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Pyroelectricity of spontaneously poled La-modified lead titanate thin films on silicon based substrates

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Abstract

Multiple deposition by spin-coating and RTP crystallisation have been used to obtain La-modified lead titanate thin films of composition $Pb_{0.88}La_{0.08}TiO_3$ (PTL) onto two types of substrates: Ti/Pt/Ti/(100)Si annealed at 650°C and Pt/TiO_2/(100)Si. The films on Ti/Pt/Ti/(100)Si present a main <111> preferred crystallographic orientation, whereas the films on Pt/TiO_2/(100)Si present a mixed <001>/<100> preferred orientation. All the films developed a net polarisation in the direction perpendicular to the film plane and a spontaneous pyroelectric coefficient. The hysteresis and switching characteristics of the films were dependent on the type of substrate. Results as a function of the number of deposited layers are presented. Poling was carried out under different electrical signals at 150°C. The highest pyroelectric coefficient achieved at room temperature was $\gamma \sim 40\times10^{-9}$ C cm^{-2} K^{-1}.

Keywords: Ferroelectric properties; Films; Functional applications; Sol-gel process; X-ray methods

1. Introduction

Ferroelectric thin films of modified lead titanate onto silicon substrates have created much interest during recent years due to the possibility of their integration into microelectronic devices, mainly as infra-red pyroelectric detectors, but also in piezoelectric microelectromechanical systems (MEMS).

Among the modified-lead titanate thin films, (Pb, La)TiO_3 compositions have been shown to be suitable for pyroelectric applications.[1]

The properties of the thin films are governed by the underlying substrate and processing conditions, thus, it is possible to promote nucleation and preferred orientation of the perovskite depending on the type of substrate. It has been shown[2,3] that Ti on the Pt electrode plays a key role in seeding of the orientation, giving place to <111> main preferred orientation in the film. For this condition, a net polarisation of about 60% of the spontaneous polarisation (P_s) can be achieved in the direction normal to the substrate. Such a net polarisation is advantageous for pyroelectric applications, because poling of the film during fabrication of the devices can be avoided.

We present here the study of the field response, by measurement of the ferroelectric hysteresis loops and the switching current curves. The poling procedure and the optimised pyroelectric properties of the self-polarised La-modified lead titanate thin films, processed by a diol-based sol-gel route onto Si-based substrates, are also discussed. The dependence of the properties on the different textures developed in the films on annealed Ti/Pt/Ti/SiO_2/Si(100) and Pt/TiO_2/SiO_2/Si(100) substrates is also analysed.

2. Experimental procedure

The precursor solution of $Pb_{0.88}La_{0.08}TiO_3$ films was synthesised by a diol based sol-gel process as reported elsewhere.[4] This solution was deposited onto silicon based substrates by the spin-on technique in a class 100 clean room. Pyrolysis of the wet films was carried out on a hot plate at 350°C for 60 s, and crystallisation by

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rapid thermal processing (RTP) at 650°C for 50 s at an average rate of 30°C/s. Films of different thickness were obtained by repeating the deposition and crystallisation steps up to six times. The thickness of the resulting films was measured in a scanning electron microscope (SEM) ISI DS-130C. Differences with thickness measured with a profilometer Taylor–Hobson Talysurf 50 were observed in some cases due to differences in substrate curvature.

Two types of substrates prepared by sputtering were tested: (1) Ti/Pt/Ti/SiO_2/(100)Si annealed at 650°C for 1800 s, hereinafter called Ti/Pt/Ti, and (2) Pt/TiO_2/SiO_2/(100)Si, hereinafter called Pt/TiO_2.

A Siemens D500 powder diffractometer with a Cu anode was used to obtain the film diffraction patterns. Preferred orientations of the films were analysed by XRD with Bragg–Brentano geometry. To avoid the overlapping of the 111 peaks of the PTL film and the Pt electrode, θ and 2θ were misaligned by an angle of ~3°. In this way, it was possible to use pseudovoigt functions for the decoupling of the two peaks and to obtain a semi-quantitative value of the orientation degree of the films, by calculating the relative intensities with respect to that of the highest peak.

Electrical characterisation was accomplished after ~0.2 mm diameter Pt top electrodes were deposited in a BAL-TEC SCD 050 sputter coater. The dielectric permittivity and losses at 1 kHz were measured on a HP4284A impedance bridge.

Ferroelectric hysteresis loops were traced with a modified Sawyer–Tower circuit using sinusoidal waves of 1 kHz and maximum amplitude of 16 V. The apparent coercive fields, E_c, were obtained from the maximum of the current density versus field cycles, according to the expression $E_c \sim (|E_c^+| + |E_c^-|)/2$. These loops were corrected by compensating the contribution of the ohmic and the capacitive linear currents, using a non-perturbative method.[5] For measurement of the hysteresis loops of the six layer films, a commercial Radiant Technologies RT66A unit was used.

