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PZT-based piezoelectric composites via a modified sol–gel route

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Abstract

A novel hybrid sol–gel approach is developed to prepare composite PZT films in the thickness range 1–20 μm at relatively low sintering temperatures (<600°C). In this approach, a dip-coating method (thickness <5 μm) is used to deposit films from a sol–gel solution with dispersed PZT powder. Thicker films (>5 μm) are fabricated using sedimentation of the PZT powder onto Pt-coated Si substrates with a subsequent multiple infiltration of powder coatings with PZT sol–gel solution. Dielectric and ferroelectric properties of thick films are studied and discussed in the framework of existing models of composites. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Composites; Dielectric properties; Films; PZT; Sol–gel method

1. Introduction

A current trend to miniaturisation and an increase in the operation frequency requires scaling down of the dimensions of ceramic electronic components. Specifically, ferroelectric thick films of moderate thickness (1–20 μm) with a controllable porosity are desired for the development of piezoelectric transducers, micro sensors, and pyroelectric detectors.[1] To date, the properties of Pb-based thick films prepared using conventional techniques (such as screen-printing and tape casting) are inferior to those of bulk ceramics, mainly due to the lead loss and insufficient densification during sintering. Using recently developed sol–gel method, a large number of deposition cycles is required for the fabrication of thick films. Moreover, thick layers deposited with this technique are prone to cracking and delamination. Thus, a modification of the existing technologies is needed.

A promising idea to fabricate 0–3 thick film composites using sintered ferroelectric powder dispersed in a sol–gel solution was proposed by Barrow et al.[2] However, this type of connectivity suggests only a small (less than 10 vol.%) powder content in the film, and, as a consequence, a small thickness of the individual layer. Otherwise, if the powder concentration exceeds the above mentioned limit, the dispersed phase starts to form continuous structure, and the type of the connectivity changes resulting in the uncontrollable porosity and poor dielectric properties.[3] Besides, high-concentrated suspension, which is necessary to obtain a large enough thickness of the individual layer (>1 μm per coating cycle), results in the aggregation of the powder leading to unstable porous coatings with a rough surface. In the present work, the above mentioned problems are solved and a novel processing route to fabricate ferroelectric thick film composites is developed. Ferroelectric and dielectric properties of composite films are discussed.

2. Experimental

A 0.6 mol/l PZT precursor solution of the composition $Pb_{1.05}Zr_{0.52}Ti_{0.48}O_3$ was prepared from lead acetate trihydrate, zirconium n-propoxide, titanium isopropoxide, and 2-methoxyethanol in accordance with the recipe of Budd et al.[4] A 5% excess of Pb was added to the solution to compensate for the lead loss during heat treatment. Commercially available PZT powders (TRS600FG and TRS200FG, TRS Ceramics) were dispersed in the solution. Powder concentrations in the slurry used in the

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dip-coating method were varied in the range 10–10 000 mg/ml. Tritone/X100 or glycerol were used to increase the viscosity of the solution. An intensive ultrasonic mixing of the slurry was performed before and during dip coating onto Pt/Ti/SiO_2/Si substrates. Sedimentation of the powder onto the same substrate was done from a low-concentrated suspension (~0.5 mg/ml) in 0.6 M PZT solution immediately after the ultrasonic mixing. Two types of centrifuges (WIFUG and L8-M Beckman) were used in this work. After rotating the substrate fixed in a plastic tube (rotation speed 3000 rpm for 3 min) the samples were dried on a hot plate at 180°C for 1 min and fired in a tube furnace at 550°C for 5 min after each sedimentation cycle. The thickness of the individual layer was about 2.5 μm for 10 mg of the powder.

Infiltration with a PZT sol–gel solution after sedimentation was made by putting a small quantity of the solution onto the coating surface (until a full coverage of the coating area) and subsequent spinning at 1000 rpm for 30 s. This allowed the solution to fill the pores in the coating and to remove the solution excess from the surface. After the infiltration, samples were dried and heated again to 550°C. Multiple infiltration cycles were performed to obtain stable PZT films with good dielectric properties. Finally, circular Pt top electrodes of 0.6 mm in diameter were deposited by sputtering.

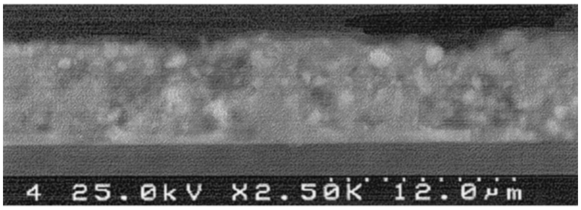
The crystalline phase and microstructure of the films (as well as the film thickness) were analysed by XRD (Rigaku, Geigerflex D/Max-B) and SEM (Hitachi S-4100), respectively. The capacitance and loss factor were measured with a Solartron 1260 Impedance/Gain-phase analyser.

