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Characterization of Seeded Sol–Gel Lead Zirconate Titanate Thin Films

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Abstract

In this paper the electrical properties of PZT (52/48) thin films derived from seeded and unseeded sol–gel precursors are presented. A pure perovskite phase was obtained at lower temperatures, 550°C for 30 min, for film prepared from seeded precursors and deposited on platinum passivated silicon substrates (Pt/Ti/SiO_2/Si). The electrical properties of these films also reflect the presence or absence of seeds in the precursors. Ferroelectric hysteresis loops began to be observed for seeded films fired at 500°C for 30 min, while in the films derived from unseeded precursors and fired in the same conditions, linear polarization versus electrical field curve is observed. © 1999 Elsevier Science Limited. All rights reserved

Keywords: seeds, films, sol–gel process, ferroelectric properties, PZT.

1 Introduction

Lead zirconate titanate, $Pb(Zr_x,Ti_{1-x})O_3$ (PZT), thin films are promising materials for a variety of microelectronics devices. Applications in microelectromechanical systems take advantage of the strong piezoelectric effect of PZT that allows electromechanical sensing and actuation.[1] Applications in integrated ferroelectric memories take advantage of the electrically switchable remanent polarization that can be used for binary data storage.[2] Device designs for these applications typically include the PZT thin film sandwiched between metal electrodes on a insulator or semiconductor substrate. For memory devices the ferroelectric capacitors are formed over an interlevel dielectric covering the completed silicon transistors and beneath the interconnect metallization.[2] For microelectromechanical devices the ferroelectric capacitors are formed over a thin layer of flexible structural material prior to the metallization and encapsulation.[1]

From the technological point of view, the ability of preparing PZT thin films with good electrical properties at low temperatures is considerably important since the interdiffusion between the different layers will be minimized, increasing the reliability of the devices.

The sol–gel processing of PZT thin films offers the possibility of close control of the stoichiometry of the chemical composition. However, sol–gel PZT thin films processing usually requires post-deposition annealing treatment of the film at temperatures between 600 and 750°C, in order to obtain the single perovskite phase. Interdiffusion between the PZT thin film and the multilayered substrate materials that can occur at these temperatures, alter the PZT composition and the electrode stability, and consequently the performances of the devices.

The effects of using perovskite seeds in PZT thin films on alumina substrates were previously studied and a decrease of the formation temperature of the pure perovskite phase was observed.[3,4] In this paper the electrical properties of seeded PZT thin films deposited on Pt/Ti/SiO_2/Si substrates are presented and compared with the unseeded ones. The influence of seeds on the electrical properties is discussed.

2 Experimental

The PZT precursor solution was prepared according to the stoichiometric formula $Pb(Zr_{0.52}Ti_{0.48})O_3$. No excess lead was added. The starting

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reagents were lead acetate trihydrate, titanium diisopropoxide bisacetylacetonate and zirconium acetylacetonate. A 0·4 M stock solution was used for the PZT thin film deposition. Ultrafine PZT (52/48) powders were used as seeds.[5] Then 1 wt% of PZT seeds were added to the solution to form a stable colloid suspension. The experimental details for the stock solution and seeds preparation have already been reported.[3] The dispersion behavior of seeds and the stability of the suspension sols were analysed by measuring their rheological behavior using a Carri-Med Controlled Stressed Rheometer at 20°C. The viscosity of the solutions with and without seeds was adjusted to ~0·012 Pa s.

PZT films of thickness around 300 nm were deposited on $Pt/Ti/SiO_2/Si$ multilayered substrates by dip-coating. The substrate was dipped and withdrawn from the precursor sol at a constant rate of 0·17 cm s^{-1}. The resulting wet films were dried on a hot plate at ~300°C for 1 min to remove residual organics. After deposition of four layers, the films were fired at different temperatures from ca 400 to 700°C for 15~30 min in air. Top electrodes (Au, 100×100 mm square) were patterned by thermal evaporation process using a shadow mask.

The thickness, stoichiometry and the interfaces quality of the films were studied by Rutherford Back Scattering (RBS) spectrometry using a He^+ beam at 1·6 MeV. The experimental set up is described elsewhere.[9]

The refractive index of both seeded and unseeded films was compared using a multi-channel ellipsometer. Surface morphology was studied by atomic force microscopy (AFM). The dielectric constant and loss were determined in unpoled samples with a HP4194A Impedance/Gain-phase Analyzer, over a frequency range of 100 Hz to 1 MHz. The hysteresis loops were measured using a Sawyer–Tower circuit at frequency range from 500 Hz to 100 KHz.

