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Characterization of $Pb(Zr,Ti)O_3$ thin films obtained by MOD

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$Pb(Zr,Ti)O_3$ thin films were deposited by dip-coating on polycrystalline alumina substrates by using an MOD method. The thickness and homogeneity of the films were measured as a function of dip rates and solution concentration. Heating and cooling schedules determined the main structure of the crystallized films. Rheology measurements and Fourier transform–infrared spectra were carried out to obtain a better knowledge of the solution features. A microstructural development study and some ferroelectric measurements were also carried out.

1. Introduction

Thin films of ferroelectric materials, such as the perovskite compounds $PbTiO_3$ (PT), $Pb(Zr,Ti)O_3$ (PZT), $Pb_3Nb_2MgO_9$ (PMN), and many others, have found wide application in electronic devices, non-volatile memory arrays, infrared detectors, saw substrates, frequency discriminators for laser diodes, etc. [1]. This development is conditioned to the large-scale deposition processes. Physical procedures, such as electron-beam vaporization, r.f. sputtering and laser ablation, require heavy and complex equipment, and do not produce large surfaces with adequate homogeneity [2].

Complex chemical procedures such as chemical vapour deposition (CVD) [3], liquid-phase epitaxy, and other precise high-temperatures (above 1600 °C) processes, for which PbO volatility is very strong, lead to a non-stoichiometric formulation. Other processes, such as spray pyrolysis [4], thermal decomposition of layers obtained from deposition of solutions [5, 6] and sol–gel procedures [7], have shown the possibility of preparing homogeneous thin films on large surfaces. These procedures have allowed transparent polycrystalline thin films to be obtained by heat treatment at temperatures in the 500–800 °C range, over a wide class of single and polycrystalline substrates.

The sol–gel method for preparing thin films requires the use of metallorganic solutions which must be processed with a rigorous control of added water to obtain stable hydroxide sols of the corresponding cations. The preparation of films by thermal decomposition of deposited layers from solutions of the cations is easier, and allows the use of organic and/or inorganic soluble salts with higher stability than the alkoxide ones. Nevertheless, the latter compounds are used very frequently.

Deposition on to different substrates can be carried out by several methods, such as dip coating [8], spin coating [9], spray drying, spray pyrolysis and others [10]. Dip coating is one of the easiest to perform. Thickness control is favoured and the film composition can be carefully controlled, which is a widely used procedure when it is necessary to prepare multicomponent films, for example from stable solutions such as hydroxide sols. In addition, this procedure allows integration of thin films of ferroelectric compounds on to microelectronic circuits.

The present work had as its main aim, the preparation of thin films of piezoelectric PZT with compositions near the morphotropic boundary, on polycrystalline alumina supports by a dip-coating procedure, starting from clear solutions of organometallic cationic precursors. The influence of molar concentration and dipping rates on film thickness have been determined. The relationships between heat treatment and microstructure, particle size and crack formation of the crystallized films, have also been studied. Finally, the ageing of solutions from environmental moisture was also performed.

2. Experimental procedure

Commercial titanium and zirconium tetrabutoxides, lead 2-ethilhexanoate and acetate trihidrate were used as precursors. Different molar solutions $X = 0.1$, 0.3, 0.5, 0.7 and 0.9 of a 53/47 PZT composition were formulated. Polycrystalline alumina substrates of 99% purity were thoroughly cleaned by lapping with potassium dichromate, washing and were then ultrasonically treated. Solution rheology was studied by measurement of viscosity in a Rotovisco model Haake RV-20. Ageing behaviour was monitored by Fourier transform–infrared determinations with a Perkin–Elmer Spectrograph 1760-X.

The dipping rates used were 12.12, 36.32 and 71.43 cm min^{-1}. Deposited films were dried in an oven at 200 °C, with different heating rates between 0.2 and 1.0 °C min^{-1}. Crystallization was attained by heat treatment at 750 °C, 4 h, with several heating rates and a constant cooling rate of 1 °C min^{-1}.

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The thickness of the dried and crystallized films was measured with a Talystep model Taylor–Hobson, with 0.1 μm sensibility. Crystalline evolution was followed by XRD (Siemens D-5000 Diffractometer) and by SEM with a DSM 950 Zeiss electron microscope.

