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Effect of the Particle Size in PZT Precursor Sols on the Orientation of the Thin Films

Q. Zhang,[a]* Z. Huang,[a] M. E. Vickers[b] and R. W. Whatmore[a]

[a]Advanced Material Group, Cranfield University, Cranfield, Beds, MK43 OAL, UK
[b]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, UK

Abstract

In the sol–gel processing of the ferroelectric thin films of $PbZr_xTi_{1\text{-}x}O_3$ *(PZT), solution precursor characteristics have long been considered as factors which affect thin film microstructure. In this study, the structures of PZT precursor sols before and after hydrolysis were characterised by using NMR (nuclear magnetic resonance), PCS (photon correlation spectroscopy), and SAXS (small angle X-ray scattering) techniques as well as the measurement of the rheological properties of the PZT precursor solutions. The measurements discovered that alkoxy ligands which were bonded to metals were completely replaced by acetate ligands in the unhydrolysed sols. The particles in our PZT sols are chain-like and their average size increases linearly after hydrolysis on a logarithmic scale due to the hydrolysis and condensation reactions. To examine the relationship between the film orientation and the particle size in the precursor sols, the films were fabricated with different particle sizes and then annealed at 480°C. The preferred orientations were investigated using X-ray diffraction. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: films, sol–gel processes, X-ray methods, ferroelectric properties, PZT.

1 Introduction

Ferroelectric $Pb(Zr,Ti)O_3$ (PZT) thin films are under investigation for a variety of applications, ranging from decoupling capacitors[1] to optical storage media.[2] Sol–gel processing is proving to be a powerful technique for generating these films with tailored properties. However, there is still a very large gap in our understanding of the causal relationships between solution chemistry and the resulting ferroelectric properties.[3–6]

One approach to building this understanding is to systematically evaluate the solution chemistry factors and develop models relating ferroelectric properties to these factors. One of these factors is solution ageing not only for hydrolysed solutions but also for unhydrolysed solutions. It is found that the viscosity of sol solutions changes with time even though the solution was sealed and stored in a dry environment after it was prepared. This change often results in the alteration of electric properties of ferroelectric thin films, and therefore reduces the reproducibility of thin films with desired properties. In addition, striation defects can also occur during spinning if the solutions have aged unacceptably.[7] Based on our previous work on determining and characterising the particle structures in $Pb(Zr_{0{\cdot}3}Ti_{0{\cdot}7})O_3$ sols,[8] the work described below reports the effects of particle size in PZT sols on the orientation and electric properties of thin films. The purpose is to shed light on such effects by elucidating the physico-chemical properties of solutions before and during hydrolysis.

2 Experimental

The composition of the solution is Pb:0·3Zr:0·7Ti with 10 (mol%) excess of Pb. Dehydrated Pb acetate and Zr n-propoxide and Ti isopropoxide were dissolved in acetic acid and methanol. Acetic acid was added with Pb:acid = 1 g:1 ml) to stabilise the solution. Hydrolysis (unless specified elsewhere) was carried out by adding distilled water directly to the solution in the ratio H_2O:Pb 1:2. ^1H and ^{13}C spectra were obtained from a 400 MHz NMR (Bruker, AM-400) spectrometer. Photon correlation spectroscopy (PCS) experiments were performed on a Malvern Zetasizer 3000 Instrument

