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A3-P13 SYNTHESIS AND CHARACTERIZATION OF PZT FOR COATINGS

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Abstract

Polycrystalline transparent lead zirconate titanate (PZT) thin films were prepared from complex metal alkoxide solutions by spin coating. Determination of reduced specific viscosities of different PZT precursor solutions indicated compact particles which was confirmed by photon correlation spectroscopy and transmission electron microscopy. Experiments led to films that appeared amorphous in X-ray investigation with a thickness up to 1 μm. Polycrystalline crack-free PZT films with a thickness of about 520 nm were obtained after heat treatment at 550°C for 6 hours, with crystallite sizes between 13 and 20 nm.

1. Introduction

Perovskite phase $Pb(Zr,Ti)O_3$ (PZT) type films have recently been used to form non-volatile ferroelectric random access memory devices and multi-layer ceramic capacitors (MLCC's) [1]. This has increased interest in the formation of PZT thin films.

Lead zirconate titanate ceramics exhibit a high dielectric constant, a large electromechanical coupling coefficient, a large spontaneous polarization, and good electro-optic properties, which suggests that thin film applications exist as electro-optical light modulators [2], infrared detectors, display, optical storage, and surface acoustic wave devices [3].

Sol-gel techniques have been widely used for the preparation of thin PZT films [4-9]. The effects of hydrolysis on the degree of polymerization during metallo-organic solution deposition of lead zirconate titanate films on platinum-coated fused-silica substrates have been investigated. The results indicated that the degree of prepolymerization controls dramatically the film morphology/4/. Ferroelectric PZT films were prepared by dip-coating and the crystallization kinetics of the porous films and powders have been studied [5]. In [6] it was investigated how the morphology of the annealed perovskite films is affected by the chemistry of the removal of organic components during processing. Using FTIR data it was found that the organics were not completely removed from the thin films after consolidation at 400°C. By comparing the X-ray diffraction data of the annealed films consolidated at different temperatures it was noted that the consolidation temperature has only little effect on the crystallinity. With the aid of an intermediate layer of Al_2O_3 on glass and fused-silica substrates it is possible to grow crack-free transparent ferroelectric polycrystalline PZT films with a thickness of up to 2 μm [7]. Recent results show that the crystal structure of dip-coated films depends strongly on the film thickness and the substrate used as well as on the annealing temperature [8]. Using quantitative X-ray analysis the entire crystallization process in thin PZT films could be described by a consecutive phase transformation process governed by nucleation [9]. So far, little work has been carried out to correlate sol properties and processing parameters with film crystallization, microstructure and electrical properties. However, the structure and size of the sol particles prepared by hydrolysis and condensation of metal alkoxides strongly influence film morphology and properties. In this paper, the influence of reaction conditions on sol formation and sol structure was studied and was correlated with the coating properties as well as the crystallization behaviour of thin PZT films on various substrates.

2. Experimental

Stoichiometric amounts of lead-2-ethylhexanoate $Pb(O_2C_8H_{15})_2$, zirconium-n-propoxide $Zr(OC_3H_7)_4$, and titanium-n-butoxide $Ti(OC_4H_9)_4$ were mixed to form a liquid precursor of $Pb_1Zr_{0.5}Ti_{0.5}O_3$ [6]. In order to get crack-free films, additives like diethanolamine (DEA) and ethylene glycol (EG) were added. All precursor solutions were prepared without the addition of water. They were diluted to 50wt% with isopropanol and then stirred in an ultrasonic bath for 30 minutes to ensure homogeneity. The precursor solutions were investigated by measuring the dynamic viscosity as a function of time, and by calculating the reduced specific viscosity as well as the intrinsic viscosity as a function of PZT concentration, and by taking Fourier-transform-infrared (FTIR) spectra of the precursor solutions. Informations about particle size distribution were obtained by using Photon correlation spectroscopy (PCS), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS).