Hysteresis loops were measured using an R.T. 66 A Standardized Test System.

3. Results and discussion

A flow chart corresponding to the procedure followed for the preparation of thin films from successive coating (up to five) is shown in Fig. 1. This procedure differs from the first one in the partial hydrolysis step prior to coating. Samples with different dip rates from 8–40 cm min^{-1} were prepared. The final thickness ranged between 1.5 and 2.0 μm as a function of dipping withdrawal.

Fig. 2 shows the evolution of water absorption with ageing time from IR spectroscopy measurements. The water bands grew with time but no hydrolysis phenomenon was found in the solutions which remained clear. According to the IR results, it seems that when the concentration falls, the water absorption rises. Although titanium and zirconium tetrabutoxides are unstable in environmental moisture, the prepared solutions were sufficiently stable to be handled for several days without degradation.

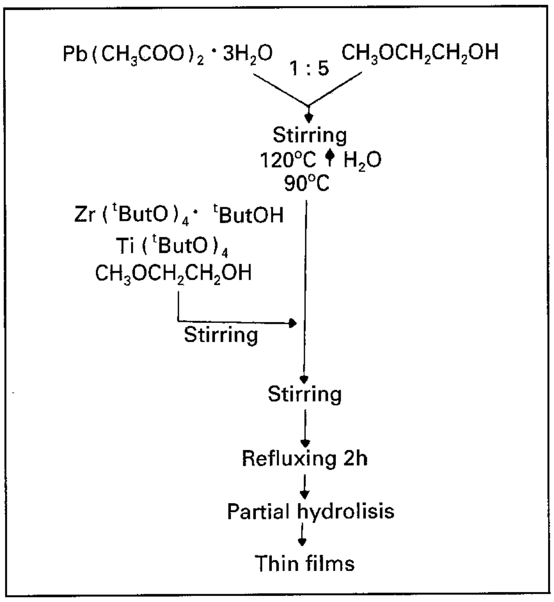


Figure 1 Flow chart corresponding to the preparation of thin films.

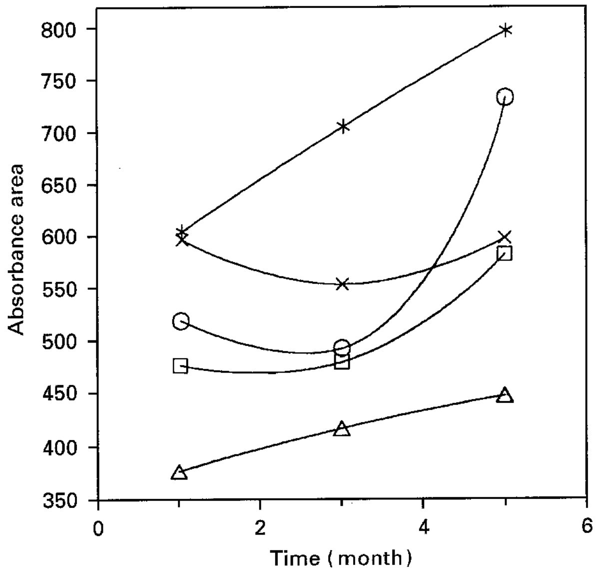


Figure 2 Variation of the moisture absorbance with ageing time in (*) 0.1 M, (×) 0.3 M, (○) 0.5 M, (□) 0.7 M and (△) 0.9 M solutions.

The viscosity changes with concentration. The increment of the viscosity values was not linear with molarity. The hydrolysis process, which would cause sol flocculation and subsequent viscosity increase, does not take place. On the other hand, the increase of absorbed water led to a correlative decrease in the viscosity. Because of the higher moisture absorption for lower concentrations, this effect is more appreciated on the diluter solutions. Ageing time is also a very important factor which increases the viscosity.

The film thickness increases quickly with molarity for low dip rates, but more slowly when the dip rate increases (Fig. 3). The reasons for such a behaviour could be related to the rheological features of the solutions, but the driving mechanisms for such a behaviour remain unclear. These results are in disagreement with those of Guchielmi and Zenezini [10] who found a higher thickness for high withdrawal rates, according to the Landau and Levich equation, but they do agree with the results described by Palma and Pascual [11].

