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Journal of the European Ceramic Society 24 (2004) 1579–1583
www.elsevier.com/locate/jeurceramsoc

Analysis of the phase content and Zr:Ti fluctuation phenomena in PZT sol-gel films with a nominal composition near the morphotropic phase boundary

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Abstract

PZT thin films are commonly used for piezoelectric sensors and actuators. Some applications require a film thickness of a few micrometers, which can be achieved by using a sol-gel process with several coating and annealing steps. We prepared sol-gel derived Nd-doped and undoped PZT (53/47) films on metallic substrates by various thermal annealing treatments. During the pyrolysis and the annealing process, a Zr:Ti fluctuation along the cross-section of the sol-gel films takes place. By means of transmission electron microscopy (TEM), electron diffraction and energy dispersive X-ray spectroscopy (EDX), the local Zr:Ti ratio and phase content have been estimated indicating a decreasing tetragonal distortion, especially for layers close to the substrate. These results are related to the microstructure of the films, taking into account the tensions resulting from the difference in the thermal expansion of the metallic substrate to the ceramic film and the crystallite size.

Keywords: Electron microscopy; Films; Grain size; Microstructure-final; PZT

1. Introduction

Ferroelectric lead zirconate titanate films can be used for several industrial applications like piezoelectric sensors and actuators. Usually they are deposited on silicon wafers with different ground electrodes to be integrated into microelectronical devices.[1] Metallic substrates are of special interest because of their flexibility and no need of an additional ground electrode.

The required film thickness of a few micrometers can be achieved by using a sol-gel process with several coating and annealing steps. The ferroelectric properties depend strongly on the resulting microstructure of the film especially from the grain size and the phase content.

It has been previously reported that the crystallization of perovskite from an amorphous sol-gel film passes off a non-ferroelectric pyrochlore phase whose residuals especially at the interfaces to the electrodes can effect the electrical properties.[2]

First results due to the microstructure of multilayered sol-gel films on metallic substrates were published by Seifert et al.[3] The investigated undoped PZT films possess columnar grains up to 600 nm height. Flat grains of 900 nm diameter are found at the surface-sided interfaces. Closed pores with diameters of 50 nm are well distributed in the whole film. The crystallization originates at the interfaces of the single layers.

A decreasing value for the coercive field with increasing film thickness is observed. But no hints of an intermediate layer between film and substrate are observable in X-ray diffraction experiments. The presence of a pyrochlore phase is ambiguous.

In comparison to similar prepared sol-gel layers on ceramic substrates[4] there seem to be no differences in the microstructure of the films.

Therefore TEM investigations of the layer which is in direct contact to the metal substrate are of special interest. TEM is one of the most suitable means to detect diffusion processes, chemical interactions and the formation of secondary phases on a nm-scale.

In sol-gel-films on ceramic substrates a gradient in the Zr:Ti ratio and the Pb content along the cross-section of each layer depending on the annealing parameters has already been observed by TEM.[5]

The aim of this work is to study the Zr:Ti fluctuation phenomena in sol-gel derived PZT films on metallic substrates with TEM. Besides the crystallisation and the resulting microstructure shall be investigated in detail,

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0955-2219/03/$ - see front matter
doi:10.1016/S0955-2219(03)00407-2

especially considering the influence of the local Zr:Ti ratio on the phase content within the layers.

2. Experiment

To understand and to optimise the properties of the films, different microstructures were prepared by various annealing treatments using Nd-doped and undoped sols. Nd is known to inhibit the grain growth and enhance the sintering process.[6]

Sols with a nominal stoichiometry of $Pb_{1,25}$ ($Zr_{0,53}$ $Ti_{0,47}$) O_3 and 2% Nd were prepared by solving amorphous PZT precursors[4] in 1.3 propandiol with lead acetate trihydrate adding a certain amount of $NdCl_3$ respectively. They were deposited by dip-coating on Hastelloy (C276) substrates.

In the first system each of four layers of a sample was annealed directly after coating in a preheated furnace at 525 °C for 5 min. The whole layer system was additionally annealed at 600 °C for 10 min.

In the second system each layer has been directly annealed at 600 °C for 5 min. The third and fourth systems consist of post annealed and directly annealed Nd-doped films respectively.

