Sol-gel deposition of PZT thin films on ceramic ZrO_2 substrates

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Abstract

$Pb(Zr_{1-x}Ti_x)O_3$ thin films ($x = 0.55$ and 0.85) were prepared on fine grained, polished ZrO_2 ceramic substrates by a sol-gel method. The high thermal expansion of ZrO_2 relative to Si allows the preparation of thicker PZT films with reduced thermal stress. For the $x = 0.85$ films, this reduction of thermal stress gives a preference of (001) over (100) oriented domains. For $x = 0.55$ films, square P-E hysteresis loops were obtained with: $P_r = 36$ µC/cm^2, and $E_c = 45$ kV/cm, at a field of 160 kV/cm. Pyroelectric figures of merit, defined as P/ε, of 0.93 were measured for a 4.0 µm thick $Pb(Zr_{0.15}Ti_{0.85})O_3$ film. The measured properties were comparable to those of highly (111) oriented films on Si. Thus, the (001) texture must be increased in order to realize improved properties

1 Introduction

$Pb(Zr_{1-x},Ti_x)O_3$ (PZT) thin films are of interest for applications including ferroelectric memories, micro-mechanical actuators and pyroelectric based microsensors. Most papers report PZT deposition on Si, although the use of oxide single crystals and metallic substrates are also described [1,2]. An advantage of single crystals and metallic substrates is that in most cases the thermal expansion coefficients (TEC) (in the temperature range of interest: 25 to 650°C) are larger than that of Si, and in some cases (e.g. MgO) greater than that of PZT. One effect of residual tensile film stresses is a preference for orientation of the polarization in the plane of the film [3,4]. In this work, PZT films of $x = 0.55$ ($T_c = 370$°C) and $x = 0.85$ ($T_c = 460$°C) were deposited by sol-gel on Y stabilized (6%) ceramic ZrO_2 substrates. The TEC of the substrate is approximately 7×10^{-6} K^{-1} in the temperature range noted above. The TEC of the PZT compositions investigated is respectively less than and greater than this value for temperatures below and above the Curie temperature, Table I [5].

ZrO_2 substrates were investigated for the following reasons. First, with a TEC greater than Si, and near to that of PZT, the preparation of thicker films is facilitated due to decreased thermal stresses. Second, the pyroelectric response of the $x = 0.85$ material can be improved due to a preference for (001) over (100) domain formation upon cooling of the films. TEC data for ZrO_2, Si and MgO and the PZT compositions investigated are summarized in Table I, for temperature ranges below and above the respective Curie points of the PZT.

The crystallographic orientation or texture of PZT thin films with respect to the substrate is another parameter which strongly effects the electrical and mechanical response of the films [6-11]. In this work, control of film orientation, through the use of TiO_2 layers and different annealing profiles, particularly to obtain (001) preferred orientation, was studied. The electrical property results are then compared with those obtained for strongly (111) textured PZT films of the same compositions prepared on Si substrates.

A number of investigations concerning grain size effects in ferroelectric ceramics have been published. At this point, no systematic studies of grain size in PZT thin films have been reported. Kwok and Desu indicated that grain size is thickness dependent for a given annealing profile, and that no significant changes in grain size occur for increasing annealing time or temperature [12]. In this paper the effect of annealing temperatures up to 950°C on microstructure development and grain growth are reported.

Table I. Thermal expansion coefficients

Material	TEC's ($\times 10^{-6}$°C^{-1})			
	25 - 370°C	25 - 464°C	370 - 550°C	464 – 550°C
$Pb(Zr_{0.45}Ti_{0.55})O_3$	2.5		7.9	
$Pb(Zr_{0.15}Ti_{0.85})O_3$		-3.0	4.0	
Si	3.4	3.5	4.0	4.0
ZrO_2	7.4	7.2	6.4	6.4
MgO	12.9	13.0	13.8	13.9

2 Experimental

2.1 Deposition of Electrodes and PZT Films

Bottom electrode structures of TiO_2/Pt (10 nm/100 nm) were deposited on the polished ZrO_2 ceramic substrates by sputtering at 650°C. No adhesion problems were encountered even after the deposition of 10 µm thick PZT films.

