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Sol-Gel Derived Lead Zirconate Titanate Thick Films and their improved pyroelectric properties

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Abstract

The single-layer thickness of $Pb(Zr_{0.3}Ti_{0.7})O_3$ (PZT 30/70) thin films made by the sol-gel process is often restricted by the appearance of cracks when a single layer is thicker than 100nm. Making a film with 1μm thick needs more than 10 times coating cycles, which is sometimes unacceptable. In this study, a sol modified with an additive was used for the preparation of thick PZT films. The thickness of the films depends upon the rotation rate. Up to 700 nm crack-free single layers could be obtained. The deposited films crystallised as the perovskite structure on platinum-buffered silicon by heating at 550 ºC. The porosity of the thick films was a function of the single layer thickness. A dense PZT film with a single layer 140nm thick was found to have a very high pyroelectric coefficient ($p=2.36 \times 10^{-4}$ $CK^{-1}m^{-2}$) and figure of merit (1.88×10^{-5} $Pa^{-0.5}$). The introduction of pores in the films reduced p. However, the figure of merit of the films exhibited a reasonably high value due to a dramatic reduction of dielectric constant.

Introduction

In recent years, the use of ferroelectric thin films of $PbZr_xTi_{1-x}O_3$ (PZT) family for memory, piezoelectric and pyroelectric devices has drawn considerable interest [1]. Deposition of PZT films on silicon substrates has been extensively investigated in thin-film form (thickness less than 1 μm). However, the needs of PZT materials in thick-film form (thickness 1-50 μm) are expanding for applications in microactuators in order to produce large piezoelectric displacements and generative forces. The advantage of film devices over bulk materials is that they can be directly deposited on platinised silicon to allow direct integration with electronics.

The sol-gel process used to deposit PZT films on substrates has been considered as one of the best methods due to its low processing temperature, precise control of composition and low cost. However, one of the drawbacks in the use of sol-gel process is its limit of single layer thickness. The thickness of a single sol-gel layer usually falls in the range of less than 0.1 μm.

Deposition of thicker layers than this usually results in cracks and /or formation of porosity. The required thickness is achieved by repeating the coating and heat treatment, which produces a sequence of thin layers free from cracking. Such repetitive coatings, however, may not be realistic in the production of coating films in industry. The limited thickness achievable without crack formation is one of the factors that discourages application of the sol-gel technique to industrial production of ceramic coatings. The origins of cracks are widely thought to come from two sources: the shrinkage during the crystallisation anneals in the sol-gel processing, and the thermal mismatch between the film and the substrate.

Many efforts have been made to prepare crack-free, thick, ceramic coating films from gels [2-7]. The largest single layer thickness has been reported to be 1.7μm [7]. However, all these thick films contain, more or less, some porosity, which will reduce the piezoelectric and ferroelectric properties.

The pyroelectric properties of sol-gel PZT thin films (≤ 1μm) reported in the literature so far are based on samples with a single layer thickness of less than 0.1μm, which tends to produce dense films. To our knowledge, the pyroelectric properties of dense sol-gel PZT films with a single layer thicker than 0.1μm have not been reported.

Most recently, Suyal et al [8] added polymer into PZT precursor sol prior to spin coating to prepare porous PZT films (the porosity is in the range of 20-25%). Introduction of pores creates a matrix void composite resulting in the increase of figures of merit for pyroelectric applications.

The purposes of the work described in the present paper are dual, first to prepare a dense crack-free thicker film (> 0.1 μm of a single layer) and compare its pyroelectric properties with a dense thin film (<0.1 μm of a single layer) and second to prepare thicker films (≥0.35μm of a single layer) in the hope of improving the figures of merit of these pyroelectric films by introducing a

porous microstructure, which largely reduces the dielectric permitivity of the materials (figures of merit, $F_d = p/c'(\varepsilon_r\varepsilon_0\tan\delta)^{1/2}$) and compare its pyroelectric properties with those obtained with dense films.