The microstructure was characterised by transmission electron microscopy (TEM) using a Philips CM12 STEM with an accelerating voltage of 120 kV.

The samples were processed by common sandwich preparation using a Gatan dual ion mill model 600.

Variations in the Zr:Ti ratio along the cross-section of the samples were investigated by energy dispersive X-ray analysis (EDX).

Crystallite diameters were estimated on the basis of TEM micrographs. According to the crystallite size, the lattice parameters for a tetragonal distortion were specified with selected area diffraction (SAED) or convergent beam electron diffraction (CBED). The results of EDX line scans along the area used for diffraction were averaged and related to the lattice parameters.

3. Results

3.1. Microstructure and chemical composition

The typical microstructure is presented by TEM darkfield images of the different samples in Figs. 1 and 2. The appropriate SAED-patterns and the Zr:Ti ratio along the cross-section of the considered crystallites are also shown.

In directly annealed samples the crystallites might be extended over the interface of two layers independently whether they are doped or not (Fig. 1).

Undoped films have a columnar structure with diameters in the range of a few 100 nm (Fig. 1a). For this reason diffraction patterns of adjoining crystallites are detected as well. The Zr:Ti ratio is almost constant, only a marginally smaller Zr content is detectable at the interface between two layers (Fig. 1a, Zr:Ti).

Nd-doped films consist of crystallites of higher extension in the layer plane (Fig. 1b). The SAED pattern confirms that they are single crystals. The EDX line scan shows a stronger fluctuation in the Zr:Ti ratio with a higher Ti content at the interface (Fig. 1b, Zr:Ti).

In post-annealed samples the crystallites are not extended over the interfaces (Fig. 2). Especially in the surface layer undoped films (Fig. 2a) contain of single crystallites (see also SAED pattern) which are spread over the layer plane and can reach diameters up to 1 μm. In the PZT layer neighbouring the substrate the crystallites are much smaller (in the range of a few 100 nm) in comparison to those in PZT films stacked on the first layer. In the center of these stacked layers a significant lack of Ti is observed (Fig. 2a, Zr:Ti).

In post-annealed Nd-doped films the average diameter of the crystallites is in the range of 70 nm in all layers (Fig. 2b). They are not particularly shaped. The great bright area in the TEM darkfield image visualizes the partially similar orientation which is confirmed by the SAED pattern.

No additional fluctuation within the crystallites aside from the lower Ti content in the center of the layer could be approved within the precision of measurement (Fig. 2b, Zr:Ti).

3.2. Crystallite size and lattice parameters

The tetragonal distortion of single crystallites located in the different layers of Nd-doped and undoped films is related separately to the local Zr content (Fig. 3) and the crystallite size (Fig. 4). Its distribution is independent of the annealing treatment.

The values of the c/a ratio versus the Zr content for crystallites in undoped samples are scattered over the whole range from values as determined for bulk ceramics [7] to almost no distortion (Fig. 3a) indicating no dependency on the size of the crystallites (Fig. 4a) or their localisation.

In Nd-doped samples the crystallites possess a smaller tetragonal distortion than known for bulk ceramics (Fig. 3b). Additionally a slight decrease towards larger crystallites is detected (Fig. 4b). For most of the crystallites, the localisation within the sample seems to have no influence. Only a few in the surface layer exhibit a higher distortion.

4. Discussion and conclusions

As investigated by Wahl[5] the energetically favoured nucleation and growth of Ti-rich perovskite and the