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*To whom correspondence should be addressed. Fax: +44-(0)1234-751346; E-mail: q.zhang@cranfield.ac.uk

with an external laser (wavelength: 488 nm, power: 10~60 mW). The photomultiplier was fixed at 90°. SAXS data were collected with Cuk_α radiation in a step scanning Kratky camera. The experimental details on the PCS and SAXS techniques have been published elsewhere.[7] A falling ball viscometer was used to measure the viscosities of the solutions and solvent. Thin films were fabricated on Pt(111)/Ti/SiO_2/Si substrates (thickness Pt/Ti/SiO_2 = 100/5/500 nm) by spin coating. A single coating generally gave a 0·08~0.1 μm crack-free film after firing. The orientation of the film was determined by standard θ–2θ X-ray diffraction (XRD) method on a Siemens D5005 diffractometer using CuK_α radiation and a Goebel mirror. Thicknesses of the films were examined using scanning electron microscopy (SEM). A Genrad 1689M RLC Digibridge impedance analyser was used to measure dielectric properties at 1 KHz and a Radiant Technologies RT66A ferroelectric test system was used to obtain ferroelectric hysteresis loops.

3 Results and Discussion

In a fresh-made unhydrolysed solution, particle size was found to be between 5 and 6 nm in our system. Although no water was added to the solution, particle size increased with time (up to ~10 nm in 3 months). Viscosity measurement of the unhydrolysed solutions shows that the reduced viscosity increased linearly with the concentration, indicating that the polymer formed in the precursor solution is chain-like. After water was added to the precursor solution, the hydrolysis and condensation reactions occurred. The limiting viscosity number (η) of the solution increased with the ageing time, indicating that the polymer chain in the solution was increasing. After hydrolysis, the particles increased more quickly (Fig. 1). It increased up to 15–20 nm in about 150 h.

SAXS data was used to extract information on the structure of the precursor. The gradient at low angles increased with time after hydrolysis, indicating an increasing scattering dimension. For a rod the scattering data can be separated into two parts: a low angle region which relates to the length and a higher angle region which relates to the diameter. The rod length $L = \sqrt{12}R_g$ and the rod diameter can be obtained from data at higher angles where $2\pi/L < Q < 1/R_c$. Figure 2 shows the change of rod length and diameter of the particles with ageing time. Both rod length and diameter increased linearly with the logarithm of the ageing time. This result agreed with that from PCS, although PCS gives the diameter of an spherical particle with equivalent volume as a rod particle. It is worth noticing that the diameter data obtained from PCS are basically equal to the length data obtained from SAXS, indicating that PCS is able to measure the particle size of a long chain polymer. However, care must be taken because the obtained data by PCS at this time actually reflect the length size of a polymer.

^1H and ^{13}C NMR did not show any obvious differences between the spectra of unhydrolysed