Experimental

$Pb(OOCCH_3)_2{\cdot}3H_2O$ was dissolved in CH_3OH with heating. $Ti(O^nBu)_4$ and $Zr(O^nPr)_4{\cdot}Pr^nOH$ was mixed together and dissolved in a mixed solution of CH_3COOH and MeOH. The molar ratio of Zr/Ti was equal to 30/70. Two solutions were then mixed together and refluxed for 2h. Pb excess was fixed at 10% extra. This was for the compensation of Pb loss later during heat treatment of films. The concentration of the solution was 0.4M based on Pb. This sol (Solution A) was used for making layers less than 150nm each layer. To make films with thicker layers, this solution was then concentrated to 1M by distillation. A small amount of organic additives was then added to the concentrated solution to increase the viscosity and avoid the creation of cracks in the preparation of thick films. Distilled water was added to the PZT precursor solution with the ratio of PZT solution to water, 10 : 1 v/v. The resultant solution (Solution B) was aged at room temperature for 24h prior to use.

The films were fabricated by applying sols onto $Pt(111)/Ti/SiO_2/Si(100)$ substrates (thickness $Pt/Ti/SiO_2$ = 100/5/500 nm) by spin coating with a photo resist spinner (Model 1-EC101D-R790, Headway Research Inc) at various spin rates depending on the required thickness. Each wet layer was initially dried at 150 °C to evaporate the solvent, rapidly heated to 400ºC to remove residual organics, and annealed at 550 °C to densify the layer and prevent further shrinkage. The orientation of the film was determined by the standard θ-2θ X-ray diffraction (XRD) method on a Siemens D5005 diffractometer using CuK_α radiation and a Goebel mirror. The cross-section

morphology of the films was observed using scanning electron microscope (SEM) (Philips XL30, SFEG). On selected films, transmission electron microscopy (TEM) Philips CM20 was used. The TEM cross-section samples were prepared using a focused ion beam system (FEI FIB200). For the measurement of electrical properties, a set of Au/Cr electrode dots was sputtered onto the film surface through a photoresist mask obtained by photolithography. The exposed Pt bottom electrode beneath the film provided the other electrode. Film thickness was determined from a Dektak surface profilometer, and compared against values taken from SEM or TEM cross-section images. The dielectric constant and loss tangent of the PZT films as a function of frequency (33Hz to 1kHz) were measured using a Genrad 1689M RLC Digibridge impedance analyzer. The polarisation hysteresis loops of PZT porous thick films showed that the porous PZT is very hard to pole as compared to dense PZT films and a relatively high poling field is needed for the poling of porous thick films. A dense thin film (700nm) could be fully poled at 20V at 130 ºC for 10 min, while a porous thick film (700nm) needed almost a double voltage to reach a saturated polarisation at the same temperature and the length of poling time. The films used in this paper for pyroelectric and hysteresis loop measurements were poled by the corona method at 130ºC at 25 kV for 5min. After poling, the films were discharged by connecting the top electrode and bottom electrode. The pyroelectric coefficient was measured using the Byer-Roundy method [9] for which the detailed procedure was described in Ref. [10].

Results and discussion

The SEM micrographs of thick films synthesised by Solution B are shown in Fig.1. Through the control of spinning rate, films with different thicknesses were obtained. A film (Fig. 1(a)) with 2 layers obtained at 1000 rpm is 1.4 μ thick and a film (Fig.1 (b)) at 2000 rpm with 3 layers is 1.5 μ

thick. It can be clearly seen that there are many pores randomly distributed through the thickness of the film. However, it has been observed that there are not any cracks in the films with the single-layer thickness up to 700nm. The thicker films could be built up by repeating the above deposition process. The porosity of the films can be observed from TEM and SEM images. Unlike the thin films of PZT, XRD patterns (not showing here) of these thick films show a random orientation, indicating that the mechanism of nucleation and growth of these thick films is different from the thin films [12].

The success of the preparation of crack-free thick films and introduction of pores into the PZT films makes it possible to examine the concept that the porous PZT films can actually have a higher figure of merit through lowering the permittivity without a sacrifice in pyroelectric coefficient (p). To compare the electric properties of thick films to those of thin films, three samples, all 700nm thick, were prepared with various single-layer thicknesses. Table 1 lists these samples and their processing conditions.