3. Results and discussion

XRD analysis of all the investigated films after firing showed single-phase perovskite structure with no indication of second phases. SEM analysis of the films deposited by dip-coating without any viscous additive demonstrated that no powder was left in the films after the deposition. Therefore, 15% of glycerol was added to the solution. As a result, the thickness of the individual layer was increased (up to 0.25 μm) with a considerable amount of powder within the film. However, this process resulted in micro pores due to the burning out of glycerol. Also, large powder aggregates were formed in the film. The best results were obtained by using continuous ultrasonic mixing during the deposition processing and no viscous additives at all.[5] Thus dense composite structures with a small number of aggregates could be achieved (thickness 0.25 μm/coating). The results of dielectric and ferroelectric measurements on these films were reported in an earlier publication.[5] In particular, the high dielectric permittivity (≅2500) and polarisation values (≅35 μC/cm^2) were demonstrated. The apparent disadvantage of this technique is a large number of layers needed for the deposition of thick films and inability to control the porosity. In the following, the results on sedimentation deposition are described, which allowed for the deposition of thick coatings with a much lower number of processing steps.

Fig. 1 compares SEM cross-sections of the PZT films before and after the infiltration of sedimented layers with PZT precursor solution. It can be clearly seen that powder deposition alone results in very porous structures with a rough surface. After infiltration (15 layers), both the densification and surface roughness are significantly improved, though some porosity is left inside the film. Fig. 2(a) shows the dependence of the effective dielectric permittivity of the films deposited by sedimentation on the number of infiltration cycles, N. It is demonstrated that the dielectric permittivity increases with increasing N reaching the saturation at about 1350 ($N = 10$). The total film thickness was about 10 μm. A similar increase in the coating weight with increasing N was observed. Fig. 2(b) shows weight of the films as a function of the number of infiltration cycles obtained for 2-, and 4-layer coatings before, and after crystallisation of the sol–gel matrix at 550°C. It can be concluded that some kind of saturation takes place at $N = 10$ for films not subjected to heating. However, after the heat treatment, the infiltration process could be started again and new saturation is reached. This can be explained by pore opening in a composite layer due to PZT gel decomposition (which takes place at the temperatures above 300°C)[4] and shrinkage of the PZT gel after infiltration. Fig. 3 shows nested hysteresis loops obtained for PZT films deposited by sedimentation of 2 powder layers with subsequent 14 sol–gel infiltrations. Saturation polarisation

a) before infiltration



b) after infiltration

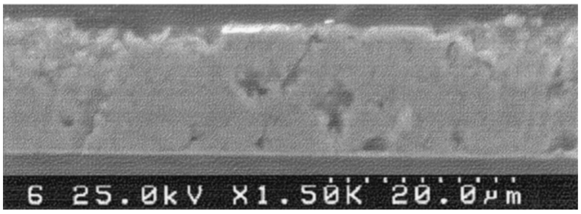


Fig. 1. SEM cross-sections of a PZT thick film: (a) before infiltration, and (b) after 14 infiltration cycles.

$P_{\mathrm{sat}} = 40$ μC/cm^2 (at 200 kV/cm) and coercive field $E_c \cong$ 50 kV/cm were observed. These values are close to those of thin PZT films deposited by chemical techniques.

Both weight and thickness of the layers were measured at various stages of infiltration. These values allowed us to estimate relative density of the composite coatings before (~34%) and after 15 cycles of infiltration (~41%). The calculations showed that the total number of the infiltration cycles of about 40 would be required to fill all the pores in the sedimented layer due to decomposition of infiltrated PZT solution.

