*Journal of the European Ceramic Society* **19** (1999) 1387–1389
© 1999 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00442-7
0955-2219/99/$ - see front matter

# Characterization of PZT Thin Films Prepared by a Modified Sol–Gel Method

Bernd Matthes,* Gerhard Tomandl and Günter Werner

Freiberg University of Mining and Technology, Institute of Ceramic Materials, Gustav-Zeuner-Str. 3,
09596 Freiberg, Germany

## Abstract

*Lead zirconate titanate (PZT) thin films with thicknesses of around 5 μm were prepared by the deposition a sol slurry. This sol slurry consists of a PZT-sol on acetic acid basis and PZT powder. The sol serves as the dispersion agent of the powder. Both are identical in composition with molar ratio Zr/Ti of 0·53/0·47. Lead in excess of 5% was used in all samples. This coating conditions enhance the possibilities of film preparation. © 1999 Elsevier Science Limited. All rights reserved*

*Keywords*: sol–gel processes, PZT.

## 1 Introduction

There is manifold potential for the application of lead–zirconate–titanate ($PbZr_xTi_{1-x}O_3$ or PZT) ceramics such as in DRAMs, nonvolatile memories, optical storage media, pyroelectric IR detectors, micromechanical applications, sensors. It has been possible to prepare thin films of PZT by physical deposition methods (e.g. sputtering,[1,2] laser ablation[3]) and chemical methods (MOD,[4] sol–gel[5]). In this paper, we present a modified sol–gel method using a sol slurry as coating medium. In this case, a PZT sol serves as dispersant of a PZT powder. Silicon discs coated either with Pt or with Ag/Pd were employed as substrates.

## 2 Chemical Characterization of Sol and Gelation

Figure 1 shows a schematic of the sol-slurry preparation. The mixture of Zr- and Ti-alcoholate (molar ratio Zr/Ti = 0·53/0·47) leads to a Zr/Ti-alcoholate. This alcoholate reacts with acetic acid to a defined Zr/Ti-acetate. Recently, we have described the reaction of Zr-, Ti- and Zr/Ti-alcoholates with acetic acid and we found that the nature of the alcoholates is not important for these reactions. The formation of acetates depends on the molar ratio of acetic acid to metal.[6]

The compound $Zr_{0\cdot53}Ti_{0\cdot47}(OH)_2(CH_3COO)_2$ is formed by sol preparation conditions (molar ratio acetic acid/$Zr_{0\cdot53}Ti_{0\cdot47}\approx 6/1$). The exact structure of this acetate is unknown. The IR-spectra show bands on 1723, 1226 $cm^{-1}$ and broad bands on 1574, 1425, 1340 $cm^{-1}$. This means that, there are monodentate ($\nu_s$ [$COO^-$] 1226 $cm^{-1}$, $\nu_{as}$ [$COO^-$] 1723 $cm^{-1}$), bridging and chelating ($\nu_s$ [$COO^-$] 1340, 1425 $cm^{-1}$, ($\nu_{as}$ [$COO^-$] 1574 $cm^{-1}$) acetates ligands. Diethanolamine (DEA) is necessary for gelation in the sol because it substitutes acetate ligands from lead(II)–acetate up to the formation of 1/1-complexes. The Pb–acetate–DEA complex and $Zr_{0\cdot53}Ti_{0\cdot47}(OH)_2(CH_3COO)_2$ form a polymeric structure by linking the free OH groups (Pb–acetate–DEA–complexes) and the monodentate acetate ligands from the $Zr_{0\cdot53}Ti_{0\cdot47}(OH)_2(CH_3COO)_2$ (hydrogen bonds). Only bridging and chelating (bidentate) acetate ligands are observed in the sol (solid content: ≈25%). Weak bands on 1710 and 1270 $cm^{-1}$ indicate free acetic acid. An excess of DEA causes slowly reactions of cross-linking under participation of $Zr_{0\cdot53}Ti_{0\cdot47}(OH)_2(CH_3COO)_2$. These reactions induce an excessive increase of carbon content and viscosity of the sol. Excess acetic acid and water evaporize during gelation (solid content of gel: ≈50%). The gel consists of the Pb–acetate–DEA complex, $Zr_{0\cdot53}Ti_{0\cdot47}(OH)_2(CH_3COO)_2$ and 4 hydrate water. All ligands (OH-groups: 3600–2500 $cm^{-1}$, acetates: 1575, 1425, 1340 $cm^{-1}$) serve in the polymer gel structure as bidentate ligands.