Fig. 2 shows the TEM and SEM cross-section images of these films. For the films PZT70 and PZT140, columnar structure with well-defined grains can be clearly observed. These two films are very dense and closely packed. For the film PZT350, the TEM cross-section does not show a columnar structure. Although no cracks are observed, there is a small amount of pores randomly distributed in the film.

X-ray diffraction patterns of these samples are shown in Fig. 3. This figure clearly shows that all the films have a perovskite structure after being annealed at 550 ºC. No second phase pyrochlore was observed which indicates that given the same length of time at 550 ºC, the thicker layer film (350 nm per layer) can also crystallise into perovskite. The x-ray diffraction patterns taken from the samples PZT70 and PZT140, derived from Solution A, demonstrates a strong (111)

reflection while the sample, PZT350, derived from Solution B, a random reflection. These observations confirm that the films made from thick single layers have no preferred orientation. In our earlier works [12] about the mechanism of the crystallisation and orientation of the PZT thin films, we had found that the formation of PZT [111] orientation is due to a close lattice match between a Pt_3Pb intermetallic phase and PZT [111], which favours a preferred orientation. However, in the case of thick single layer films (PZT350), the mechanism has become more complicated. The thicker single layer decreases the influence of the Pt bottom electrode on the nucleation and preferred orientation of the deposited PZT film. Nucleation also occurs at other sites at the surface and in the bulk of the film [13], which produces crystallites whose orientations are not constrained by the Pt orientation. The intensity $I_{111}/(I_{111} + I_{110})$ through deconvolution decreased from 0.92 in the sample PZT140 to 0.15 in the sample PZT350, indicating the decline in 111 preferred orientation. The corresponding ratio for powder prepared from bulk gels was ~0.15, which shows that there was still a considerable degree of orientation in the sample PZT350.

Table 2 shows the electrical properties of the PZT 30/70 films with different single-layer thickness. Dielectric constant largely decreases from 372 in the dense film (PZT70) to 210 in the porous film (PZT350). It was observed that the porous film (PZT350) has a lower pyrocoefficient ($1.60 \times 10^{-4}\ CK^{-1}m^{-2}$) compared to the dense films (PZT70 $2.11 \times 10^{-4}\ CK^{-1}m^{-2}$ and PZT140 $2.36 \times 10^{-4}\ CK^{-1}m^{-2}$). This behavior may be due to the fact that the films with porosity have a reduced charge density and hence a reduced pyrocoefficient. The reduction in pyrocoefficient in the film with porosity was in agreement with the observation in Ref [8]. It must be noticed that PZT140 has a higher pyrocoefficient than PZT70, indicating that increasing a single layer thickness from 70nm to 140nm increases the pyrocoefficient. There are many possible explanations for these observations, for example, PZT thin films have been reported to have composition variations in the

crystallisation interface [14-15]. Thicker single layer may help reducing such variations in the film stoichiometry or microstructural inhomogenities. The pyrocoefficient of dense thick film is one of the highest values reported for PZT films prepared on silicon substrate. The figure-of-merits F_d of three samples have been calculated using $F_d = p/c'(\varepsilon_r\varepsilon_0\tan\delta)^{1/2}$ and c' value of 2.5 x 10^6 J m^{-3} K^{-1} known for PZT ceramics [11]. The thicker dense film (PZT140) almost has a double F_d value (1.88 x 10^{-5} $Pa^{-0.5}$) compared to the thin dense film (PZT70)(1.07 x 10^{-5} $Pa^{-0.5}$). The figure of merit of the porous thicker film (PZT350)(1.50 x 10^{-5} $Pa^{-0.5}$) has shown a much higher value than the dense thin film (PZT70) due to a dramatic decrease of dielectric constant.