Deposition of a PZT layer was carried out by spin coating at 5000 rpm in a dust-free environment. Precursor films were coated onto fused silica, single-crystal silicon, and alumina. The films were dried at 110°C to evaporate the solvent, and then heated at 275°C for 60 minutes. The coating/drying/consolidating process was repeated

several times. Crystallization was carried out at 550°C for 6 hours. The effects of drying and annealing were characterized using X-ray diffraction (XRD), transmission FTIR spectroscopy for silicon wafers, and optical microscopy (Fig. 1).

3. Results and discussion

3.1 PZT precursor solutions

Dynamic viscosities of different PZT precursor solutions without additives show an increase with increasing PZT concentration C_{PZT}, and viscosities between 2.4 mPa·s (0.01 mole·l^{-1} PZT) and 8.3 mPa·s (0.75 mole·l^{-1} PZT) were found. A simple quadratic relationship ($\eta = 2{\cdot}4 + 10{\cdot}C^2$) between the dynamic viscosity η and the PZT concentration was found (Fig. 2).

In order to get crack-free PZT films additives like diethanolamine and ethylene glycol were added to different PZT precursor solutions. With increasing values of the ratios D and E (D = mole DEA/mole Alkoxide; E = mole EG/mole Alkoxide) the dynamic viscosity increased (Fig. 3). In Fig. 3 optimal coating conditions are marked, which will be discussed below.

The dynamic viscosity of PZT precursor solutions with and without additives was independent of time up to five month and could be adjusted by the PZT concentration as well as by the addition of additives.

For determining the reduced specific viscosity η_{sp}/C (η_{sp}: specific viscosity) two PZT precursor solutions (0.25 mole·l^{-1} and 0.50 mole·l^{-1} PZT) were diluted with different amounts of iPrOH. All diluted solutions were heated to evaporate the solvent. The residual powders were heated at 550°C for 6 h to get perovskite phase PZT. Figure 4 shows the reduced specific viscosity η_{sp}/C as a function of PZT concentration C_{PZT}:

In both cases the reduced specific viscosity is independent of PZT precursor concentration and the intrinsic viscosity is below 0.05 cm^3/g indicating compact sol particles in the PZT precursor solution [10]. No agglomeration and gelation in the solutions have occurred. Further information about the sol properties was obtained from PCS measurements. For a monodisperse suspension of rigid particles, the autocorrelation function decays exponentially, and τ_{CE} is the characteristic relaxation time given by

$$1/\tau_{CE} = 2D_TK^2$$

where D_T is the translational diffusion coefficient, and K is determined from the wavelength λ of the light source, the index of refraction n, and the scattering angle θ [11]:

$$K = (4\pi n/\lambda)\sin(\theta/2)$$

For the PCS measurements all solutions were prepared under clean room conditions using ceramic filters to avoid the existence of dust particles in the solutions. Figures 5 and 6 show an autocorrelation function of a 0.50 mole·l^{-1} PZT precursor solution as well as the calculated particle size distribution.

Two relaxation processes (region A and B) could be predicted from the autocorrelation function in Fig. 5. From the first relaxation process (region A in Fig. 5) a particle diameter of about 6 mm was calculated. These particles form in a dynamic process clusters with an average size of about 1.2 µm which corresponds to the second slower relaxation process (region B in Fig. 5). There were no differences between autocorrelation functions of a 0.1 mole·l^{-1} and a 0.50 mole·l^{-1} PZT precursor solutions and no dependence of time up to five months was detected. The angle-dependent measurements of relaxation times τ_A and τ_B for processes A and B showed a linear relationship between the relaxation times and $\sin^2(\theta/2)$ (Fig. 7).

These results indicate that there are two diffusion controlled processes (A and B) [11]. Process A corresponds with non-interactive and monodispersed particles (average size of 6 mm) which form loosely packed clusters with a size of about 1,2 µm (process B).

Figure 8 shows the autocorrelation function of a 0.37 mole·l^{-1} PZT precursor solution with ethylene glycol as additive (E = 0.5) and the calculated particle size.