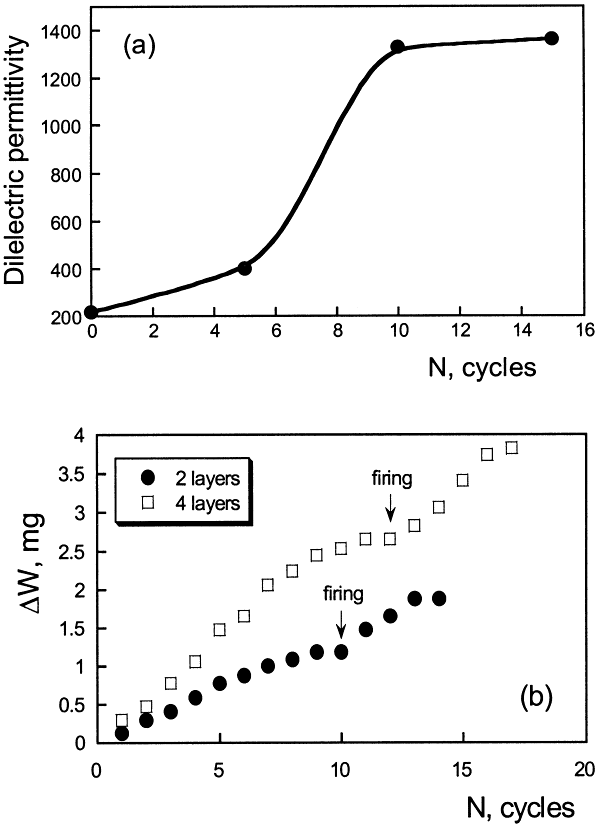


Fig. 2. (a) Effective dielectric permittivity (a) and (b) weight increase vs. number of infiltration cycles for PZT thick films deposited by sedimentation of PZT powder.

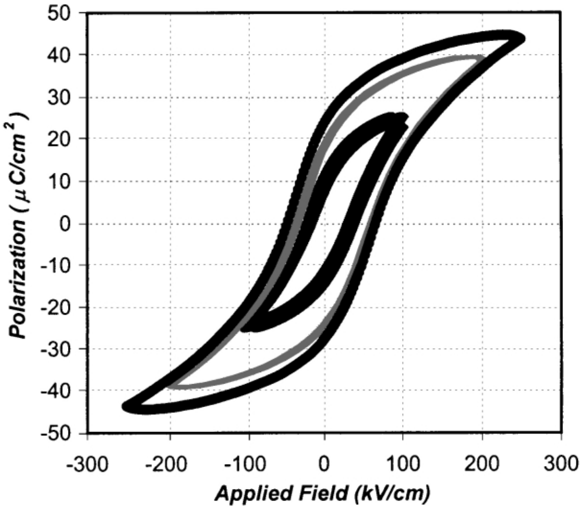


Fig. 3. Hysteresis loops under increasing maximum field in PZT thick film deposited by sedimentation (2 powder layers + 14 infiltrations with PZT sol).

Before the discussion of the dielectric properties of the films, it is instructive to consider the infiltration kinetics. According to Darsy's law, the infiltration depth x versus time t may be expressed as:[6]

$$x = \left(\frac{2KP}{\eta}\right)^{\frac{1}{2}} t^{\frac{1}{2}}, \tag{1}$$

where η is the viscosity, $K = D^2(\mathrm{I}-\rho)^3/36C\rho^2$ is the permeability of the porous body, and $C \approx 5$ is a constant that defines the shape and tortuosity of the pore channel.[7] $P = P_{\mathrm{c}} + P_{\mathrm{a}} - P_{\mathrm{i}}$ is the total pressure which is defined by the capillary pressure P_{c}, applied pressure P_{a} and pressure of displaced gas P_{i}. Capillary pressure is given by equation $P_{\mathrm{c}} = \frac{6\gamma\cos\theta\rho}{D(1-\rho)}$, where D is the particle diameter, γ and θ are surface tension, and contact angle, respectively. Using experimental values of $D \cong 1$ μm (mean particle size of the TRS600FG powder), $\eta = 2.65 \times 10^{-3}$ Pa s, $\gamma \cong 3.2 \times 10^{-2}$ N/m, $\theta \cong 0$, and $\rho \cong 0.4$, one can get $P_{\mathrm{c}} \cong 1.3 \cdot 10^5$ Pa. In the absence of applied pressure, the total pressure is $P = P_{\mathrm{c}} - P_{\mathrm{i}} \cong 2 \times 10^4$ Pa assuming that the pressure of the displaced gas is equal to the atmospheric one ($P_{\mathrm{i}} = 1.1 \times 10^5$ Pa). According to Eq. (1), the infiltration depth $x \approx 2$ mm is calculated for the used infiltration time (30 s). This value is much greater than the thickness of the sedimented layer (~10 μm). Since the replaced gas is not evacuated during the infiltration procedure, the difference $P_{\mathrm{c}} - P_{\mathrm{i}}$ becomes zero after filling in of nearly 20% pores due to the corresponding increase of P_{i}. Thus, infiltration of the powder layer without evacuation of the replaced gas results in a slowing rate of infiltration kinetics before all the pores are filled in.

Apparently, the above mentioned increase of the dielectric properties of composites after multiple infiltrations is due to partial filling of the pores inside the film. However, it is difficult to explain a nearly 6-fold increase in the dielectric permittivity [Fig. 2(a)] after infiltration where the composite density is increased by only 20%. The existing models of two-phase composites (see e.g. Ref. 8 and references therein) seem to fail in predicting the dielectric properties of the composite films. To solve this problem, the composite layer should be considered as a three-component system containing PZT powder, sol–gel PZT, and air (pores).

