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Bi-layered PZT films by combining thick and thin film technology

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Abstract

PZT thick films on various substrates are of great interest for applications as pressure sensors, micropumps, ultrasonic and pyroelectric transducers, deformable mirrors and ferroelectric printing forms. Until now, functional properties and microstructure of such films were still not sufficiently solved. Concerning the application as a printing form in an electrostatic printing process a homogeneous microstructure of the PZT film is necessary in order to homogenize the relevant surface potential. Though PZT thin films show very fine grains and thus allow excellent resolution, their surface potential is unstable due to the low internal resistance. Therefore, we have performed an investigation in order to find out whether the combination of thick and thin film technology results in films which can be homogeneously polarized on a scale <20 μm, corresponding to a printing resolution better than 1200 dpi. Results on preparation, characterization and modeling of bi-layered PZT films are presented.

Keywords: Defects; Electrical properties; Films; PZT; Sol-gel process

1. Introduction

The preparation of PZT thick films on various substrates with thicknesses between 5 and 150 μm has been an area of active research for the last 15 years. Sintering of such films turned out to be difficult due to constrained sintering conditions and decomposition by PbO loss which results in high residual porosity and minor functional properties.

The best results have been obtained using liquid phase sintering by means of PbO excess [1,2] or an addition of a low melting glass[3–5] or an eutectic oxide composition.[6–11]

In our investigation reduction of the sintering temperature is achieved by combining a commercially available PZT–PMN powder with a low melting point glass and the eutectic forming oxides Bi_2O_3 and ZnO.[6–8] By this method PZT thick films with high dielectric, ferroelectric and piezoelectric properties can be produced which are suitable for actuator and sensor applications.

For use in a ferroelectric printing process attention has to be directed to the microstructure of the PZT thick film. The size of inhomogeneities like pores, secondary phases or coarse grains has to be reduced drastically below 20 μm to succeed in a resolution of 1200 dpi.

Our approach is based on a combination of thick and thin film technology and is governed by the idea of shielding inhomogenities in the PZT thick film by a PZT thin film on top.

2. Experimental procedure and basic modeling considerations

2.1. Preparation

Experiments were based on a PZT–PMN formulation (Sonox P51, CeramTec, Lauf, Germany) with a high

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sintering temperature $T_s = 1200$ °C. T_s was reduced to 950 °C by the addition of 3 wt.% Bi_2O_3 and ZnO (2:1 wt.%) and 6 wt.% borosilicate glass as described elsewhere.[6–8] The powder was mixed with a solvent and a binder and screen printed onto a dense Al_2O_3-substrate (99.7%Al_2O_3) with screen printed Au electrode. A simple 45 × 45 mm^2 square printing pattern was chosen. Sintering was performed at 950 °C/5 h. Thereby, a shrinkage of approximately 45% in the thickness direction occured. Lateral shrinkage was suppressed, and no cracks were generated.

The PZT thick films were subsequently ground and polished to a thickness of about 100 μm. For the deposition of the PZT thin film an undoped PZT sol was used. The amounts of the alcoholates were adjusted to a final composition of $Pb_{1.05}(Zr_{0.53}Ti_{0.47})O_{3.05}$. The sol was deposited by spin coating. To reach a thickness of 1–1.5 μm typically 10–15 layers had to be applied. Sintering was performed after each layer at 700 °C/10 min.

2.2. Measurement equipment

PZT films were poled at room temperature with 30 kV/cm for 1 min before measurement of the dielectric and piezoelectric properties. Measurement of the parameters was done at least 24 h after poling. For investigation of the print quality, poling was carried out by corona until polarization of the PZT film reached at least 18 μC/cm^2.

The dielectric constants were measured at 1 kHz, using a Hewlett Packard 4194A Impedance Analyzer. The measurement of the piezoelectric coefficient $d_{33,\mathrm{eff}}$ was performed at the Department of Physics of the Martin-Luther-University Halle at 130 Hz, using equipment based on a capacitive detector.[12] A modified Sawyer–Tower circuit was used to determine ferroelectric hystereses. Internal resistance was measured by a Hewlett Packard 4339A High Resistance Meter.

To investigate the polarization distribution in the PZT film in correlation with the film microstructure the Laser Intensity Modulation Method (LIMM) was applied.[13,14] Thereby, the pyroelectric response in planes at different distances from the film surface was measured. The technique was combined with a laser scanning microscope for recording x–y scans of the polarization distribution. The equipment was improved for enhancing the resolution to $\leqslant 10$ μm in lateral dimensions and to 0.2 μm in the depth of the sample.