On the other hand, it can be seen that film thickness decreases when the withdrawal rate increases. This effect is stronger for the higher concentration.

Film drying is a crucial step with respect to the cracking behaviour during thermal crystallization at high temperatures. Heating rates of 1 °C min^{-1} from room temperature to 200 °C lead to crack formation on films crystallized at temperature of 750 °C. Lowering the drying rate of 0.2 °C min^{-1} allowed the preparation of crack-free, dried and crystallized thin films at the same crystallization temperature. The heating

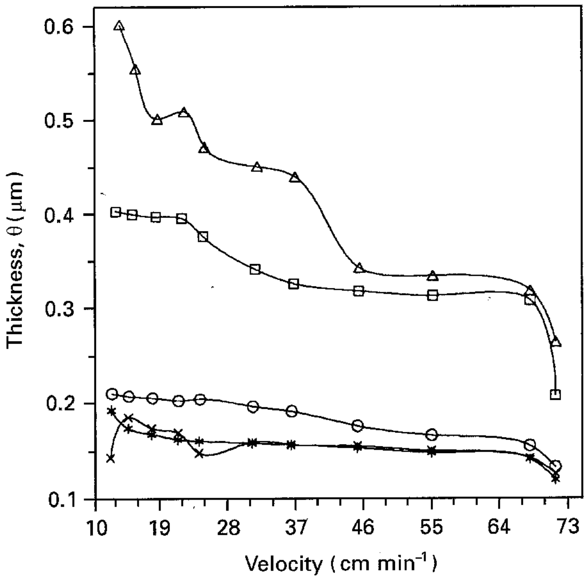
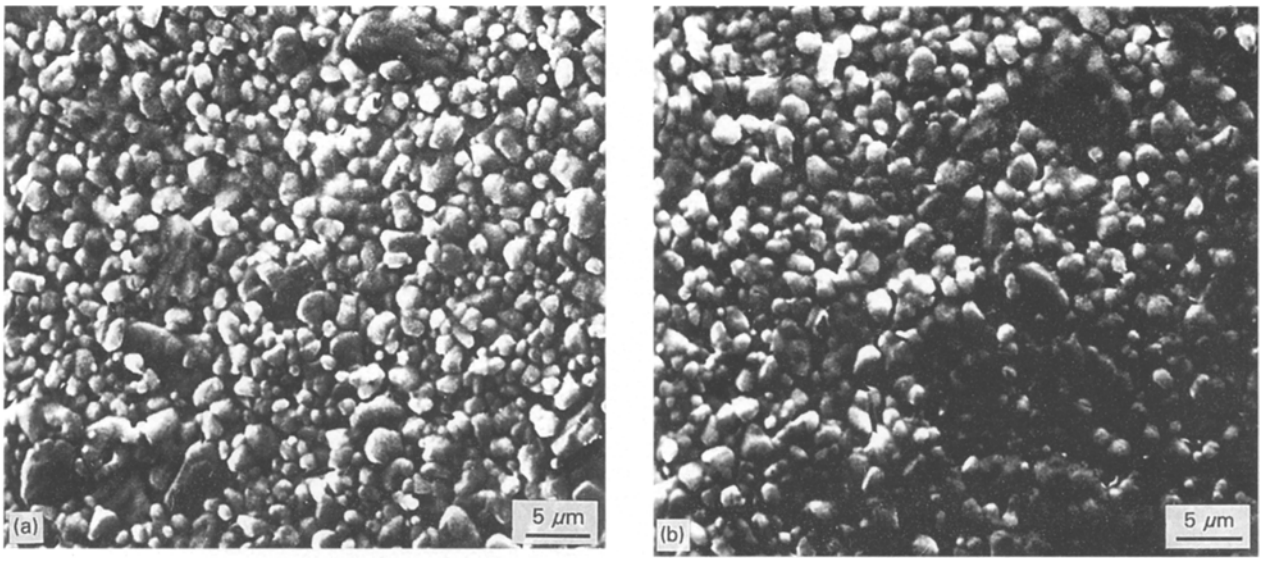


Figure 3 Film thickness variation with the withdrawal rates for different molar solutions: (*) 0.1 M, (×) 0.3 M, (○) 0.5 M, (□) 0.7 M and (△) 0.9 M.