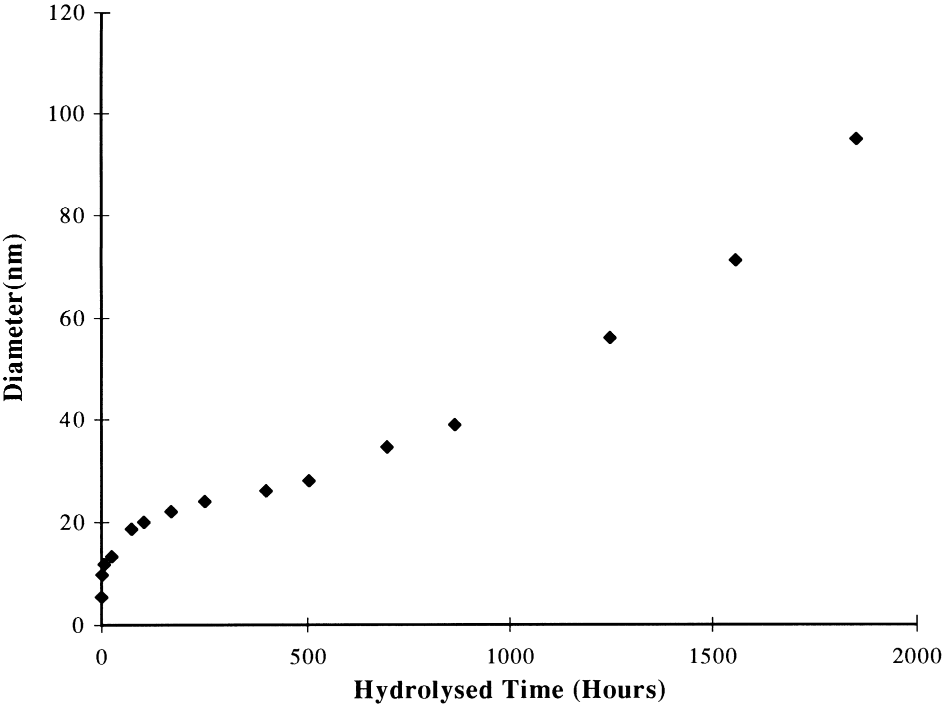

Fig. 1. Change of particle size with ageing time for the hydrolysed PZT sols. Water was added to the system with the ratio of water:ethylene glycol 5:1.

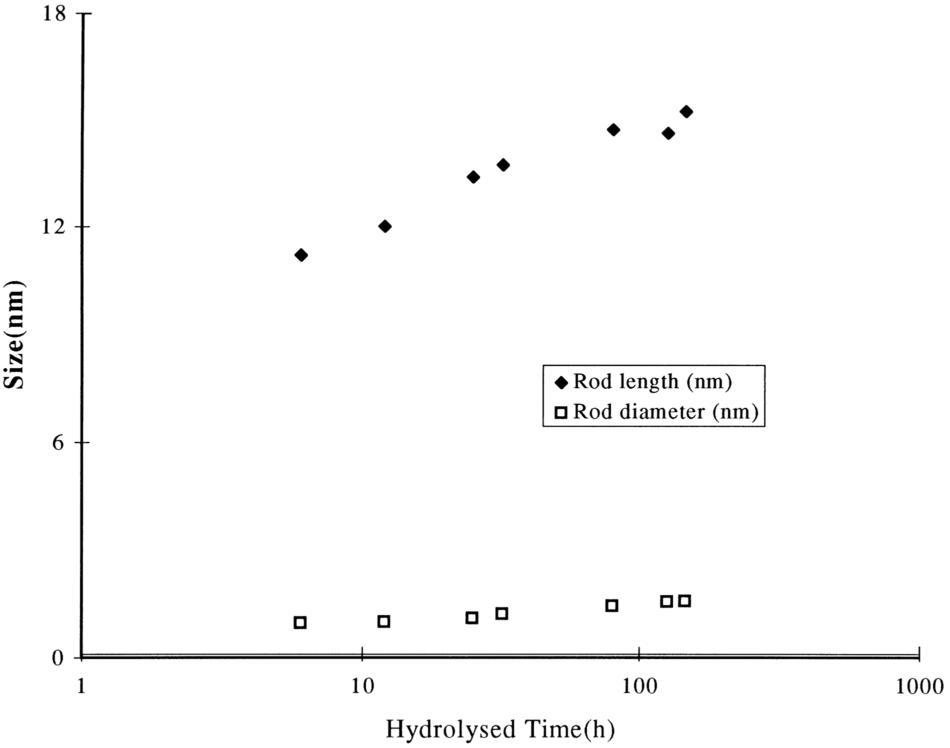

Fig. 2. Change of particle size with the ageing time by SAXS.

precursor sample and hydrolysed samples. They were also similar to the spectra reported by Assink *et al.*[3] except that in our spectra, no isopropyl acetate and n-propyl acetate were observed. However, methyl acetate could be identified. No alkoxy ligands of the starting precursors were found in the final PZT solution precursor species before and after hydrolysis. Due to the similarity in NMR spectra of unhydrolysed precursor solution and hydrolysed solution, we might expect that before and after hydrolysis, the basic structure of the polymer did not change except for the increase in the polymer size.