Pyroelectric coefficients were calculated from the pyroelectric currents measured on a Keithley 6512 electrometer, obtained by application of a triangular wave of 5×10^3 Hz and amplitude of 2°C, with a heating and cooling rate of ±1.8 K/min. These coefficients were obtained before and after a poling process at 150°C for 5 min with a train of square pulses of ±12 V amplitude.

3. Results and discussion

Films on Ti/Pt/Ti substrate show a <111> preferred orientation with also important <001> and <100> contributions to the texture (Table 1). This result was confirmed by XRD pole figure analysis,[6] together with the decrease of the texture index as the thickness increases. As shown in Table 1, this decrease corresponds to the relative decrease of the <111> component of the texture, while the <001>/<100> ones become, for the six layer films, the most important texture components. The <111> orientation is a consequence of the existence of heterogeneous nucleation at the film-substrate interface, due to the interaction with the titanium on the platinum during crystallisation.[2,3] Films on Pt/TiO_2 substrate show <001>/<100> preferred orientations. In both types of films the preferred orientations are promoted by the successive deposition and crystallisation processing of thin layers (100 nm). As reported previously,[6] in films on Pt/TiO_2 substrate there is no remarkable change of the texture index with thickness.

Table 1
Relative XRD pattern intensities of PTL films

Number of layers	PTL on Ti/Pt/Ti (%)				PTL on Pt/TiO_2 (%)	PTC theoretical values (JCPDD[a] file no. 39-1336)
	1	2	3	6	3	
I_{001}	15	23	49	–	85	14
I_{100}	19	28	54	100	100	21
I_{101}	13.7	9.5	28	10	1	100
I_{110}	14.6	19.4	27.8	18	7	45
I_{111}	100	100	100	79	15	35
c/a	–	–	1.011	–	1.009	–

[a] Joint Committee of Powder Diffraction Data.

Hysteresis loops for the two kinds of films are shown in Fig. 1. A decrease of the coercive field, E_c, as the thickness increases is found for both of them (Table 2). This fact, together with the increase of the dielectric permittivity with the thickness,[6] points to the existence of a modified layer at the ferroelectric-substrate interface.[7,8] Higher values of the remanent polarisation (P_r) were found for films on Ti/Pt/Ti substrate. These films have a texture with two components, <111> and <001>, that results in contributions to a net polarisation in a direction normal to the substrate, whereas films on Pt/TiO_2 only have one component <001>, contributing to this net polarisation.

All the films show spontaneous pyroelectricity (Table 3), which also reveals the existence of self-polarisation with a net component in the direction perpendicular to the plane of the film in all of them. The sign of the measured currents indicates that this net polarisation in all the films points upwards from the substrate. These results on the self-polarisation indicate the existence of an internal bias field. It has been suggested[9] that a built-in field of a Schottky barrier between the film and the bottom electrode is responsible for the observed effect.

Different poling experiments with trains of square pulses were carried out to achieve the maximum pyroelectric coefficients. A temperature of 150°C was used since higher temperatures may cause increase in the film dielectric loss and irreversible damage, and for lower temperatures saturation poling is not achieved.

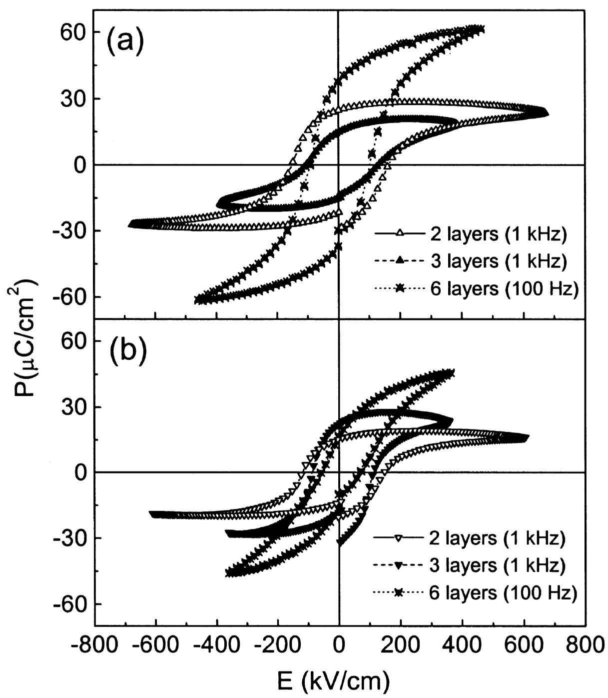

Fig. 1. Hysteresis loops of the films on (a) Ti/Pt/Ti substrate and (b) Pt/TiO_2 substrate.

Table 2
Results of the ferroelectric characterisation of the films

Number of layers	Thickness (nm)	$+P_r$ (μC/cm^2)	$-P_r$ (μC/cm^2)	E_C (kV/cm)
PTL on Ti/Pt/Ti substrate				
2	240	25.0	−25.5	145.6
3	338	14.8	−14.3	103.7
6	429	37.5[a]	−37.0[a]	96.8[a]
PTL on Pt/TiO$_2$ substrate				
2	266	15.4	−17.9	128.0
3	335	22.0	−26.7	96.3
6	547	16.8[a]	−16.5[a]	64.0[a]

[a] Radiant Techn. RT66A unit measurement. Frequency 100 Hz.