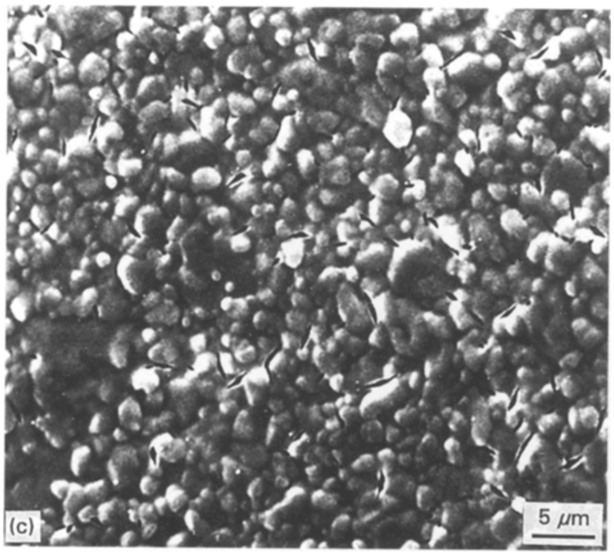


Figure 4 Scanning electron micrographs of surfaces of films obtained from solutions of 0.3 M concentration with different withdrawal rates: (a) 12.12 cm min^{-1}, (b) 36.32 cm min^{-1}, (c) 71.43 cm min^{-1}, dried at 200 °C.

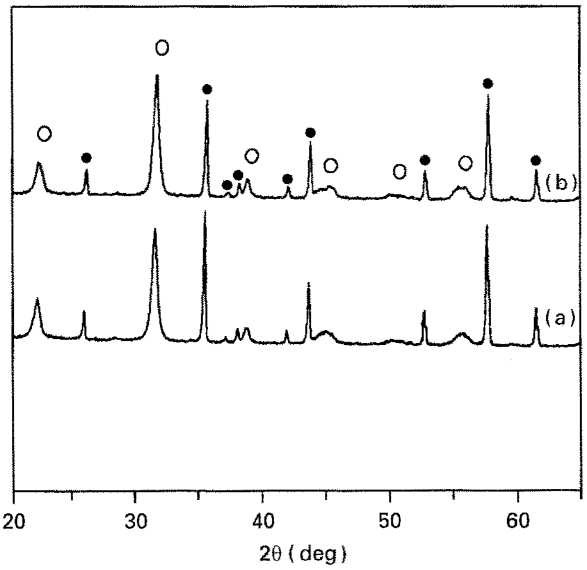


Figure 5 XRD patterns for samples at 750 °C (a) 2 h and (b) 4 h; (○) PZT, (●) Al_2O_3 substrate.

rates from 200 °C to the crystallization temperature were less critical for crack formation. Fig. 4 shows micrographs of films obtained with different withdrawal rates, and the same drying treatment. It can be seen that crack formation is almost independent of the deposition rate, except for the lower one which shows a somewhat better microstructure.

The solution concentration also influences crack formation. Films prepared from the higher concentrated solutions showed a lower tendency to crack. The most stable films were prepared from M values $\leqslant 0.5$. Dried films showed an amorphous structure by X-ray diffraction (XRD) analysis. Heat treatment at 750 °C for 2 and 4 h developed a well-crystallized microstructure (Fig. 5). The final phase was PZT perovskite and no pyrochlore formation was detected. XRD patterns displayed broad bands which corresponded to small-sized grains, calculated using Klug and Alexander's equation [12]. The obtained result was 22 nm for 750 °C 4 heat treatment, although, the size was independent of the film preparation parameters. The broadening of peaks makes it difficult to establish the symmetry of the perovskite structure. Nevertheless, indexing according to a rhombohedral cell led to the following lattice parameters: $a_0 = 0.4076$ nm, $\alpha = 89°36'$, which correspond well with those reported in the literature [13].

The relative thickness shrinkage after thermal treatment depends on the dried film thickness and increases with increasing withdrawal rate. Nevertheless, the shrinkage is quite low (3%–6%). This fact seems to indicate that cracking depends more strongly on the drying step than on crystallization.