Fig. 4 shows the hysteresis loops of the PZT70, PZT140 and PZT350 films. The P-E hysteresis loops show that the remnant polarisation of the porous film (PZT350) is not as large as the dense films. The reason for poor ferroelectric properties is the porous nature of the film, leading to a large leakage current. The hysteresis loop of the porous thick film (PZT350) shifts to the positive field, called the 'imprint' phenomenon, and indicates the magnitude of internal bias field, which is proportional to the polarisation. With the increase of the densification of the films, the symmetry of the hysteresis loops improves, indicating that the internal bias fields decrease. It is implied that the PZT porous thin films may possess less spontaneous polarisation responses. Therefore, they are probably less suitable for the piezo- or ferro-applications.

Conclusions

(1) Dense crack- and pore-free PZT thick films (single layer thickness =140 nm) have successfully prepared by adjusting the spinning rate of deposition.

(2) Through incorporating an additive to the precursor solution, the thickness of a single layer without cracks can be up to 700 nm. However, These films are porous and their porosity is a function of single-layer thickness.

(3) The films prepared with thicker single layers (140nm per layer) have showed a higher pyroelectric coefficient (p) and figure-of-merit (F_D) compared to the films prepared with thinner single layers (70nm per layer) or with porous microstructure thick layers.

(4) The films prepared with thicker layers (350nm /per layer) possessed a certain amount of porosity. The permittivity of such a film was largely reduced (almost one half of dense films) due to the existence of pores. However, their pyroelectric coefficients remained relatively high so that their figures-of-merit were also relatively high compared to the films prepared by thin dense layers (<100nm /per layer).

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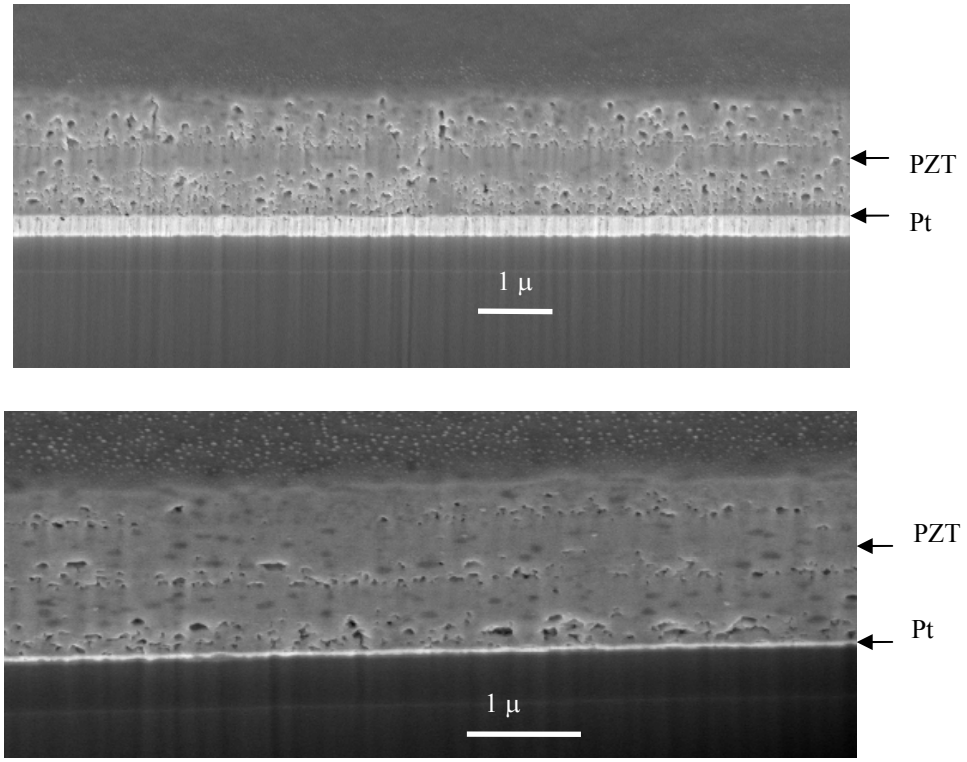
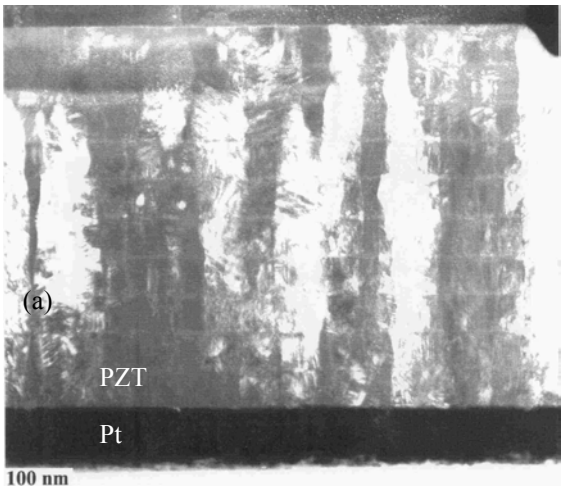
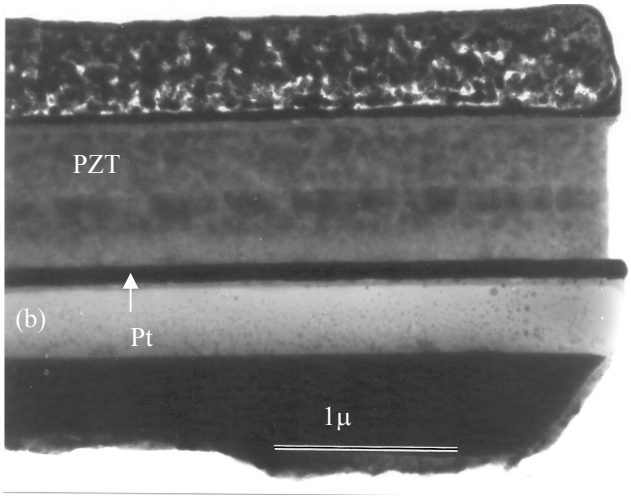