3 Results and Discussion

Thin films were amorphous after deposition. During firing a pyrochlore type phase is formed prior to the PZT perovskite phase formation. The effect of seeds on the crystalline phase development with firing temperature is shown in Fig. 1. The X-ray diffraction patterns of samples prepared without seeds are presented in Fig. 1(a). From 500 to 550°C the (110) peak of perovskite (Pe) phase ($2\theta = 31{\cdot}0°$) increase in intensity with respect to the pyrochlore (Py) phase ($2\theta = 29{\cdot}8°$), but pyrochlore is still detectable. Single perovskite PZT phase was only obtained after firing at 600 °C 15 min^{-1}.

Figure 1(b) illustrates the phase development of films containing 1% of seeds at different crystallization temperatures. A marked improvement on the perovskite phase formation was observed when 1 wt% of PZT seeds was added, indicating a faster

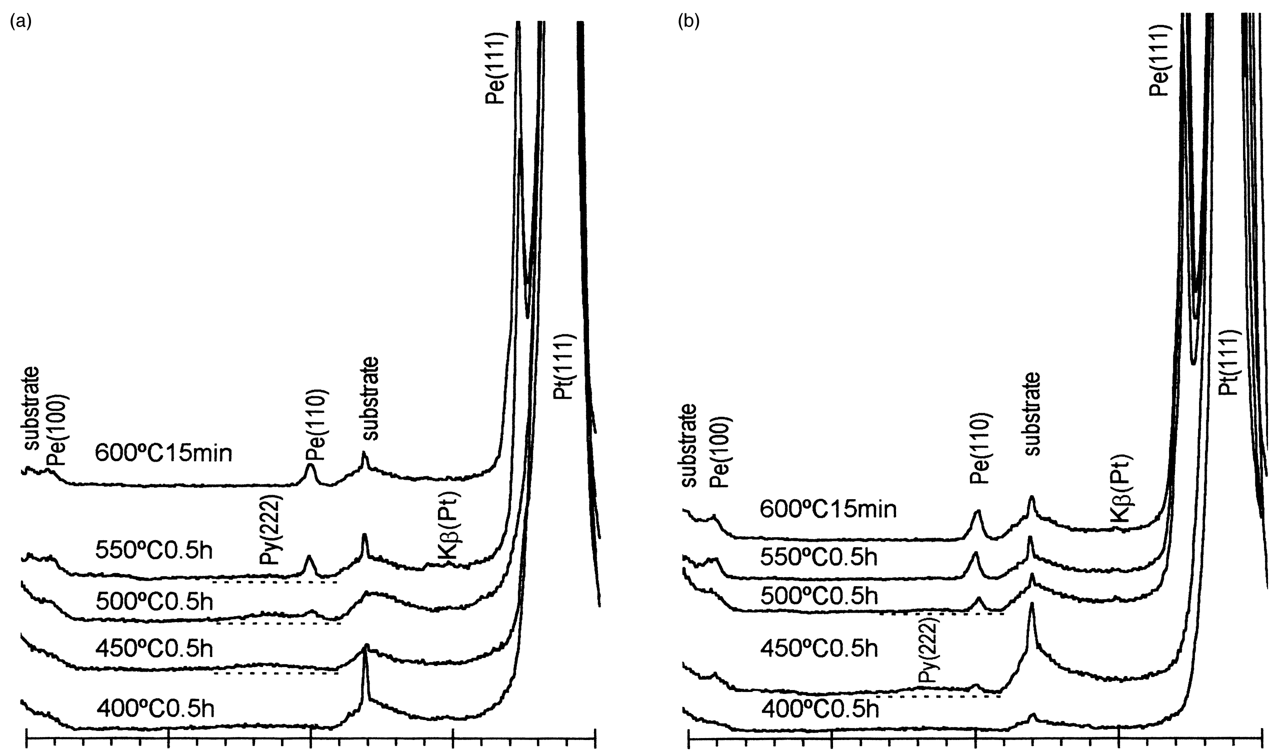

Fig. 1. XRD patterns of (a) unseeded films and (b) seeded films heat treated at different temperatures.