Fig. 6 shows the microstructure of thin films prepared from 0.3 M solutions, with different withdrawal rates. The films had a final thickness varying from 0.13–0.17 μm. The grains were smaller than 0.1 μm and formed planar agglomerates uniformly distributed with about 1.5 μm size. These results are in accordance with those of Guppy and Atkinson [14] which found that only for a thickness below 0.5 μm is

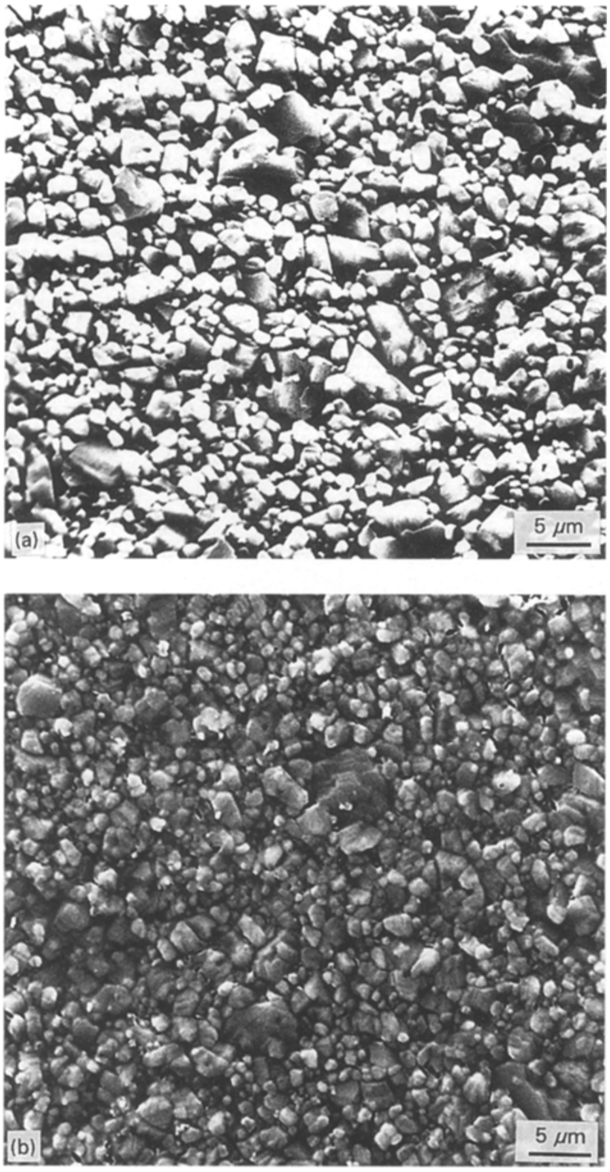


Figure 6 Scanning electron micrographs of surfaces of films obtained from solutions of 0.3 M concentration with different withdrawal rates: (a) 12.12 cm min^{-1}, (b) 36.32 cm min^{-1}, sintered at 750 °C.

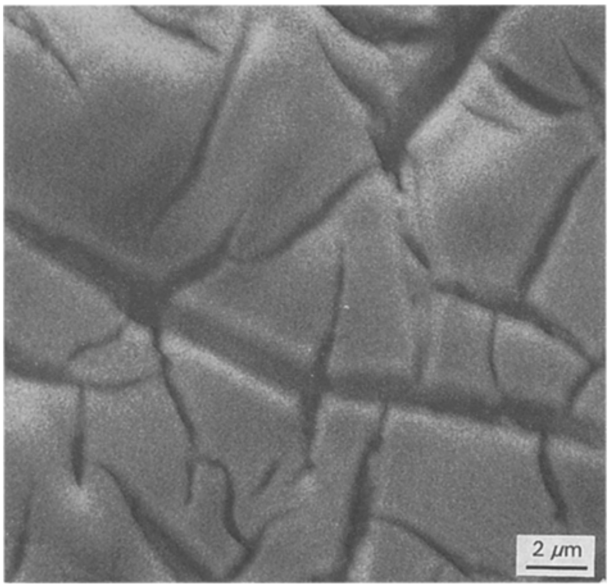


Figure 7 Surface micrograph of five layers thin film samples sintered at 800 °C.