2.3. Basic modeling considerations

The effect of a PZT thin film on shielding inhomogeneities of the PZT thick film can be demonstrated by calculating the electric fields inside the bi-layered system. An axissymmetric finite element model has been developed which uses the fully coupled linear piezoelectric material law with remanant strains and remanant polarizations. The model consists of a piezoelectric thick film of 100 μm thickness and a thin film with different electromechanical properties and variable film thickness. A spherical pore, located directly under the interface between the two layers, is considered as a weakly polarizable region. Furthermore, it is assumed that both ferroelectric materials are homogeneously poled within each region. The bottom surface of the bilayer system is set to zero potential and mechanically clamped by the Al_2O_3-substrate. The boundary conditions at the top surface are rather undefined in the real printing process. However, the effect of a thin film, which is to improve the surface conditions, can be shown under fixed potential as well. Thus, the upper surface was also set to zero potential in the model. Then, in the absence of a defect, the internal fields will be homogeneous within each layer and depend on the dielectric constants and the relative thickness of the films. Details to the modeling of multilayer films are given elsewhere.[15]

3. Results and discussion

The PZT thick films showed very good dielectric, ferroelectric and piezoelectric properties as shown in Table 1 which makes them suitable for sensor and actuator applications. An example of the ferroelectric hystereses is given in Fig. 1.

For the ferroelectric printing process, the microstructure of the PZT film plays the key role. The process is based on a ferroelectric printing form, e.g. a PZT thick film, which is polarized homogeneously in a first step. The polarization is then switched locally according to the image structure. e.g. by an appropriate charge generation device. Charged toner particles move along electric field lines on the surface of the PZT layer, mainly between the regions of different polarization and surface charges, and are attracted to the image regions and are repelled from non-image areas. Thus, quality defined by uniformity and resolution of the print image depends mainly on the homogeneity of the polarization

Table 1
Properties of PZT thick film on Al_2O_3

Property	PZT thick film on Al_2O_3
Dielectric constant $\varepsilon_{33}{}^{T}/\epsilon_0$	1600–2000
Dielectric loss tan δ	<0.04
Piezoelectric coefficient d_{33} [pC/N]	150–210
Remanent polarization P_r at 5 Hz, 30 kV/cm (μC/cm^2)	12–16
Coercive field E_C at 5 Hz (kV/cm)	12–13
Internal resistance R_{is} (Ω)	$>10^{10}$

state, which corresponds to the microstructure of the film. To reach a resolution of 1200 dpi and to avoid visible artefacts in the printed image, the size of defects in the resulting electric field above the PZT layer has to be reduced below 20 μm.

Fig. 2 shows a typical micrograph of a PZT thick film. Inhomogeneities in the polarization state result from pores, secondary phases or coarse grains which are not polarized or have a remarkable lower remanent polarization than the matrix. The resulting gradients of the electric field at the surface influence the toner attraction.

Beside a fine grained matrix with grain sizes between 0.2 and 4 μm there is a closed porosity of 8.6 vol.% with pore sizes between 0.5 and 19 μm. The amount of coarse grains with sizes between 4 and 23 μm yields 10.7 vol.%. Even greater defect sizes are caused by the segregation of secondary phases (Bi_2O_3/ZnO, borosilicate glass).

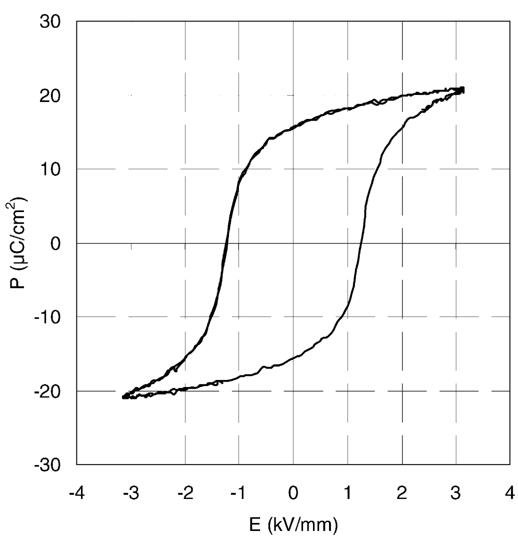

Fig. 1. Ferroelectric hystereses of a PZT thick film on Au electroded Al_2O_3.