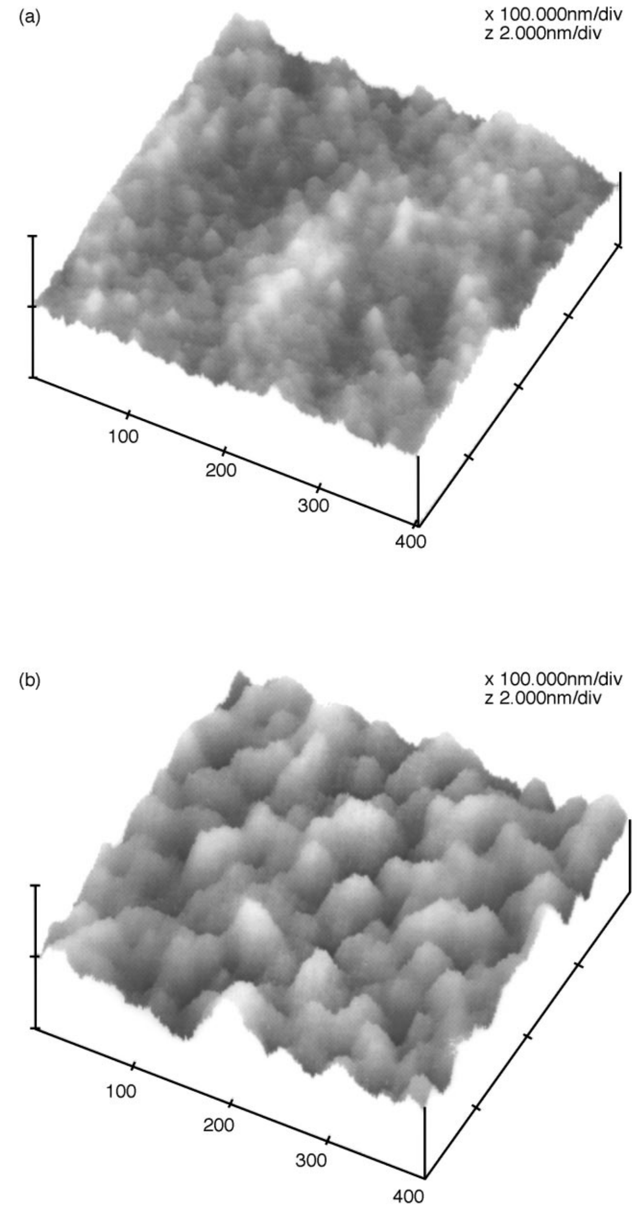

Fig. 2. Surface morphology observed by atomic force microscopy for (a) seeded and (b) unseeded films heat treated at 550 °C for 15 min.

phase transformation. At 500°C the perovskite peaks are more intense and the pyrochlore one is less intense, when compared to XRD pattern of unseeded films. For the seeded films single perovskite PZT phase was obtained after firing at 550°C for 30 min. A single perovskite phase could also be obtained at 500°C but for an extended firing period (6 h). As already discussed for the crystallization of PZT on alumina substrates[3–5] the PZT seeds distributed in the film act as preferential nucleation sites, and the perovskite phase formation in the film is promoted at lower temperatures.

The atomic force micrographs (Fig. 2) show the surface morphology of the seeded and unseeded films, heat treated at 550 °C/15 min. Different surface morphologies are clearly identified. The seeded films are characterized by a uniform distribution of small grains. On the contrary, the surface morphology of unseeded sample reveals bigger grains not so uniformly developed. The presence of the nanoparticles and their action of heterogeneous nucleus sites seems to be the reason for the uniform and small grain growth of seeded films.

Figure 3(a)–(c) show the RBS spectra of unseeded films. After the deposition there is an enrichment of lead at the surface of the film [Fig. 3(a)]. Also, the interfaces between the Pt and the PZT film are well defined. After the annealing treatment at 550°C during 30 min, the film looks homogeneous. The lead peak disappears but the interfaces are not so well defined, indicating a diffusion of Ti from the Ti substrate layer into the Pt electrode layer. This is shown in Fig. 3(b) with the analysis of a thicker sample. The losts of sharpness of the interface increases with the annealing temperature [Fig. 3(c)]. Preliminary analysis of seeded samples seems to indicate similar results.