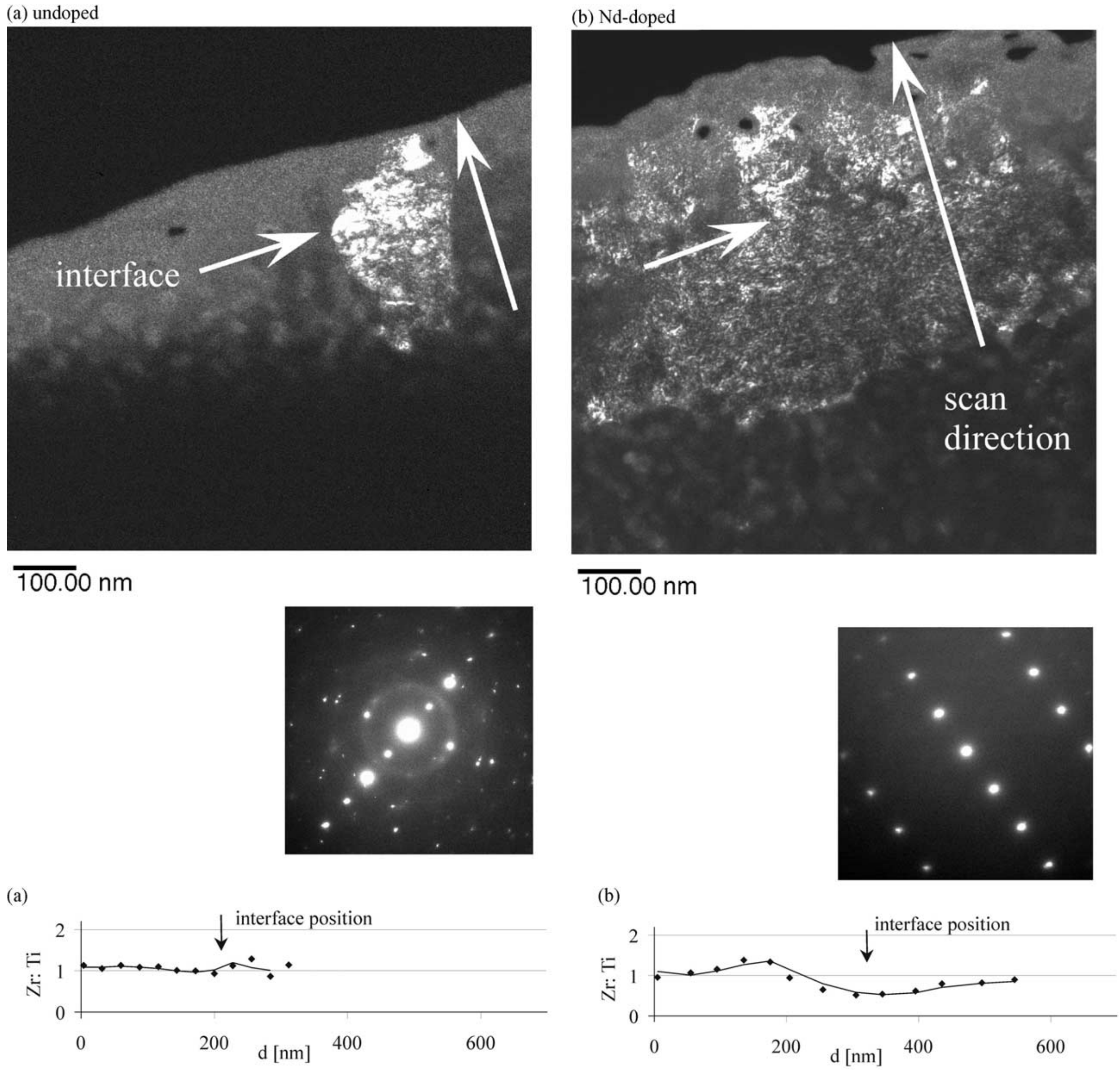

Fig. 1. TEM darkfield images, SAED patterns and local Zr:Ti ratio of directly annealed (a) undoped and (b) Nd-doped samples along the cross-section of crystallites within the third and the surface layer (interface marked with arrows).

higher crystallization temperature of Zr-rich perovskite[8] might be possible for the Zr:Ti fluctuation within the layers.

The maximum fraction of pyrochlore formation in PZT is reached at a temperature around 525 °C where the transformation to perovskite is suppressed actually. Simulation of the crystallization kinetics indicates a shift of the nucleation maximum of perovskite to lower temperatures for Nd-doped samples, which can be confirmed by XRD-measurements (data not shown) causing even a stronger Zr:Ti fluctuation at higher temperatures such as 600 °C.

Therefore the films contain Ti-rich and Zr-rich perovskite which leads to the assumption that they may contain the accompanying[7] tetragonal and rhombohedral phase as well.