The addition of additives leads to different results in the PCS measurements; only one fast relaxation process could be detected approximately leading to the same average particle size as mentioned above. Compared with the results of the PCS measurements on solutions without additives, the particles in solutions with additives do not form clusters. Interpreting these results the additives act after an unknown mechanism as dispersing agents inhibiting the agglomeration of particles. Comparing the PZT precursor solutions with ethylene glycol and diethanolamine no differences in particle size distribution were found. In the range between 50 to 500 mm no particles could be detected in any solution when studied by SAXS.

With the aid of an image processing system the TEM pictures of different PZT precursor solutions with

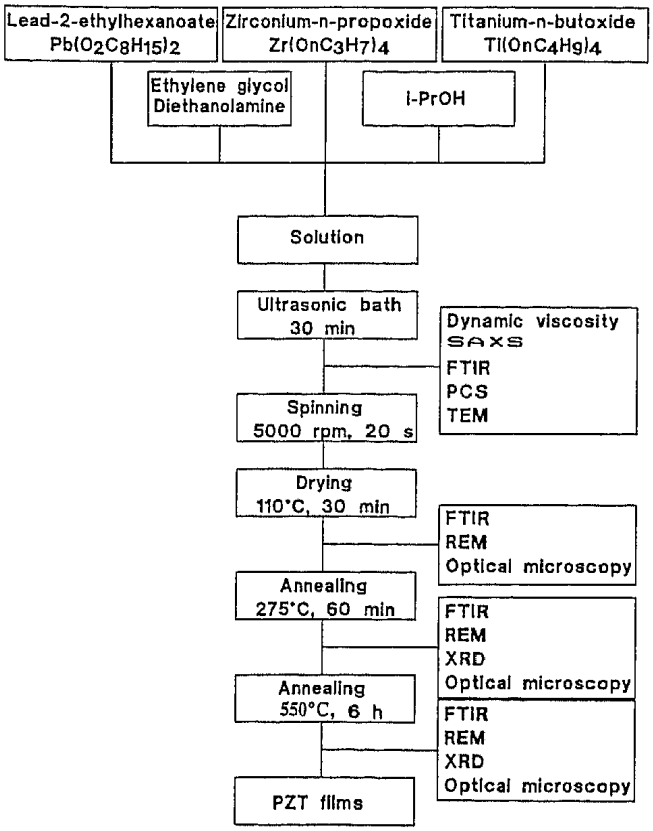


Fig. 1 Flow diagram for the preparation and characterisation of PZT precursor solutions and films.

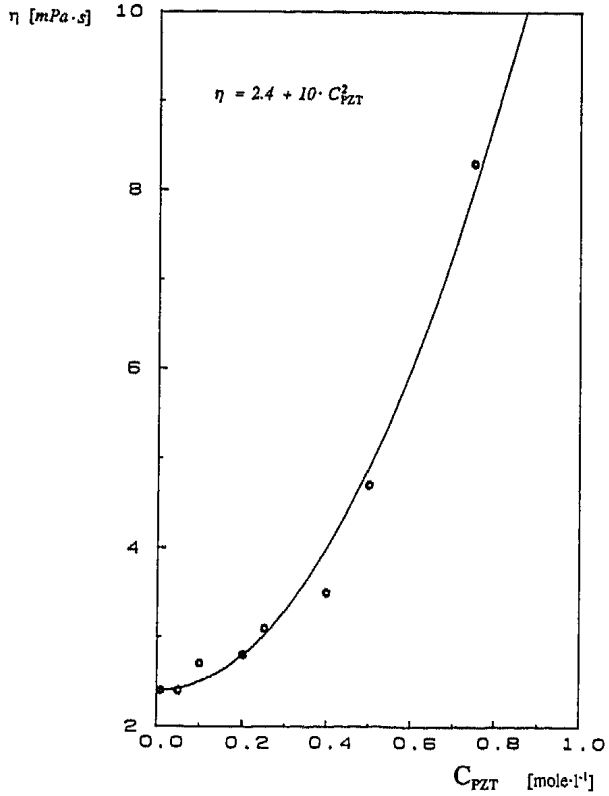


Fig. 2 Dynamic viscosities of different PZT precursor solutions without additives.