The solution with different particle sizes at different times was used for preparation of thin films. These films were made under the same conditions. Each film was dried at 200°C for 3 min. and fired at 480°C for 4 min. The films have ten layers. Figure 3 shows the XRD patterns of four films made with the solutions having particle sizes from 5–6 nm to 16·5 nm. With the increase of the particle size, the intensity of (111) orientation decreased and the pyrochlore phase appeared. The intensity of the perovskite (111) peak decreased when the particle size increased. However, no other orientations, apart from (111) peak, are obviously present. The above observations actually support the opinion that the degree of branching of the precursor has a direct effect on the resulting morphology of the deposited film.[4,5] Weakly branched precursor systems allow for the interpenetration and rearrangement of polymer molecules during the film deposition process, resulting in the formation of a thermodynamically favorable configuration of efficient packing and high density. In contrast, highly branched precursor hinders such rearrangement because of a high rate of irreversible entanglement of molecules, leading to the formation of a non-homogeneous film.

Our recent study on the transformation mechanism of perovskite phase of PZT (30/70) thin films on Pt(111)/Ti/SiO_2/Si substrates shows that the PZT transformation follows the formation of a transient intermetallic phase process.[8] Our TEM cross-section images directly show for the first time, to our knowledge, the existence of intermetallic phase and the EDX element analysis proved that the composition of intermetallic phase is Pt_3Pb instead of $Pt_{5-7}Pb$ as claimed by Chen and Chen.[9] This intermetallic phase was found to precede the formation of perovskite [111] texture. Chen and Chen thought that the formation of intermetallic phase is due to the relative easiness of Pb^{2+} reduction. Pb^{2+} can be reduced at even modestly reducing atmosphere ($P_{O_2} \sim 10^{-5}$ atm). This reducing atmosphere can be attained because of the depletion of oxygen within the ceramic film during the initial stages of pyrolysis. When Pb^{2+} is reduced to Pb, Pb can easily and quickly reacts with Pt in the interface of PZT and Pt to form Pt_3Pb.[9,10]

To explain the effect of the particle size on the texture development of thin films, we can also refer to the formation of the intermetallic phase Pt_3Pb. When the films were directly heated on a hot plate at high temperature for a very short time (ex.

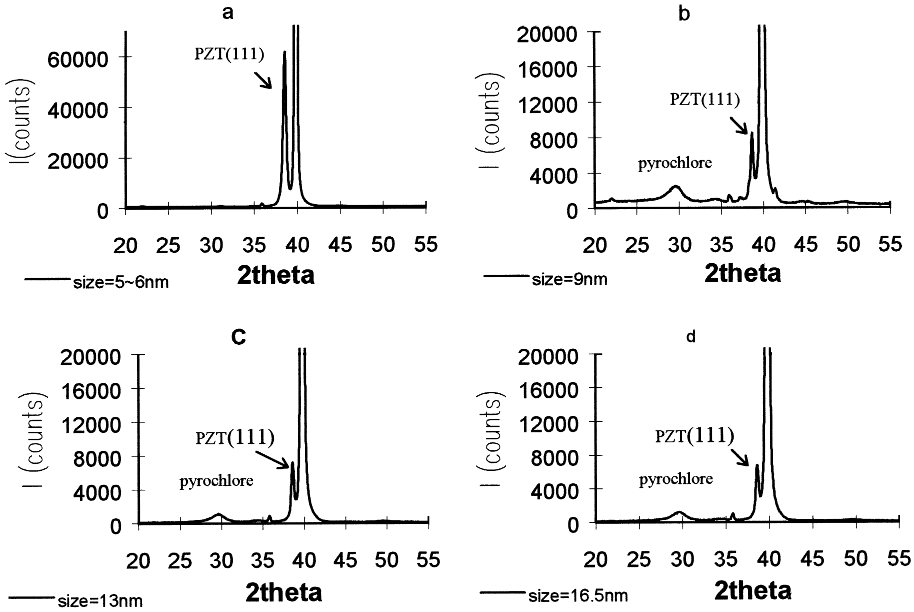

Fig. 3. Effect of particle size in sol–gel precursors on crystallisation and orientation of PZT thin films.