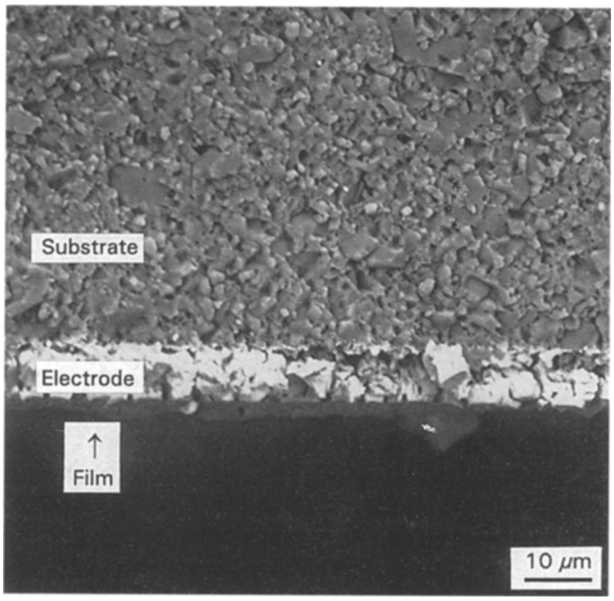


Figure 8 Cross-section of a sintered sample obtained by five dipping steps.

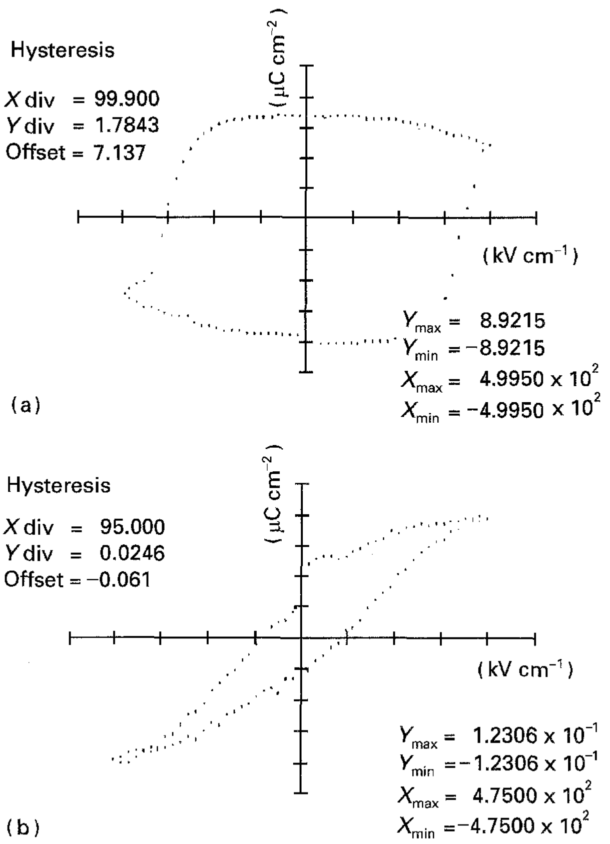


Figure 9 Hysteresis loop of samples obtained at withdrawal rates of (a) 8 cm min^{-1} and (b) 20 cm min^{-1}.

it possible to prepare crack-free CeO_2 thin films from solutions or sol–gel procedures.

Multilayers were subsequently prepared by a continuous process of dipping. Fig. 7 shows a micrograph of the free surface of films prepared by heating the coatings obtained after five dipping steps at 800 °C. Each layer was dried and calcined at 800 °C before the application of the next one. The existence cracks on the surface can be seen, but there is a continuity of the film across the whole sample.

TABLE I Remanent polarization and coercive field values corresponding to the films on Al_2O_3 and silicon substrates after five and one dipping steps, respectively

Substrate	Dip rate ($cm\,min^{-1}$)	P_s ($\mu C\,cm^{-2}$)	$+P_r$ ($\mu C\,cm^{-2}$)	$+E_c$ ($kV\,cm^{-1}$)	$-P_r$ ($\mu C\,cm^{-2}$)	$-E_c$ ($kV\,cm^{-1}$)	No. of layers
Al_2O_3	8	4.429	6.066	340.823	6.709	305.721	5
	20	0.096	0.030	83.573	0.026	78.018	5
Si	12.12	0.544	0.054	49.481	0.202	35.797	1