---

*To whom correspondence should be addressed. Fax: +49-3731-393-662; e-mail: matthes@anw.ikw.tu-freiberg.de

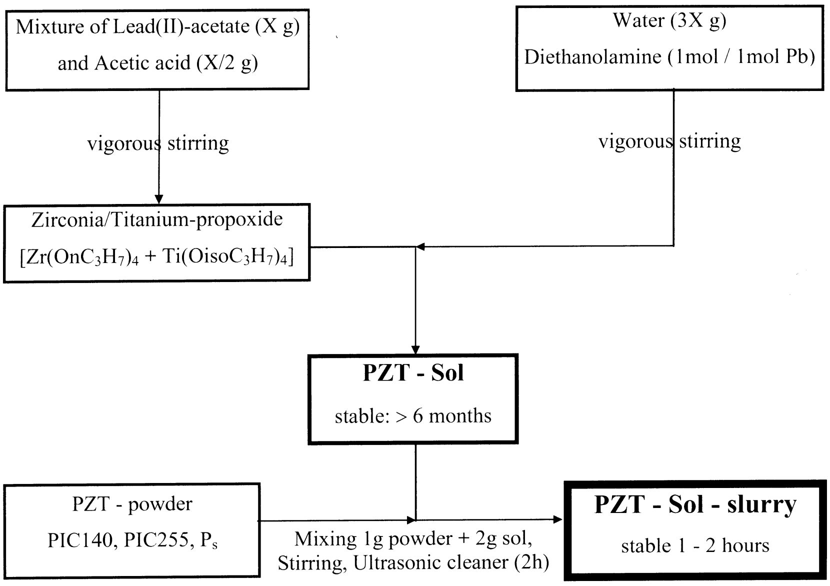

**Fig. 1.** Preparation of PZT sol slurry, lead excess 5%, Molar ratio Zr/Ti = 0·53/0·47.

## 3 Slurry Preparation

It is possible to use the sol for preparation of PZT thin films. The film thickness is approximately 0·7 μm. A molar ratio $1/2 \leq$ DEA/Pb $< 1/1$ in the sol allowed for good handling properties (viscosity, $\eta_{\mathrm{sol}}$ = 0·10–0·12 Pa s) as coating medium and dispersion agent for PZT powders. The powders and the sol are identical in composition.

The acetic acid causes a low acidic pH value in the sol. For dispersion we have used powders with isoelectrical points > pH 7: PIC140 (Physics Instruments Lederhose Germany, $d_{50}$ = 450 nm), PIC255 ($d_{50}$ = 900 nm) and $P_s$ (reaction of Zr/Ti(OH)$_4$ aq. and Pb(OH)$_2$ at 550°C, $d_{50} \approx 900$ nm). The OH groups on the surface of the powder particles are also a part of the polymeric network of the sol. The prepared slurries are stable for 1–2 h. We dispersed 0·5 g powder completely in 1 g sol.

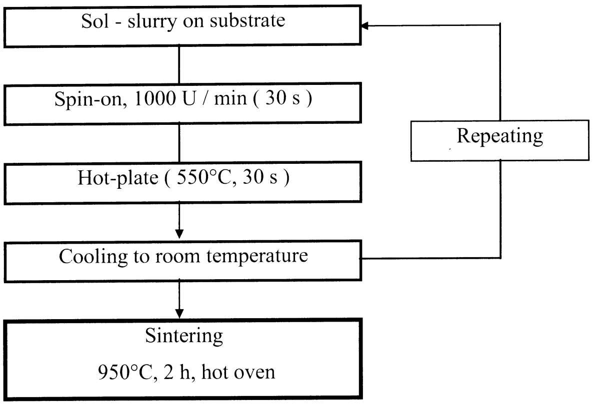

**Fig. 2.** Film preparation.

## 4 Preparation and Characterization of Films

The ratio of PZT powder to PZT from the sol is suitable for dense films on sintering below 1000°C. The viscosity ($\eta_{\mathrm{slurry}}$ = 0·12–0·15 Pa s) of the slurry allowed to use the spin-coating process for the film preparation. Figure 2 shows the procedure of film preparation. An advantage of this procedure is its simplicity: spin coating, drying through the rotation of the substrate, heating on a hot-plate and sintering in air. The film thicknesses (2·5 and 7 μm) are dependent on the number of coating cycles and on the rotary speed. The gelation was realised during the rotation due evaporation of water and acetic acid. After the subsequent temperature treatment (hot plate) the PZT layers consist of particles which were homogeneously surrounded an amorphous PZT precursor. This film contains no residual organics at all. Repeating cycles are possible. There is a limit to the number of coating cycles due to a high number of PZT layers which inhibit the rapid heat input from the hot-plate through the layers to the last layer. A result of this effect is the volatilization of the organics from the top into the body of the last layer by the heat radiation from the hot-plate. This induce big cracks in the top layer. The fabricated films are dense and crack–free. Figure 3 shows a mono-layer PZT film prepared by the conditions shown in Fig. 2. The film thickness is 5·5 μm.