PZT films were prepared by spin-coating a methoxyethanol based precursor solution. Solution preparation follows the method of Budd [131 and is described in more detail elsewhere [7]. For both $Pb(Zr_{0.45}Ti_{0.55})O_3$ and $Pb(Zr_{0.15}Ti_{0.85})O_3$ compositions, 10% excess lead was contained in the precursor solutions. Layers of approximately 0.1 µm thickness were deposited from a 0.4 M precursor solution by spin coating at 1400 rpm for 30 s. Each layer was then crystallized on a hot plate at 600°C for 60 s. Subsequent layers were deposited and crystallized to obtain films of thicknesses in the range of 1 to 10 µm. In some cases, additional conventional anneals between 650 and 950°C, with 5°C/min. heating and 20°C/min. cooling rates were carried out. Furnace anneals were done in closed crucibles which contained $PbZrO_3$ powder.

In order to obtain partial (001) texture, thin TiO_2 layers were deposited on the Pt bottom electrodes before deposition of the PZT layers. A 0.05 M solution of TiO_2 prepared from Ti-isopropoxide in 2-methoxyethanol was spun on the wafers at 2000 rpm for 30 sec and pyrolyzed at 350°C for 30 sec. Two depositions yielded TiO_2 layers of approximately 12 nm in thickness. These TiO_2 layers served to reduce the nucleation energy of the perovskite, and prevent nucleation of (111) oriented grains by removing contact with the (111) Pt. Thus partial (001) orientation was obtained.

For the electrical measurements, top electrodes of 0.6 mm diameter were deposited. Evaporated Cr/Au electrodes were applied to the pyroelectric, $Pb(Zr_{0.15}Ti_{0.85})O_3$, films and sputtered Pt to the piezoelectric $Pb(Zr_{0.45}Ti_{0.55})O_3$ films.

2.2 Microstructure and Electrical Properties

Crystallinity and texture of the films were characterized by x-ray diffraction, using Cu kα radiation and theta-two theta step scans. Surface microstructure was characterized using a field emission SEM operated at 5 kV. Characterization of the film/electrode interfaces and film transverse section was done by TEM. TEM specimens in transverse section were prepared as described previously [14].

Electrical property measurements consisted of dielectric constant and loss measurements, ferroelectric hysteresis, pyroelectric coefficient, and piezoelectric measurements. An HP 4194 impedance gain phase analyzer was used to obtain E and tan δ at 1 and 10 kHz and 50 mV. *P-E* hysteresis loops were measured with a Sawyer-Tower circuit at a frequency of 50 Hz. Samples were cycled five times and data for the last two loops recorded. The pyroelectric coefficient of the $Pb(Zr_{0.15}Ti_{0.85})O_3$ films was determined by

measuring the current induced by a 10 mHz, 1°C temperature modulation [15]. A double beam interferometer was used to measure the piezoelectric response of the $Pb(Zr_{0.45}Ti_{0.55})O_3$ films as a function of applied field. Strain field loops and effective d_{33} coefficient data are reported.

The Y stabilized ZrO_2 substrate was characterized by SEM and XRD. The average grain size of the ZrO_2 is 0.4 µm as quoted by the manufacturer. Average linear thermal expansion values for the substrate, for the temperature ranges of interest, as calculated from the data of [5], are given in Table I.

3 Results

3.1 *$Pb(Zr_{0.45}Ti_{0.55})O_3$ films*

SEM images of the surfaces of 2.4 µm thick films as prepared and with additional anneals at 750 and 850°C for 1 hour are shown in Fig. 1. The as-prepared and 750°C films exhibit very fine grain sizes of < 0.1 and < 0.2 µm respectively. After annealing at 850°C, a microstructure with bimodal grain size distribution (fine grains <0.2 µm and large grains >1.0 µm) develops. Transmission electron microscopy revealed that the grain structure was approximately the same throughout the thickness of the film and that the SEM images of the surface were representative of the overall microstructure.

XRD results for the films shown in Fig. 1 are presented in Fig. 2. Here, the effect of increasing grain size is manifest in the splitting of the (00l)/(l00) and (200)/(002) peaks. This film was prepared without the TiO_2 layer, and random orientation occurs.

Nested *P-E* hysteresis loop are shown in Fig. 3 for a 10.25 µm film with $x = 0.55$. This film, prepared using the application of the TiO_2 layer on the bottom electrode, was partially 001 oriented. The loop is square with a P_r/P_s value of ~ 0.8, average P_r of 36 µC/cm^2, and average E_c of 45 kV/cm, at 160 kV/cm applied field. The piezoelectrically induced strain response as measured by interferometry is shown in Fig. 5. Maximum strains of greater than 0.2% were achieved with an applied field of 175 kV/cm. Analogous properties have been measured on strongly (111) textured films of thickness > 0.7 µm thick on Si. Thus for any advantage to be obtained by the use of ZrO_2, nearly perfectly (001)oriented films would be required.