Our results suggest that even in the Zr-rich parts near the morphotropic phase boundary a tetragonal distortion occurs and no precise indication of the presence of the rhombohedral phase is observable. A reason for these experimental results may be thermal induced vectored stresses probably caused by the different thermal expansion of the metallic substrate and the thin ceramic film aside from different densities of pores.

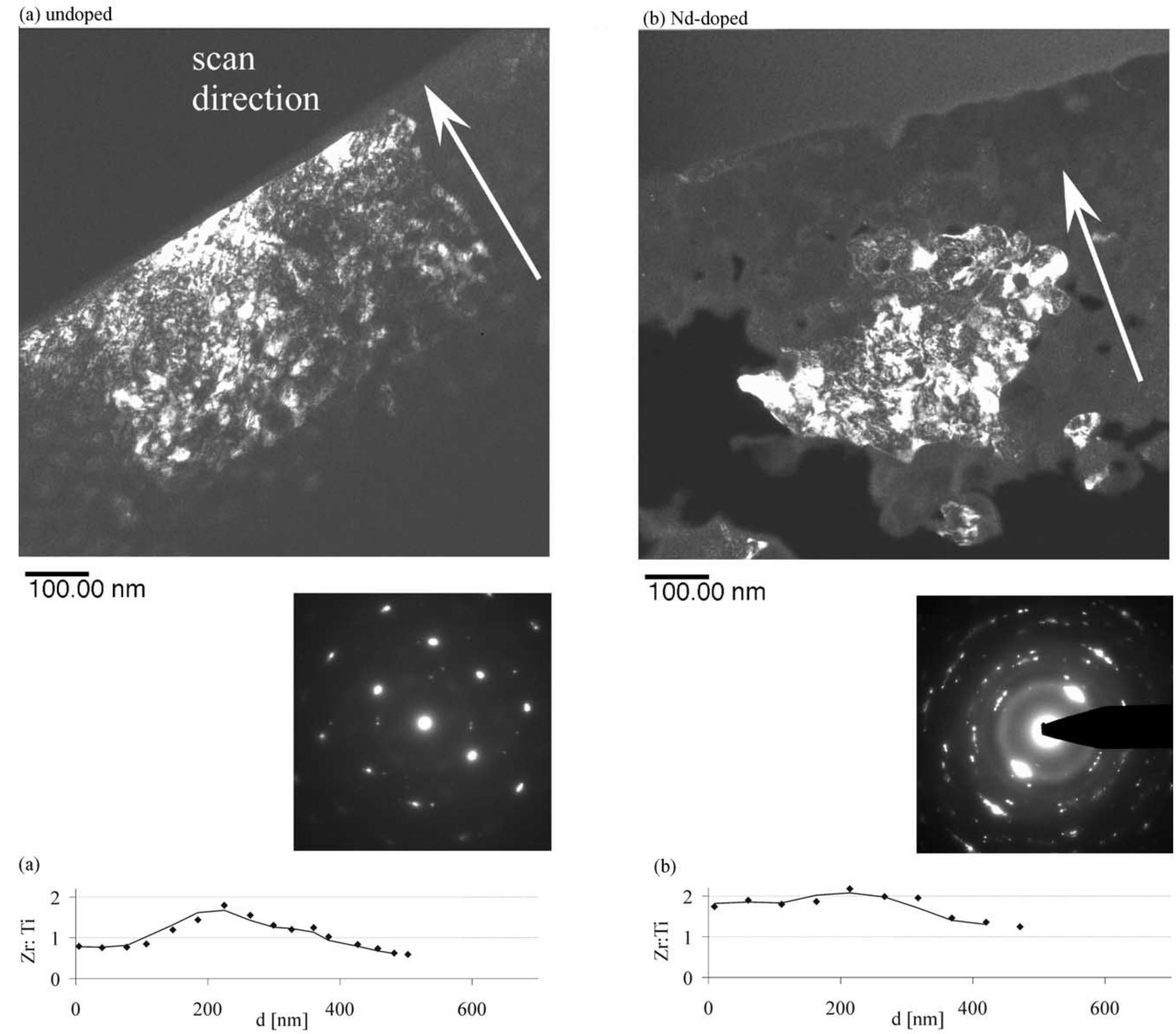

Fig. 2. TEM darkfield images, SAED patterns and local Zr:Ti ratio of post annealed (a) undoped and (b) Nd-doped samples along the cross-section of crystallites in the surface layer.