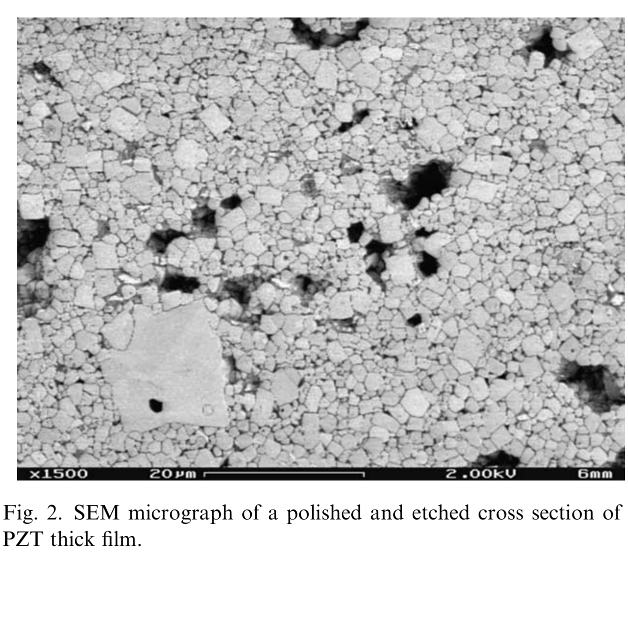

Fig. 2. SEM micrograph of a polished and etched cross section of a PZT thick film.

Our investigation is focused on the shielding of these defects by the deposition of a PZT thin film on top of the PZT thick film. Numerically calculated electric fields E_y (field in normal direction) for a pore diameter of 10 μm and a thin film thickness of 1 μm are shown in Fig. 3. An appropriate measure of the effect of the pore is the maximum difference of the dielectric displacement at the surface $\Delta D = D(x \to \infty) - D(x = 0)$. Results for different thin film thicknesses and materials are plotted in Fig. 4. There the effect of a PZT thin film with lower dielectric constant than the PZT thick film is compared to the

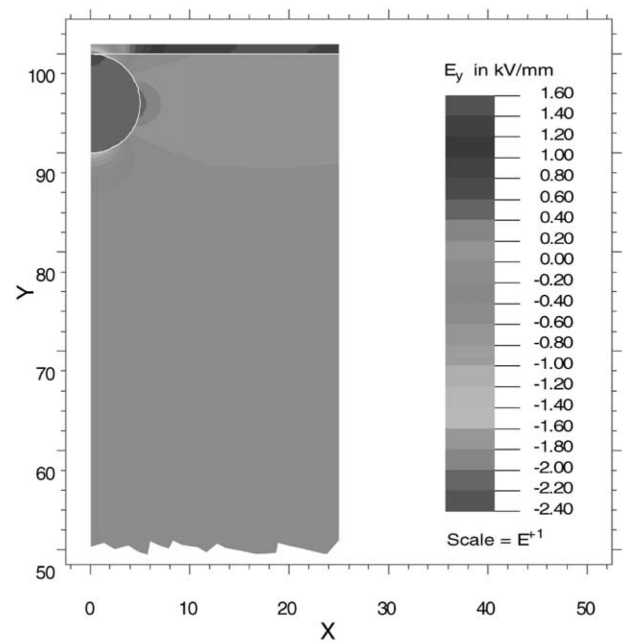

Fig. 3. Calculated electric field in normal (poling) direction for fixed (zero) electric potential at the surface of a bi-layered PZT film with included pore.

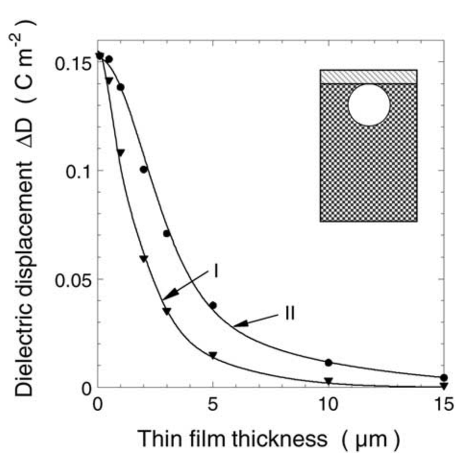

Fig. 4. Calculated differences in the dielectric displacement at the surface of a bi-layered PZT film: (I) PZT thick film with surface pore covered by a PZT thin film with lower dielectric constant than the PZT thick film and (II) PZT thick film with surface pore covered by a PZT thin film with the same properties as the PZT thick film.

effect of a thin film with the same properties as the PZT thick film. The PZT thin film with lower dielectric constant than the PZT thick film (e.g. an undoped PZT with a composition at the morphotropic phase boundary) has a greater impact on shielding inhomogeneities of the PZT thick film than a PZT thin film with same properties as the PZT thick film would have. It can be concluded that a film thickness close to 2 μm is necessary to reduce the ΔD by more than 50%. A thickness in the same order of magnitude of the defect size is necessary to eliminate inhomogeneity effects at the surface completely.