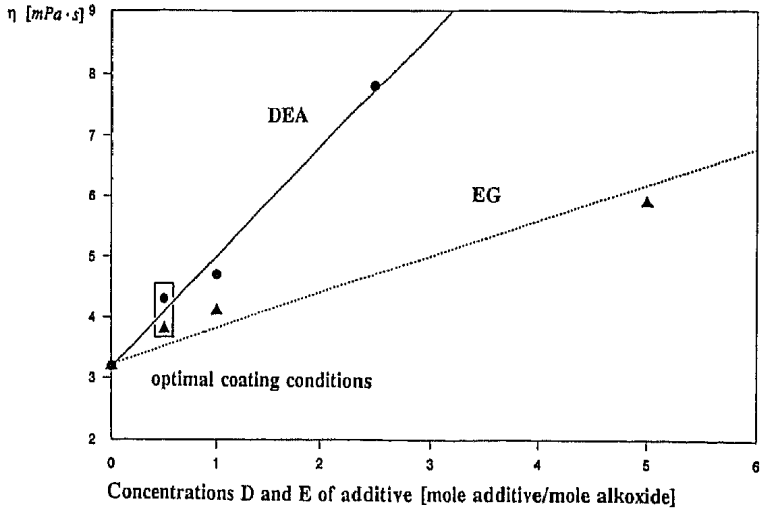


Fig. 3 Dynamic viscosities of PZT precursor solutions with additives.

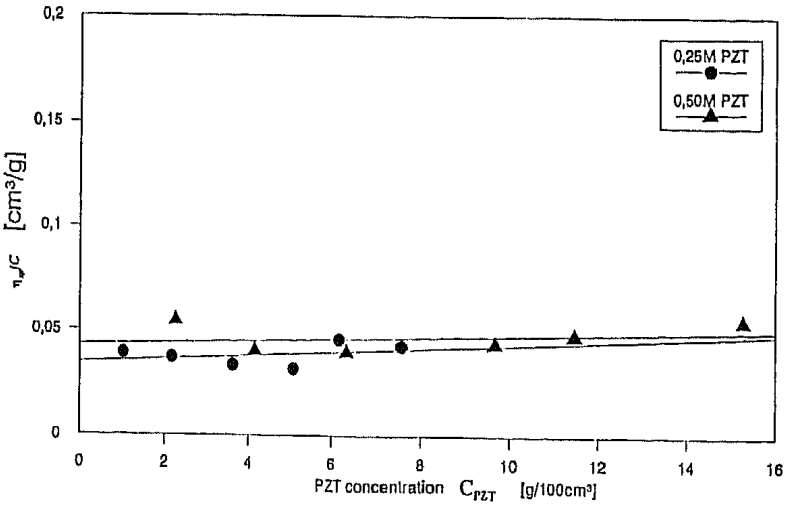
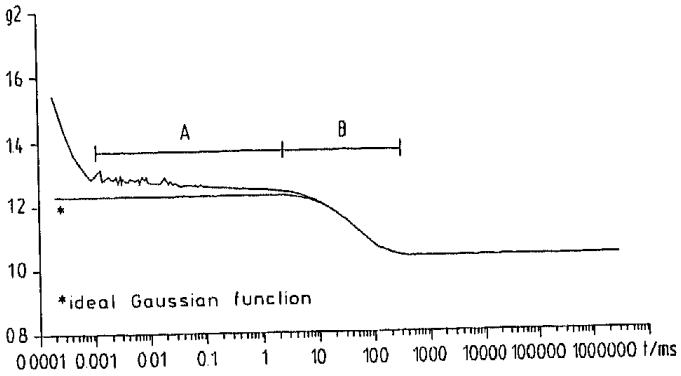