The big powder particles reduce the internal stress caused by the gelation of the sol. The smaller powder particles and the amorphous PZT precursor serves as a sintering aid (improve the sinter activity), resulting in a sintering temperature

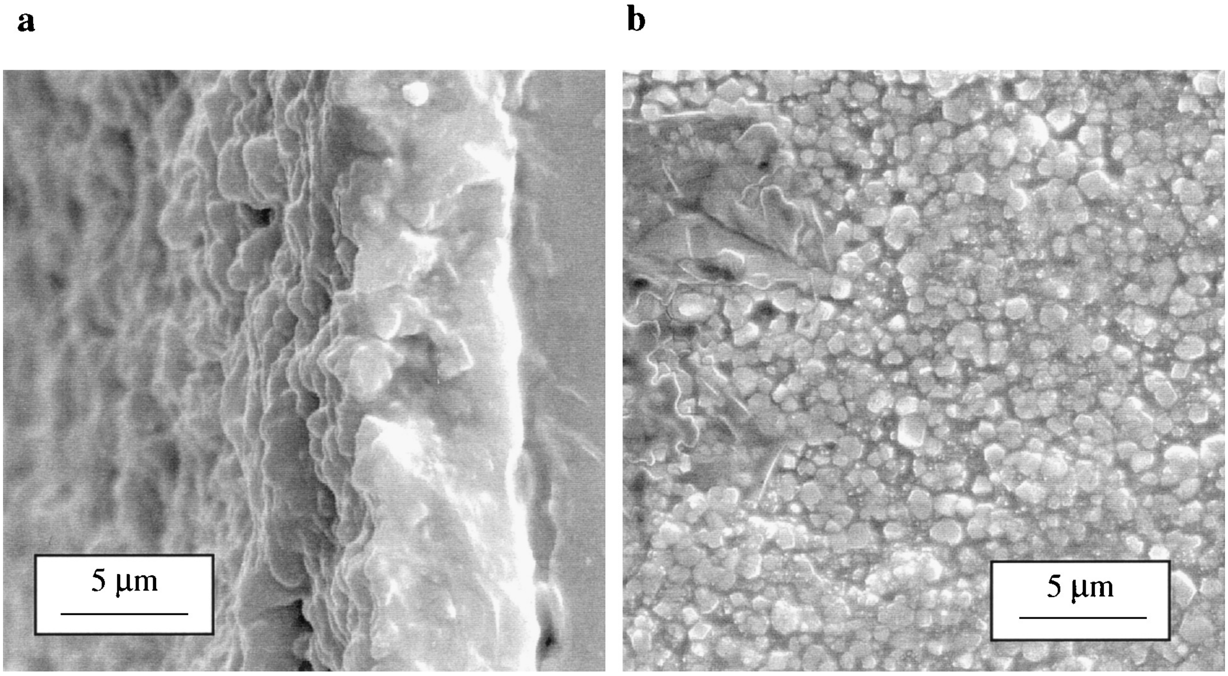

**Fig. 3.** PZT mono-layer film on sol-slurry basis: (a) fracture surface, thickness, 5·5 $\mu$m; (b) film surface.

around 950°C. This temperature range between the temperatures for sol–gel films (about 750°C) and for slurry films and bulk materials (about 1200°C, for example PIC140: 1260°C).

The sintering temperatures are still too high for making this process suitable for the manufacturing of microelectronic devices based on silicon wafers. There is no homogeneous succession of the layers (new phases, silicon diffusion), and ferroelectric properties of PZT are decreased ($P_r < 0{\cdot}3\ \mu\mathrm{C\ cm}^{-2}$, $E_c < 50\ \mathrm{V}\ \mu\mathrm{m}^{-1}$) until the films are only a dielectric. In the future, our investigations will include the use of other electrode and substrate materials as well as further adjusted powder characteristics.

## 5 Summary

In this study, we have shown, that it is possible to prepare PZT films having thickness (around 5 $\mu$m) in between those deposited by conventional thin and thick film techniques. Here the coating medium is a sol slurry consisting of PZT sol and PZT powder. All preparation steps including the coating procedure are comparatively simple and can be carried out in air. After thermal treatment, films consist of PZT-powder particles surrounded by an amorphous PZT precursor. This allowed sintering at temperatures of around 950°C. A better adjustment of substrate, electrode material and powder characteristics is still necessary.

## Acknowledgements

This project is supported by the Deutsche Forschungsgemeinschaft.

## References

1. Krupanidhi, S. B., Maffei, N., Sayer, M. and El-Assal, K., Rf planar magnetron sputtering and characterization of ferroelectric Pb(Zr,Ti)$O_3$ films. *J. Appl. Phys.*, 1983, **54**, 6601–6609.
2. Okada, A., Electrical properties of lead-zirconate-lead-titanate ferroelectric thin films and their composition analysis by auger electron spectroscopy. *J. Appl. Phys.*, 1978, **49**, 4494–4499.
3. Davis, G. M. and Gower, C., Ferroelectric thin films by laser ablation. *Appl. Phys. Lett.*, 1989, **55**, 112–117.
4. Vest, R. W., Metallo-organic decomposition processing of ferroelectric and electrooptic films: a review. *Ferroelectrics* 1990, **102**, 53–68.
5. Budd, K. D., Dey, S. K. and Payne, D. A., Sol–gel processing of PbTi$O_3$–PZT and PLZT thin films. *Br. Ceram. Proc.*, 1985, **36**, 107–121.
6. Matthes, B., Tomandl, G. and Werner, G., Production of dense lead zirconate titanate (PZT) films. *ECERS V in Key Engineering Materials*, 1997, **132–136**, 1139–1142.