The results from modeling were confirmed by experimental results. Fig. 5 shows a micrograph of a PZT thick film before and after deposition of a PZT thin film. Pore size at the surface could be considerably reduced when film thickness of the PZT thin film reached 1–1.5 μm.

This resulted also in an obvious reduction of the flaw size in the toner picture (Fig. 6).

The polarization state in the bi-layered system was characterized by LIMM. For it, an artificial pore was introduced by a Vickers indentation. The defect was then covered by the PZT thin film. The signals of the pyroelectric coefficient from the PZT thin film in 0.3 μm distance and from the PZT thick film in 32 μm distance from the surface is compared in Fig. 7. The size of the defect could be reduced from about 600 μm to 200 μm by the thin film deposition. Fig. 8 shows the pyroelectric response of a bi-layered film consisting of a PZT thick film with approximately 98 μm thickness covered with a PZT thin film of approximately 2 μm thickness independent of the distance from the sample surface. The transition between the thin and the thick film is very smooth which can be explained by an infiltration of the surface pores with the PZT sol. The whole film could be already polarized with a voltage of 200 V. The understanding of the poling mechanism and the polarization state of bi-layered PZT films will be the topic of further research.

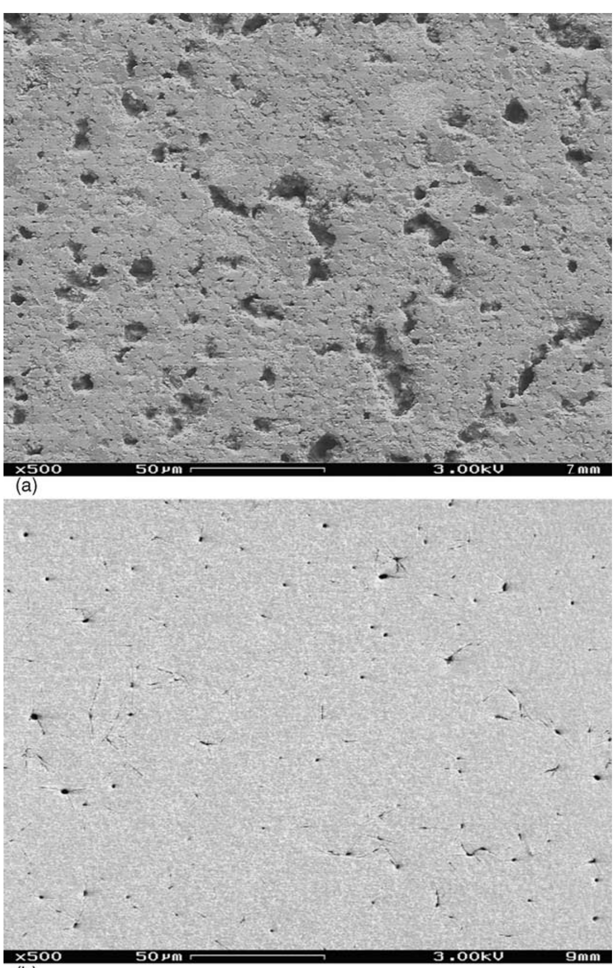

Fig. 5. SEM micrograph of a PZT thick film surface before (a) and after (b) deposition with a PZT thin film of 1–1.5 μm thickness.

