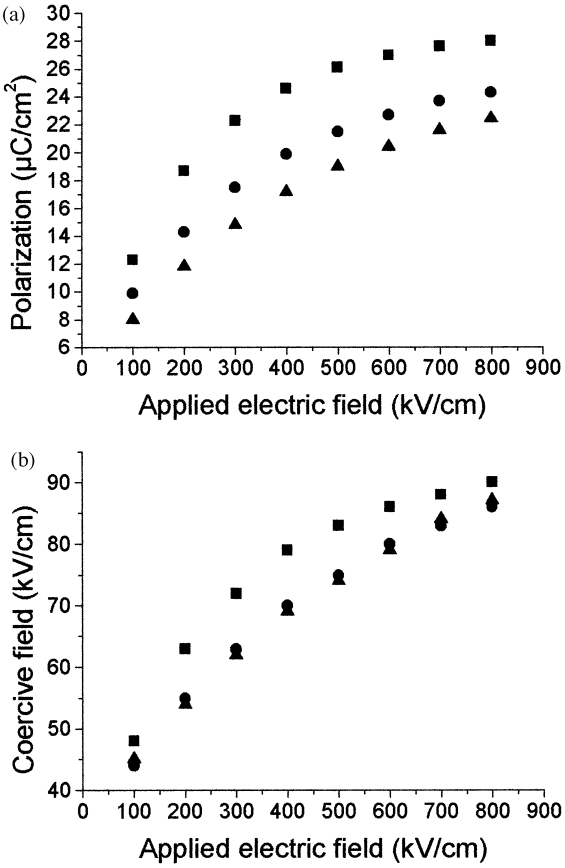


Fig. 5. Remanent polarization and coercive field as a function of the applied electric field of a 2 μm thick $PbZr_{0.45}Ti_{0.55}O_3$ film on stainless steel for different annealing temperatures (▲ = 600°C, ● = 650°C, ■ = 700°C).

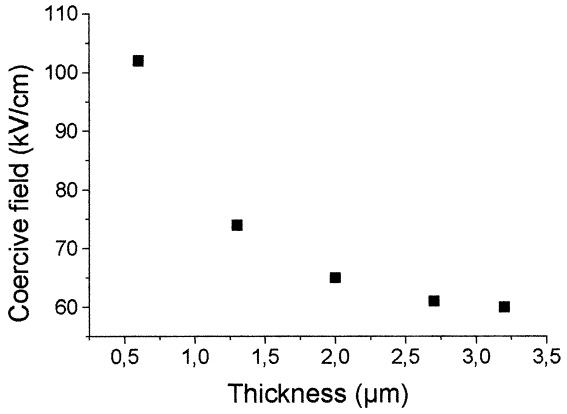


Fig. 6. Coercive electric field as a function of the thickness of a $PbZr_{0.45}Ti_{0.55}O_3$ film obtained at an applied electric field of approximately 400 kV/cm.

4. Conclusions

$PbZr_{0.45}Ti_{0.55}O_3$ films of up to 3.2 cm thickness were successfully deposited by multi-layer sol–gel method with alkoxid precursor compounds onto stainless steel substrates. The individual coatings had an uniform thickness and the overall film is homogenous. Rather good values for the remanent polarization are in contrast to a coercive electric field, which appears to be higher than cited in literature for deposition on Si-wafers. This disadvantage, probably stemming from a non-adapted interface between the PZT film and the substrate, is assumed to be healed by the introduction of an additional oxide layer which should improve the conditions for the ferroelectric crystallization process and thus decrease the coercive electric field and while increasing remanent polarization. The modification of the sol–gel process might be envisaged for depositing thicker mono-layers of the PZT in order to obtain thicker overall films; the utilization of stainless steel substrates, as an alternative to the traditional Si-wafer, seems to be promising.

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