A shift of the morphotropic phase boundary towards the rhombohedral part of the phase diagram has been calculated for tensile and compressive stresses on epitaxial PZT thin films.[9] Moreover very small c/a ratios are found in the Ti-rich parts of the investigated films. A decreasing c/a ratio for grain sizes down to approximately 200 nm has already been observed.[10]

For Nd-doped thin films a general reduction of the c/a ratio has been reported[11] as also observed in this investigation. The porosity provokes the higher c/a ratio for small crystallites (Fig. 4b) because of the easier stress compensation, while the larger crystallites are located in the denser area of the film. The few greater values for crystallites in the surface layer confirm this assumption.

As no fluctuation of the Nd content is detected by EDX and no Nd enrichment at the interfaces of the crystallites in particular, a homogeneous distribution of the dopants in the film can be assumed which lead to the consistent decrease of the c/a ratio.

In undoped samples a more inhomogeneous reduction of the tetragonal distortion is observed. External tensions, which might be higher in the layer close to the substrate seem not to have any effect on the distribution of the c/a ratios. The shape of the crystallite whether it is columnar or not does not play a role either. Maybe

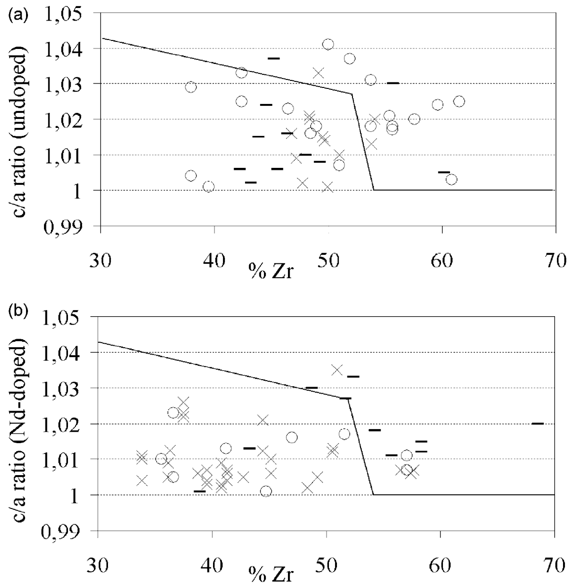

Fig. 3. *c/a* Ratio depending on the Zr content for undoped (a) and Nd-doped (b) samples. Literature values are presented by the line. –, ca 1st layer on substrate; ×, c/a center, 2nd/3rd layer; O, c/a surface layer.

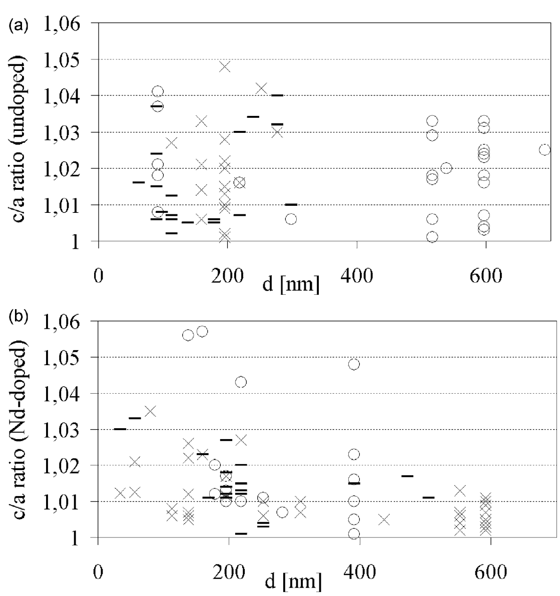

Fig. 4. *c/a* Ratio depending on the crystallite size *d* for undoped (a) and Nd-doped (b) samples. –, ca 1st layer on substrate; ×, c/a center, 2nd/3rd layer; O, c/a surface layer.

the orientations of the crystallites relative to each other are responsible for the effect.

The authors have come to the conclusion that the strong scattering of the *c/a* ratio for an identical Zr content depends on both the local directed tensions within a sample and the crystallite size.

Acknowledgements

The authors would like to thank the DFG for financial support of this research projekt (ME 1721/1-2).

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