Fig. 4(a) shows the effective dielectric pemittivity of the composite ε as a function of volume concentrations of the components V_{i} for the simplest case, where the phases are connected in parallel, $\varepsilon = \varepsilon_1 V_1 + \varepsilon_2 V_2 + \varepsilon_3 V_3$, where $\varepsilon_1 = 3420$, $\varepsilon_2 = 500$, and $\varepsilon_3 = 1$ are the dielectric

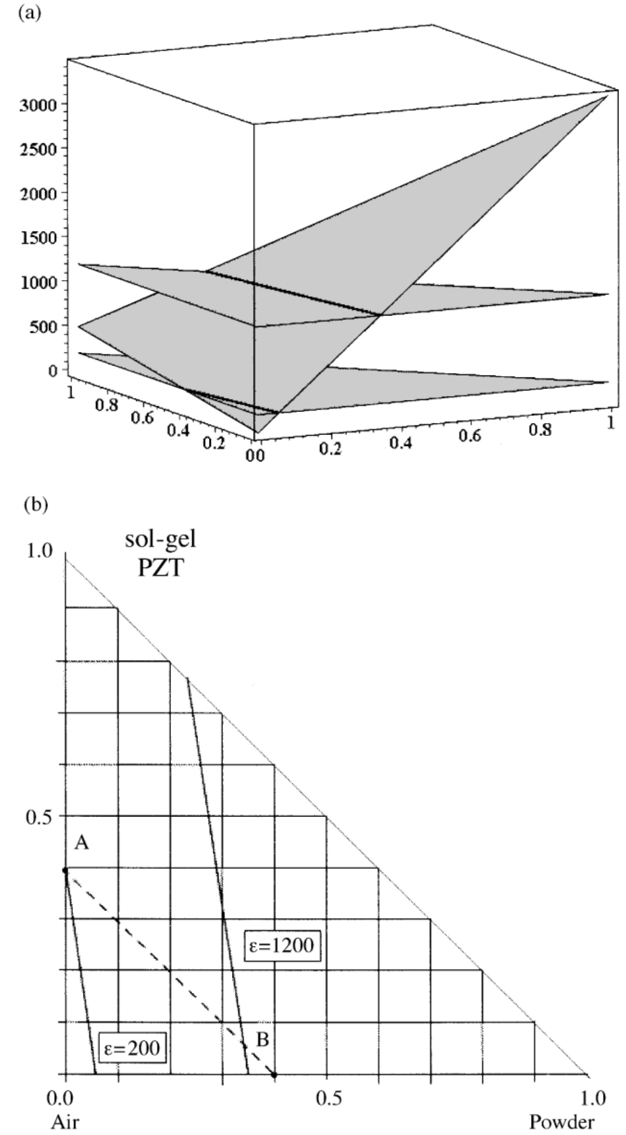


Fig. 4. (a) ε (V_i) 3D diagram of PZT composite thick film, and (b) diagram interceptions with $\varepsilon = 200$ and 1200 planes (solid lines); dashed line corresponds to the relative density of 40%.

permittivities of TRS600FG powder, sol–gel PZT, and air, respectively. Horizontal planes in the diagram correspond to the effective dielectric permittivity measured in the film before ($\varepsilon = 200$) and after infiltration ($\varepsilon = 1200$). Fig. 4(b) shows interception lines (solid) of 3D diagram with these planes, and the line (dashed) corresponding to constant relative density of the film ($\rho = 40\%$.). It is seen from Fig. 4(b) that there are two points (A and B) where solid lines intercept with the dashed one. These points correspond to different volume ratios of the ferroelectric phases (ceramic powder and sol–gel PZT) at the same relative density of the film (air content). An increase in the powder volume concentration obtained after infiltration (point B on the diagram) can be a result of the increased powder contribution to the effective dielectric permittivity of the film. It can be regarded as some kind of percolation [9] where the continuous filling with PZT sol–gel solution results in the appearance of intermediate PZT layers connecting powder particles.

4. Conclusion

A modified sol–gel method was developed, which allows for the deposition of composite PZT films in the thickness range up to 20 μm. The processing conditions were optimised in order to produce films with improved dielectric and ferroelectric properties: $\varepsilon = 2500$, $P_{\text{sat}} \cong 35\ \mu\text{C/cm}^2$ (dip-coating method, thickness up to 5 μm) and $\varepsilon = 1350$, $P_{\text{sat}} \cong 40\ \mu\text{C/cm}^2$ (sedimentation technique, thickness up to 20 μm). A large increase in the effective dielectric permittivity of composites is explained based on the simple three-component parallel model taking into account the evolution of the sol–gel phase connecting powder particles.

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