These observations confirm the importance of low temperature heat treatments of PZT thin films and highlights the role of seeds in achieving this purpose.

Table 1. Dielectric and ferroelectric characteristics of PZT thin films (at 1 KHz)

Sample designation and heat treatment	*Thickness (nm)*	ε_r	*tan* δ	*Pr* ($\mu C\ cm^{-2}$)	*Ps* ($\mu C\ cm^{-2}$)	*Ec* ($KV\ cm^{-1}$)
No seeds 500°C/30 min	363	—	—	—	—	—
1% seeds 500°C/30 min	240	797	0·071	13·1	22·4	65
No seeds 550°C/30 min	363	567	0·055	10	15·38	63·8
1% seeds 550°C/30 min	240	1234	0.097	20·8	31·6	69·6
No seeds 600°C/15 min	360	1053	0·073	14	34·2	60
1% seeds 600°C/15 min	240	1200	0·091	13.8	30	74
Literature report[1,6–8]		400~ 1850	0·02~ 0·08	13~40		45~140

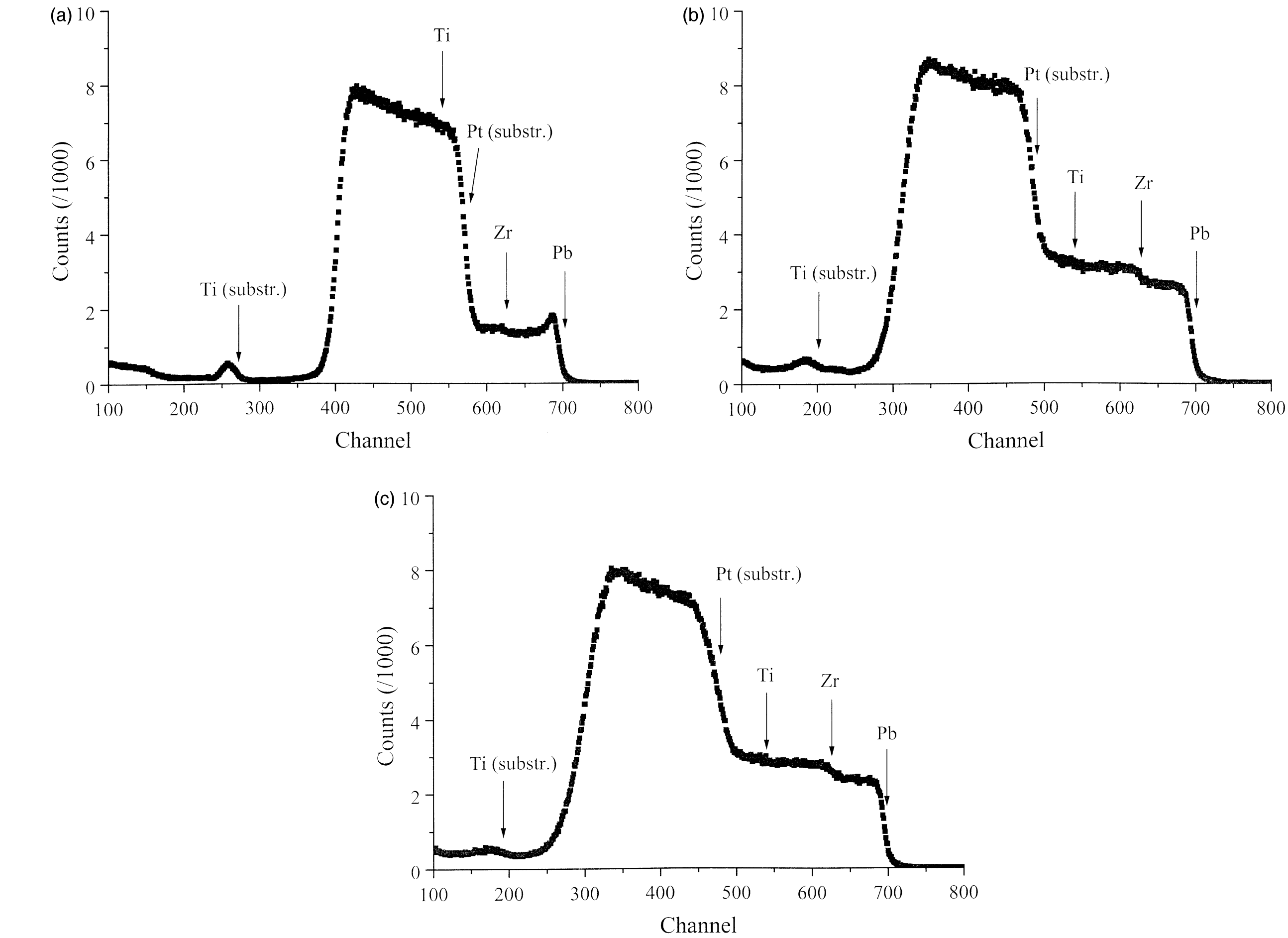

Fig. 3. RBS spectra of unseeded PZT films (a) as deposited; (b) heat treated at 550°C/30 min; and (c) heat treated at 600°C/5 min.

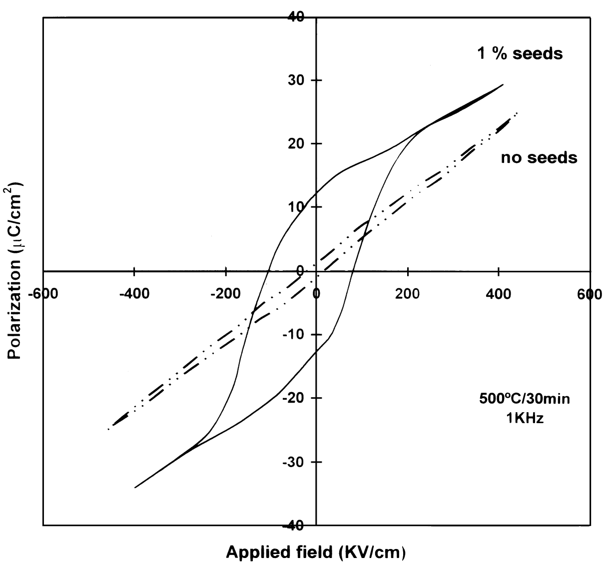

Fig. 4. Hysteresis loops of PZT films with and without seeds after firing at 500°C/30 min.

Optical measurements by ellipsometry shows similar thickness non-uniformity for seeded and unseeded films (1·77% for seeded films and 1·68% for unseeded films), and a slightly higher refractive index for seeded films, 2·40 ($\lambda = 632{\cdot}8$ nm) compared with unseeded films 2·32 ($\lambda = 632{\cdot}8$ nm) both being fired at 550°C.

The phase and microstructure difference of unseeded and seeded films are reflected in the electrical measurements. The dielectric and ferroelectric properties of unseeded and seeded PZT films are summarized in Table 1. In addition properties of PZT (52/48) films reported in the literature are also tabulated for comparison. After the heat treatment at 550°C/30 min the seeded films show much better properties than the unseeded films. At this temperature the ε_r reaches a maximum.