480°C for 5–10 s), a redox reaction at the buried PZT/Pt interface, where a low oxygen partial pressure temporarily prevailed during fast heating, was formed because of depletion of oxygen for pyrolysing organics. This caused the reduction of Pb^{2+} into metallic Pb, which in turn formed Pt_3Pb on the substrate interface. PZT(111) could then be nucleated on Pt_3Pb before its reoxidation by surface influx of O_2. Because the organic content of sol–gel precursor decreases in polymer species due to hydrolysis and condensation reactions and larger particles form, the oxygen partial pressure is probably not low enough or the organic content is not high enough in the subsequent thin films to reduce Pb^{2+} or to maintain Pt_3Pb during fast heating. Thus, the (111) texture could not be obtained or was suppressed in the sol–gel films. This was exactly the situation, as observed when we used the solutions containing higher chain polymers.

Ferroelectric hysteresis was not observed in the samples exhibiting pyrochlore phase when using the solutions with large particles. However, the use of the solutions with small particles which produced a perovskite phase resulted in the films which demonstrated excellent ferroelectric switching behaviour. Figure 4 shows the hysteresis loop of sample a in Fig. 3 (10 layers, 0·8 μm thick). Relative dielectric constant and loss tangent were 440 and 0·014, respectively. The saturation polarisation, remnant polarisation and the coercive field were about, 36 $\mu C\,cm^{-2}$, 24 $\mu C\,cm^{-2}$ and 66 $kV\,cm^{-1}$, respectively, at a maximum applied voltage of 19 V.

The particle size threshold value at and beyond which a highly branched polymer is expected to form depends on many factors, such as precursor alkoxides, solvents, synthesis routes, mixed time and temperature of multi-components, by-products and so on. In our investigation of the system of acetic acid–2-methoxyethanol,[8] we observed that freshly-made sols contain particles having average size of 4–5 nm, which is smaller than the particles in the acetic acid–methanol system. It has been observed that when the average particle size increases to 6–8 nm, a Pb-containing compound often precipitates and the resultant films do not give good physical properties. This implies that particle size must be strictly monitored, which, in turn, can help to determine the shelf life of a PZT precursor sol.

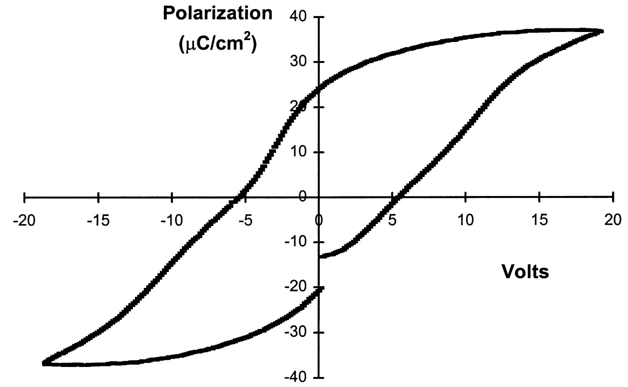

Fig. 4. Ferroelectric hysteresis loop for a PZT thin film prepared with a PZT precursor having an average particle size of 5–6 nm.

4 Conclusion

Various techniques have been combined to monitor the changes of the PZT precursor structure and polymer size in PZT precursor solutions. Experiments showed that the ageing of PZT precursor solutions was found to occur not only in the hydrolysed sol solutions but also in the unhydrolysed sols, although particles in unhydrolysed sols are only slowly increasing in size. When the solutions with large polymer particles were used to make coatings, a non-ferroelectric pyrochlore phase appeared and perovskite phase PZT(111) was largely suppressed, which resulted in the failure of the ferroelectric properties. Our observations support the contention that weakly branched polymer molecules in the PZT precursor solutions are responsible for the formation of a thermodynamically favourable configuration of efficient packing and high density.

Acknowledgements

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