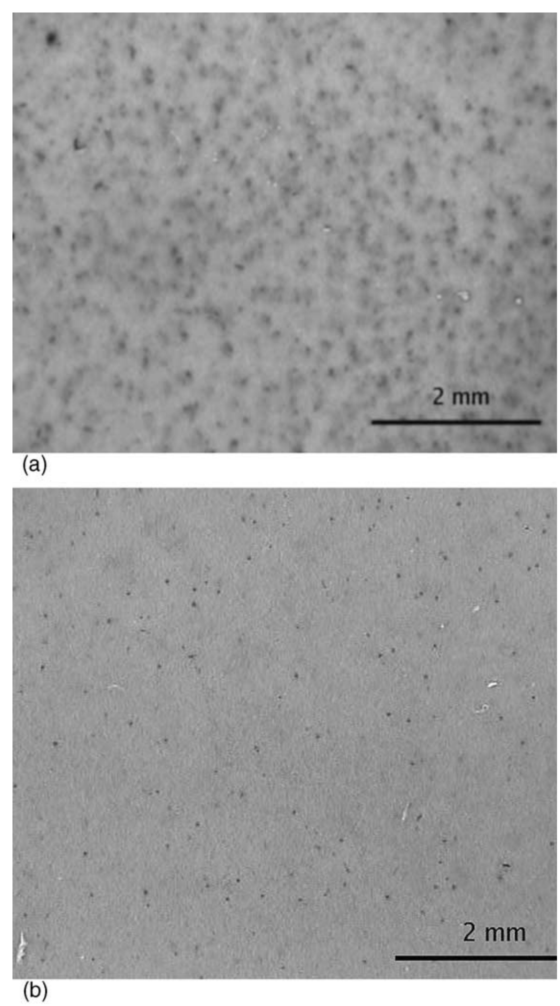

Fig. 6. Stereomicroscopic picture of a tonered PZT thick film without (a) and with (b) PZT thin film deposition. (PZT film is toner repelling polarized.)

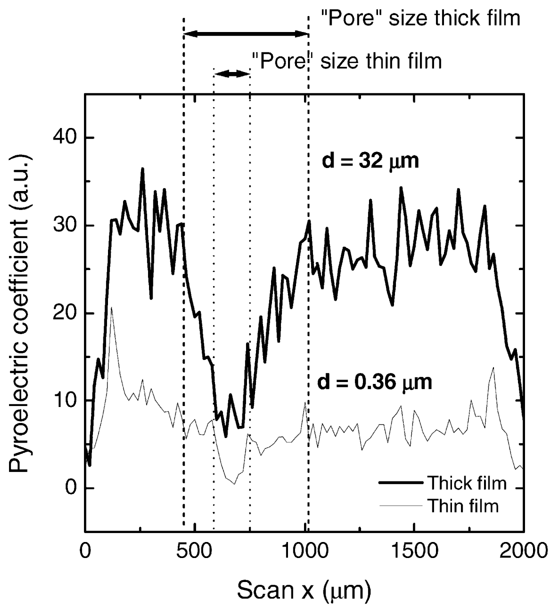

Fig. 7. Results from LIMM: pyroelectric coefficient near a Vickers indentation at 0.35 μm distance from the surface in the PZT thin film and at 32 μm distance from the surface in the PZT thick film.

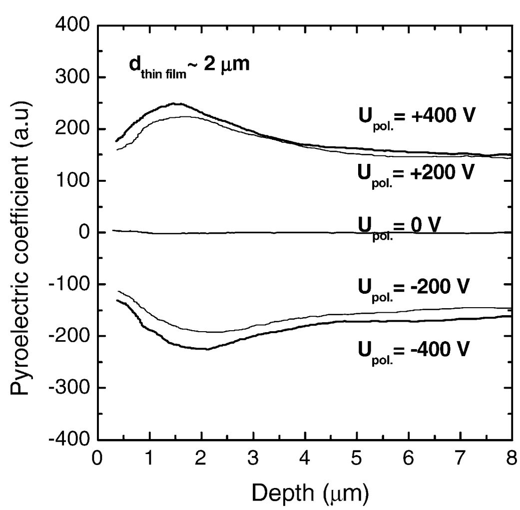

Fig. 8. Results from LIMM: signal of the pyroelectric coefficient of a bi-layered PZT film in dependence on the depth from the sample surface and the applied voltage. The thickness of the bi-layered film is ca. 100 μm with a thin film thickness of ca. 2 μm.

4. Conclusion

PZT thick films with very good dielectric, ferroelectric and piezoelectric properties have been manufactured successfully using low sintering material. These films have already been applied for pressure sensors, ultrasonic transducers and deformable mirrors. The application in a ferroelectric printing process desires PZT films with raised homogeneity. Defects in the PZT thick film, e.g. pores, coarse grains and secondary phases, cause inhomogeneities of polarization. The combination of thick and thin film technology gives the opportunity to homogenize the surface of such films which leads to a more uniform surface potential, shown by modeling and experiment.

Acknowledgements

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