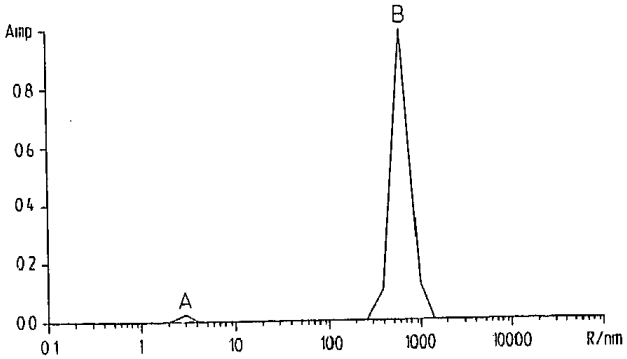
Fig. 4 Reduced specific viscosity η_{sp}/C as a function of PZT concentration C_{PZT}.



Region A: fast relaxation process

Region B: slow relaxation process

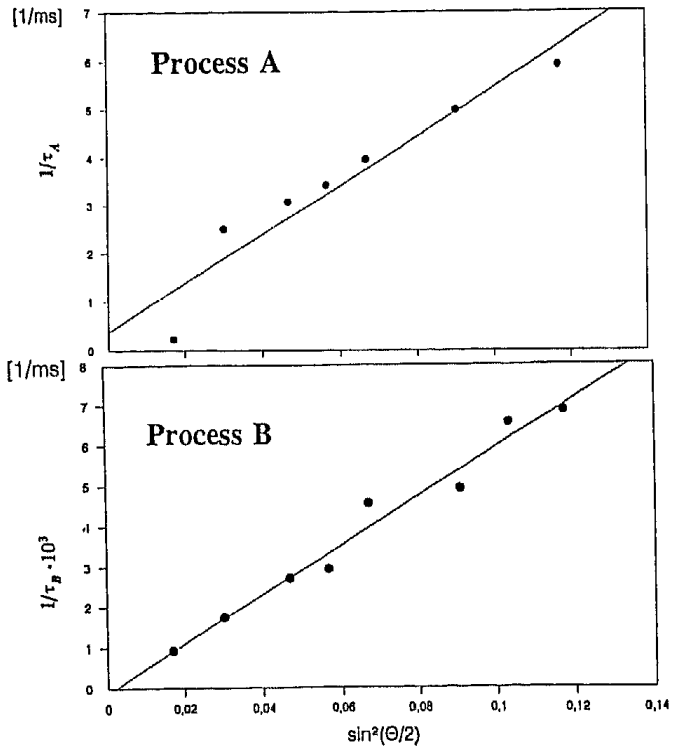
Fig. 5 Autocorrelation function of a 0.50 mole·l^{-1} PZT precursor solution.

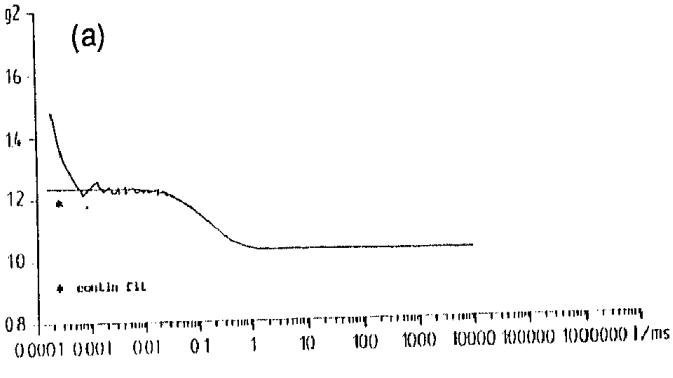


A: particle size

B: cluster size

Fig. 6 Calculated particle size distribution of a 0.50mole·l^{-1} PZT precursor solution.