3.2 *$Pb(Zr_{0.15}Ti_{0.85})O_3$ films*

The microstructural evolution with increasing annealing temperature of a $Pb(Zr_{0.15}Ti_{0.85})O_3$ film was analogous to that observed for the $Pb(Zr_{0.45}Ti_{0.55})O_3$ films (see Fig. 1). XRD patterns of $Pb(Zr_{0.15}Ti_{0.85})O_3$ films annealed at different temperatures and being partially (001) oriented, are shown in Fig. 5. For this film, the TiO_2 buffer layer method was employed to obtain the partial (001) texturing. The film texture was not effected by the post preparation anneals. Further, as was the case for the $Pb(Zr_{0.45}Ti_{0.55})O_3$ films, the increase in grain size with higher annealing temperature lead to more distinct splitting of the (100)/(001) and (200)/(002)peaks.

For films annealed at 850°C and 950°C, a grain boundary phase was observed by TEM. EDS analysis (in TEM) indicated the phase to be Pb rich. The rounded morphology of the grain boundary triple points suggests that mass transport has occurred in the liquid phase. In the PbO- TiO_2 binary system, a eutectic exists at 15% TiO_2 which has a melting point of 838°C. Although EDS only identified this phase as Pb-rich it is very likely to be the PbO-TiO_2 eutectic. For films annealed above 850°C, electrical property measurements were not possible due to degradation of the bottom electrode structure (recrystallization of the Pt). This degradation was readily observed by TEM. The Pt bottom electrode was no longer present as a continuous layer, but existed as hemispherical particles on the surface of the ZrO_2. Consequently, PZT was in direct contact and reacted with the ZrO_2. Dielectric and pyroelectric data for several of the $x = 0.85$ films are summarized in Table II, with data for a strongly (111) oriented film prepared on Si given last. Again, the properties of the partially (001) textured film on ZrO_2 and the strongly (111) oriented film on Si are similar.

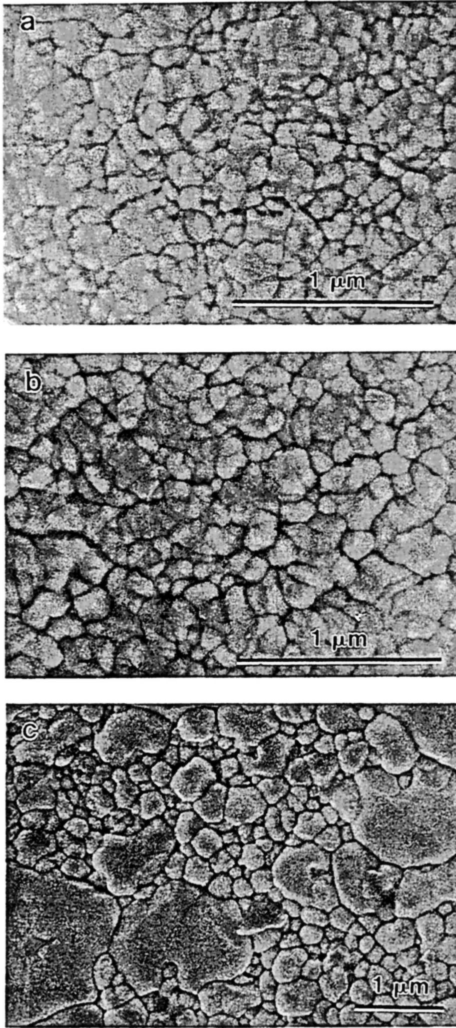

Fig. 1 SEM images of the surface of 2.4 μm $Pb(Zr_{0.45}Ti_{0.55})O_3$ films annealed at a) 630, b) 750, and c) 850°C.

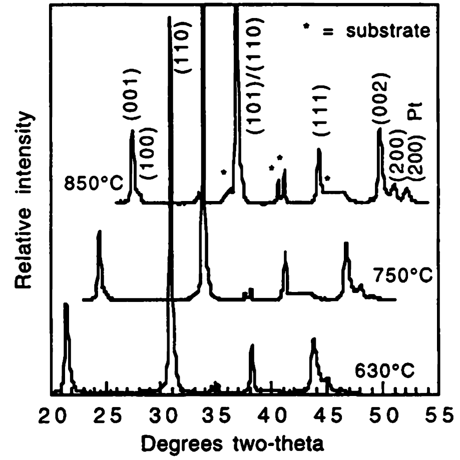

Fig. 2 XRD patterns of the films shown in Fig. 1. Note offsets in x and y for clarity. The substrate peaks have also been subtracted.