Fig.1 SEM micrographs of porous PZT films by Solution B (a) 2 layers (1.4 μ) with each layer obtained at 1000 rpm (b) 3 layers (1.5 μ) with each layer obtained at 2000 rpm.





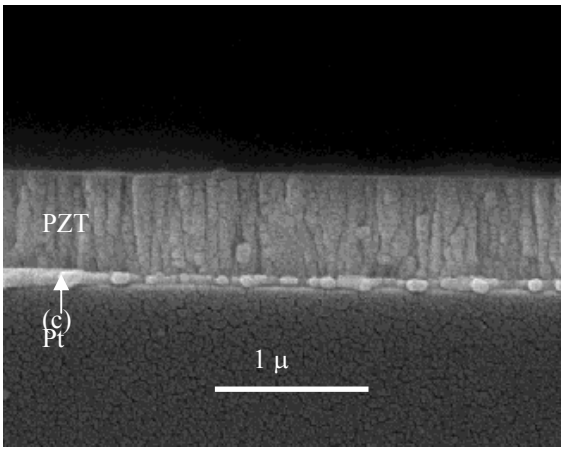


Fig. 2 TEM micrographs (a) PZT thin film with ten layers each having 70nm thick; (b) PZT thick film with 2 layers each having 350 nm and (c) SEM micrograph PZT thin film with 5 layers each having 140 nm. All the films showing here have a thickness of 700nm.