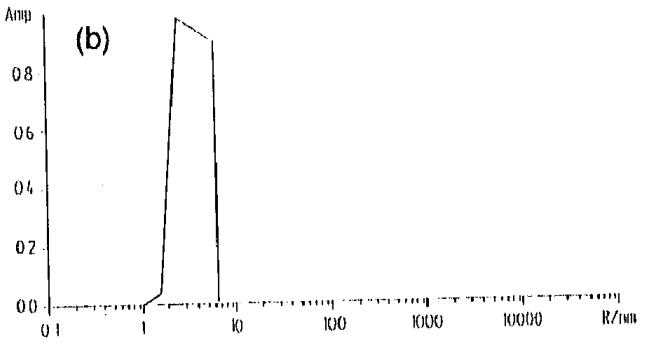


Fig. 8 Autocorrelation function (a) and calculated particle size distribution (b) of a 0.37 mole·l^{-1} PZT precursor solution with ethylene glycol as additive (E = 0.5).

Fig. 7 Angle-dependent measurements of relaxation times for processes A and B.

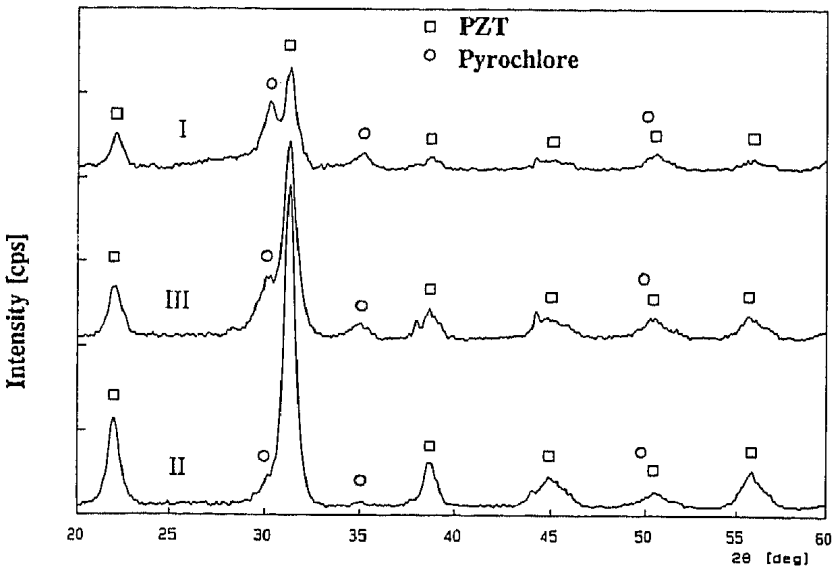


Fig. 9 X-ray patterns on silicon for PZT films prepared with different precursor solutions (550°C for 6 hours).

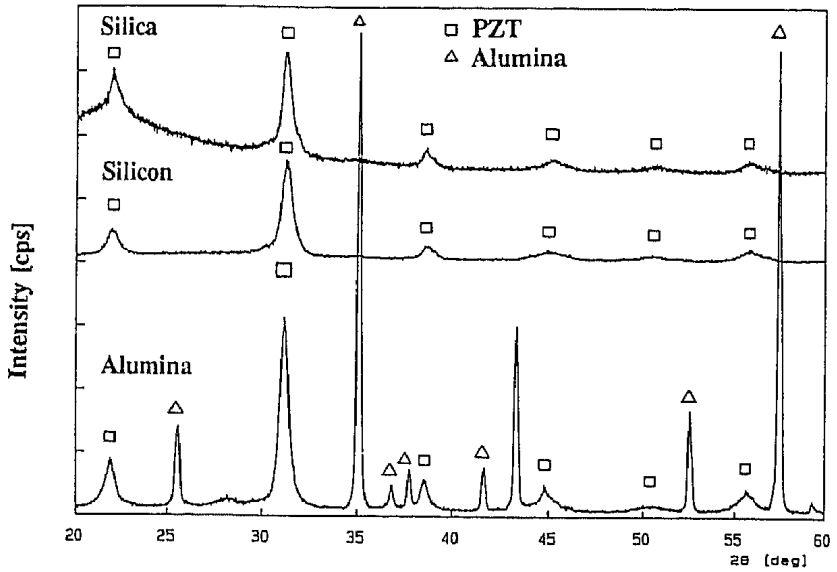


Fig. 10 X-ray patterns of films prepared with solution II on different substrates (550°C for 6 hours; film thickness about 520mm).