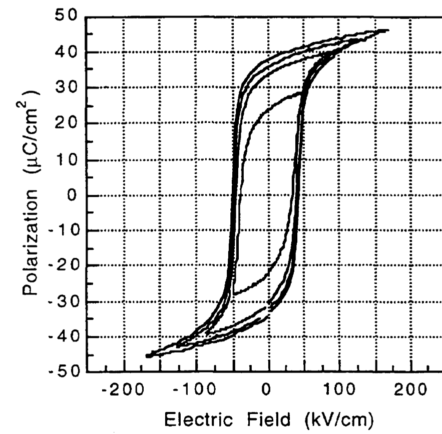

Fig. 3 Nested hysteresis loops of 10.25 μm $Pb(Zr_{0.45}Ti_{0.55})O_3$ film of partial (001) texture.

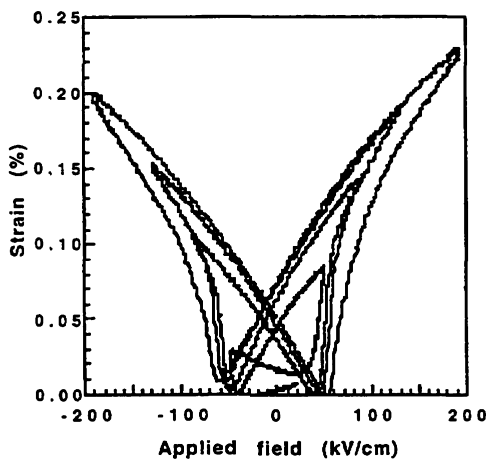

Fig. 4 Strain-field loops of as-crystallized 10.25 μm $Pb(Zr_{0.45}Ti_{0.55})O_3$ thin film of partial 001 texture.

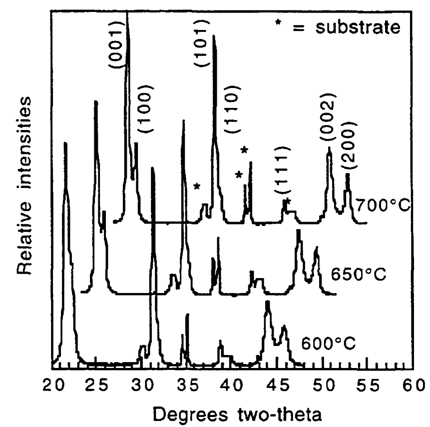

Fig. 5 XRD patterns of 1.0 μm $Pb(Zr_{0.15}Ti_{0.85})O_3$ film annealed at the temperatures indicated.

Table II. Poling and pyroelectric results for $Pb(Zr_{0.15}Ti_{0.85})O_3$ films.

Sample	Poling conditions*		Properties		
thick. / anneal temp.	Temp. (°C)	Electric Field (kV/cm)	Pyro. Coef. ($\mu C/m^2K$)	Dielectric Constant (1 kHz)	Loss (%)
1 µm /	-	-	-	270	3.5
600°C	130	-200	193	210	1.3
1 µm /	-	-	-	310	1.5
650°C	150	-150	176	270	1.4
1 µm /	-	-	-	290	1.6
700°C	130	-100	138	260	1.7
4.0 µm /	-	-	32	310	6.1
600°C	140	-200	181	220	3.7
7.0 µm /	-	0	-	200	4.9
600°C	150	-100	147	170	1.6
7.0 µm /	-	-	-	330	3.9
750°C	140	+200	171	290	0.5
**0.8 µm					
650°C	125	+250	168	287	1.6

** Poling time is 10 minutes*
*** film prepared on Si substrate*

4 Conclusions

PZT thin films of up to 10 µm thickness, of compositions $Pb(Zr_{0.45}Ti_{0.55})O_3$ and $Pb(Zr_{0.15}Ti_{0.85})O_3$ were prepared on ZrO_2 ceramic substrates. Partial (001) texture was achieved for both compositions. The partially oriented $Pb(Zr_{0.45}Ti_{0.55})O_3$ films exhibited square hysteresis loops with maximum remanent polarizations of 36 $\mu C/cm^2$ and coercive fields of approximately 45 kV/cm. Randomly oriented films yielded less well defined hysteresis loops. For the $Pb(Zr_{0.15}Ti_{0.85})O_3$ films, maximum pyroelectric coefficients of 193 $\mu C/m^2/K$ were measured. The properties obtained are approximately the same as those measured for strongly (111) textured films of the same compositions prepared on Si. Thus, in order to gain advantage from the higher TEC of the ZrO_2 substrate, the (001) texture must be improved.

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