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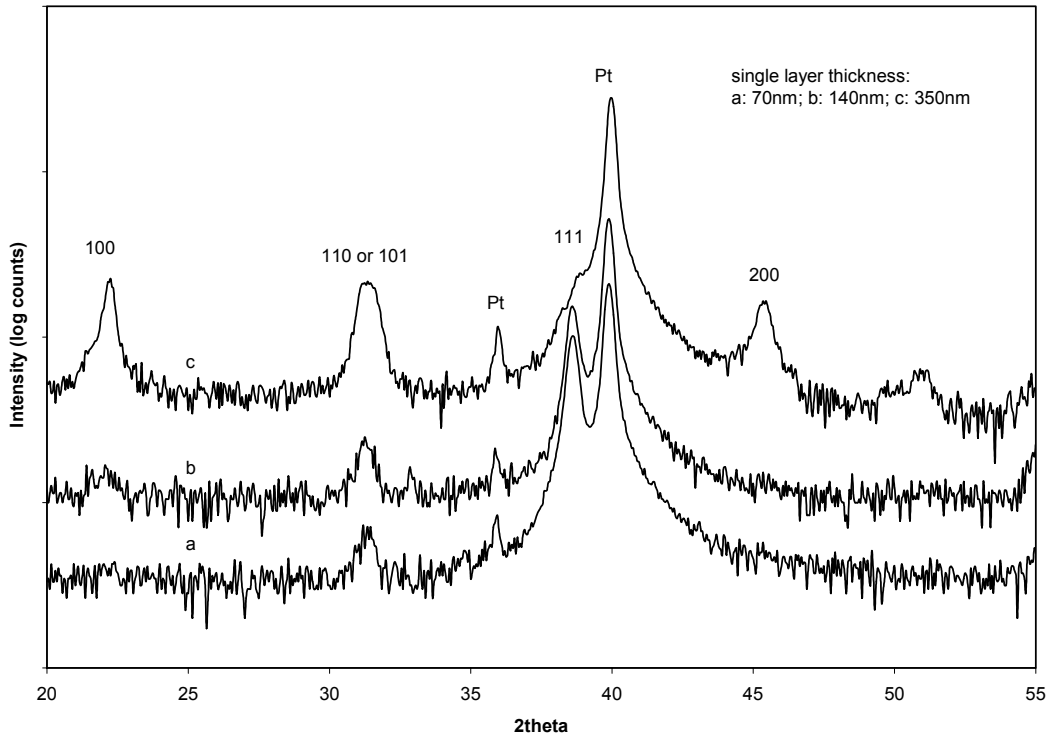


Fig.3 X-ray diffraction patterns of PZT films a: PZT70; b: PZT140 and c: PZT350.

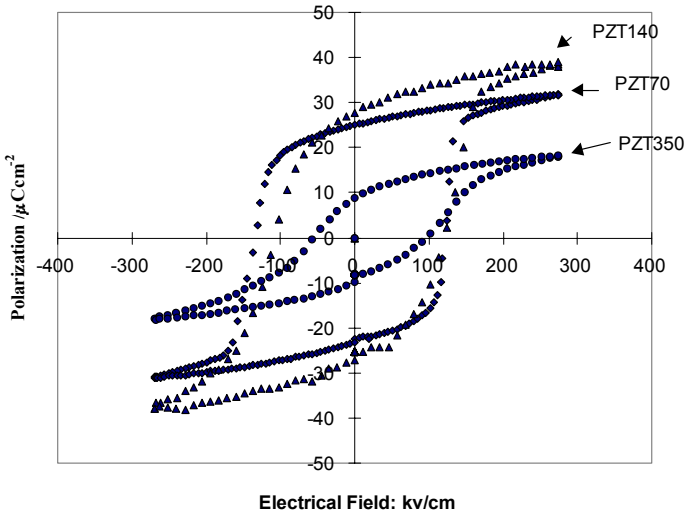


Fig. 4 Hysteresis loops of PZT thin films with various single layer thicknesses.

Table 1: Three PZT films and their processing condition. Total thickness of each film is 700nm.

Sample	Solution	No. of layers	Single layer thickness (nm)	Time (min.) of each layer annealed at 550 ºC
PZT70	A	10	70	5
PZT140	A	5	140	10
PZT350	B	2	350	25

Table 2 Electrical parameters of the PZT 30/70 films with different single-layer thickness

Sample	PZT70	PZT140	PZT350
ε at 33 Hz	372	356	210
tanδ at 33Hz	0.016	0.008	0.01
p ($CK^{-1}m^{-2}$)	2.11×10^{-4}	2.36×10^{-4}	1.60×10^{-4}
F_D ($Pa^{-0.5}$)	1.07×10^{-5}	1.88×10^{-5}	1.50×10^{-5}
$2P_s$ ($\mu C/cm^2$)	62	77	36
$2P_r$ (($\mu C/cm^2$)	48	55	19
$2E_c$ (kV/cm)	255	225	150



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