The optimum poling treatments were trains of square pulses with amplitude ±12 V, 400 μs width and separated by 300 and 500 μs for films on Ti/Pt/Ti and Pt/TiO_2, respectively. For the six layer films, trains of square pulses of 250 μs width and intervals of 1000 μs were the best. In all the films (Table 3), the pyroelectric coefficient increases when the poling field is applied to build-up polarisation in the same sense of the self-polarisation. When the poling field is applied in the opposite sense a change in the sign of the pyroelectric coefficient occurs. Therefore, the poling treatment promotes domains switching, however even at 150°C there is a "memory" effect of the sense of the net polarisation of the film meaning that a bias field is present.

Fig. 2(a) and (b) shows the time stability of the highest pyroelectric coefficients after poling for the films onto the two types of substrates.

The films prepared here have the highest pyroelectric coefficients (Table 3) reported to date for chemical solution deposited (CSD) modified lead titanate films. A pyroelectric coefficient of 14×10^{-9} C cm^{-2} K^{-1} was previously obtained after poling, for PTL films with 8% of La prepared by the same sol-gel route with a <100> <001> orientation on Pt/TiO_2, by multideposition and a single crystallisation at 500°C/min, by direct insertion in a pre-heated furnace.[7] For MOCVD prepared PTL films with a <111> orientation, coefficients of 9 and 13×10^{-9} C cm^{-2} K^{-1} were reported after a poling step for films with 8 and 20% of La, respectively.[10] Only for sputtered films of modified-lead titanate[11,12] have been reported higher pyroelectric coefficients.

For practical use, the figure of merit $F_d = \gamma/C^E(\varepsilon'\varepsilon_0 tg\delta)^{1/2}$, is the parameter to take into account to select a material. Due to the high permittivity, the films under study here have moderate figures of merit. Higher figures of merit could be obtained by processing films with important porosity, due to the consequent reduction of the dielectric permittivity.[13] However, this could be detrimental of the mechanical properties of the films. Other ways of reducing permittivity while maintaining these high pyroelectric coefficient values will be sought to improve the practical use of these films.

Table 3
Pyroelectric coefficients of the films

Number of layers	γ ($\times10^{-9}$ (cm^{-2} K^{-1})					
	PTL on Ti/Pt/Ti substrate			PTL on Pt/TiO$_2$ substrate		
	Spontaneous	Pol −12 V at 150°C	Pol +12 V at 150°C	Spontaneous	Pol −12 V at 150°C	Pol +12 V at 150°C
2	22.0	33.5	−22.6	4.8	21.5	−16.4
3	18.0	40.0	−40.0	5.4	15.8	−15.7
6	1.6	36.7	−25.6	7.0	20.0	−22.7

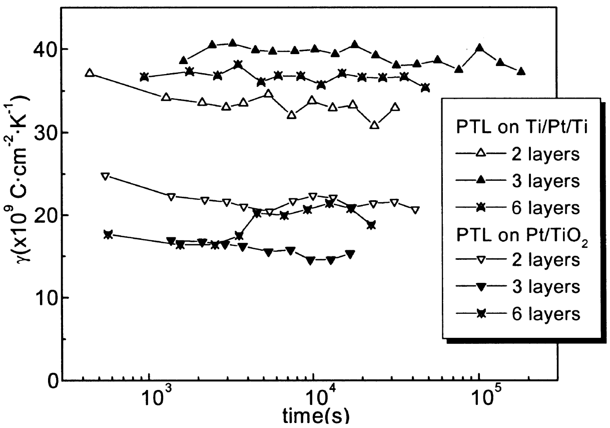

Fig. 2. Highest pyroelectric coefficients after poling of the films onto the two types of substrates.

4. Conclusions

A multiple spin-on deposition and RTP crystallisation process has been used in order to promote preferential orientations in $(Pb,La)TiO_3$ with 8% La thin films by a diol-based sol-gel route.

Higher remanent polarisations have been obtained from the measured hysteresis loops for films on Ti/Pt/Ti substrate. This is consequence of the two texture components, $<111>$ and $<001>$, of these films that result in two important contributions to a net polarisation in a direction normal to the substrate, whereas the texture of the films on Pt/TiO_2 substrate only have one component, $<001>$, contributing to this net polarisation.

Spontaneous pyroelectricity has been found in all the films, as a consequence of the self-polarisation. Higher values of pyroelectric coefficient have been obtained for films on Ti/Pt/Ti substrate. An enhancement of the coefficients has been achieved by the application of a poling treatment at 150°C. The films here prepared have the highest pyroelectric coefficients reported to date for chemical solution deposited (CSD) modified-lead titanate films, $\gamma \sim 40 \times 10^{-9}$ C cm^{-2} K^{-1}.

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