Table 1 Different PZT precursors and their film formation characteristics

Nr.	C_{PZT} *[mole l^{-1}]*	*D [mole DEA/ mole alkoxide]*	*E [mole EG/ mole alkoxide]*	*Cracks after heat treat-ment at 550°C*
I	*0.37*	*0.5*	*0*	*few*
II	*0.37*	*0*	*0.5*	*none*
III	*0.50*	*0*	*0*	*many*

and without additives were analysed. The TEM micrographs showed spherical particles with a calculated average diameter of 4 mm, which agrees with the results of photon correlation spectroscopy and the results of calculation from the intrinsic viscosity measurements. Again no time dependence of the particle size was observed.

Due to the results mentioned above, the question arises how the sol properties influence the film formation and the crystallization behaviour. It can be expected that the microstructure of the dry films prepared from cluster-free PZT precursor solutions with an almost monodisperse particle size distribution is very homogeneous exhibiting a narrow pore size distribution, which is important for the formation of crack-free films[12]. In contrast, coating solutions containing clusters might be expected to result in a heterogeneous microstructure with a broad pore size distribution. Therefore, a deterioration of the drying behaviour of the wet films can be expected.

3.2 Film preparation

The influences of sol type on crack formation are shown in Table 1. For one coating/drying/annealing cycle PZT films with a thickness of about 100 mm were obtained from a 0.50 mole·1^{-1} PZT precursor solution. Films with a thickness up to 1 μm could be prepared by repeating this procedure seven times. The dry films were amorphous according to X-ray analyses and further heat treatment at 275°C for 60 min led to the crystallization of the metastable cubic pyrochlore phase independent of the substrate used. Tetragonal perovskite PZT could be detected after annealing up to 550°C on all substrates used. Only ethylene glycol as additive led to crack-free films after heat treatment at 550°C. This can be attributed to the slowing down of the drying process compared to DEA. The film thickness of the crack-free films was about 520 nm after four repeated coating/drying/annealing cycles with a subsequent heat treatment at 550°C. The different sols show different crystallization behaviour (Fig. 9). Sol II after 550°C treatment is almost pyrochlore-free compared to I and III, indicating a strong effect of sol structure on crystallization, the mechanism of which is not quite clear up to now.

The X-ray patterns were rather broad, and from the line width a crystallite size between 13 and 20 mm was calculated [13].

In order to study the influence of the substrate sol II was used for the preparation of films on silicon, silica and alumina as substrates. The annealed PZT films were slightly yellow on silica and alumina and grey on silicon. In Fig. 10, X-ray diffraction patterns show, that in all three cases films without pyrochlore are found.

On alumina the PZT phase shows narrower peaks. The comparison of sols I and III on silicon, silica and alumina shows the pyrochlore formation of I and III on silica and silicon, but not on alumina. Summarizing one can say that by sol tailoring it is possible to obtain crack-free PZT films on various substrates and to avoid pyrochlore phase even under low temperature crystallization conditions. A strong influence of the substrates could be found, indicating a quasi epitaxial effect on Al_2O_3.

4. Conclusions

Drying control chemical additives (DCCA's) like ethylene glycol and diethanolamine are widely used for the preparation of crack free gel films because they reduce capillary forces during the drying step. Due to the results of this investigation these compounds can also act as surface active additives by preventing the agglomeration of nanosized sol particles. Therefore, the successful use of DCCA's for the preparation of crack-free gel films leads to a homogeneous microstructure with a narrow pore size distribution and an improved drying and crystallization behaviour.

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