The P–E curves for the seeded and unseeded films heat treated at 500°C/30 min are presented in Fig. 4. The hysteresis loops of these films are completely different. The seeded film shows a well defined hysteresis curve, compared with the unseeded film where a much slimmer loop was observed. As shown by these results the elimination of the pyrochlore phase at low temperatures lead to a significant improvement in the dielectric and ferroelectric properties. The difference in densification, the presence of the pyrochlore type second phase, differences in grain size and grain orientation and/or in chemical homogeneity can be reasons that determine the final quality of the PZT films. A systematic study of all the variables is in progress.

4 Conclusions

In summary, PZT (52/48) films derived from seeded solutions present different phase transformation kinetics, microstructure and electrical properties from films derived from unseeded solutions. Higher perovskite formation rates at lower temperatures (500∼550°C) occurred in films with 1 wt% seeds. Single PZT perovskite phase can be grown on $Pt/Ti/SiO_2/Si$ substrates at ∼550°C using a 1 wt% seeded diphasic precursor sol. The microstructure of the films and their dependence on the seeds are well reflected on the electrical properties. The presence of seeds allows a high amount of the perovskite phase and a high degree of densification for the films heat treated at lower temperatures. The dielectric and ferroelectric properties were found to be superior for seeded films. The relative dielectric constant ε_r of 1234 and remanent polarization of $20{\cdot}8\,\mu C\ cm^{-2}$ were obtained for 1 wt% seeded film heat treated at 550°C/30 min.

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