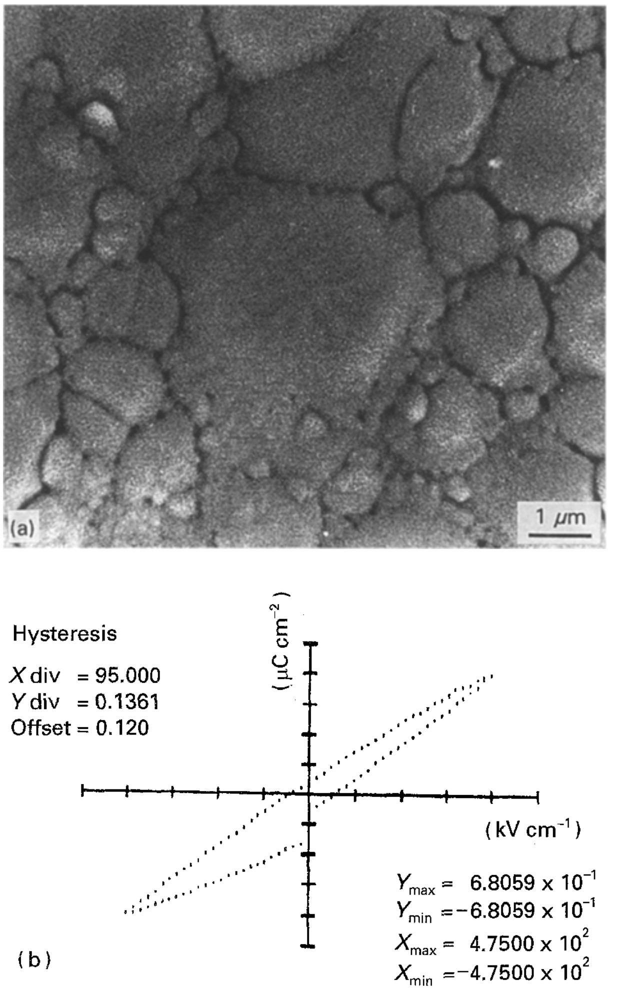


Figure 10 (a) Micrograph of the surface of a monolayer sample on a silicon substrate at 750 °C for 4 h from 0.9 M solution and a dip rate of 12.12 $cm\,min^{-1}$; (b) a hysteresis loop of this sample.

Substrates were Ag/Pd 70/30-coated alumina. The silver palladium coating was applied by a serigraph method, dried at 200 °C and was co-fired with the first PZT layer.

Fig. 8 shows a cross-section of a thin film sample in which the ceramic substrate, the metallic coating and the PZT film can be seen. Apparently there is no reaction between PZT and the metallic phases. The electrode has a thickness of $\approx 6\ \mu m$.

The hysteresis loops measured on samples prepared by consecutive dipping with different withdrawal rates can be seen in Fig. 9. The shape of loop is seen to be more rectangular for that sample with a smaller thickness. The relatively higher coercive field obtained in this case, may be associated with the small-grained microstructure of the films, see Table I.

When silicon is used as substrate, replacing Al_2O_3, the typical microstructure obtained is as shown in Fig. 10a. It corresponds to the free surface of a monolayer sample prepared on a silicon substrate with the same treatment as that used for the Al_2O_3 ones. The micrograph shows the microstructural development of the measured sample. The surface is homogeneous, almost crack-free, and well crystallized as shown by XRD. No pyrochlore phases were observed.

Hysteresis loops measured on the sample prepared by dipping on a silicon substrate are shown in Fig. 10b for the experimental conditions of dip rate 12 $cm\,min^{-1}$, solution molarity 0.3 M, and crystallization temperature 750 °C, 4 h. Table I gives the remanent polarization and coercive field for this monolayer, compared with those obtained on Al_2O_3 substrates after five dipping steps.

4. Conclusion

An adequate control of heating rate for drying at relatively high temperatures leads to almost crack-free PZT thin films being obtained from low concentration, non-aqueous solutions by a dip-coating procedure. Better results are obtained with low withdrawal rates. The microstructure of the films after crystallization is homogeneous and independent of the solution concentration. The films are constituted by perovskite phases. No pyrochlore was detected throughout the whole crystallization process. The coercive field is very high, as a consequence of the small-grained microstructure.

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