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The Effect of Film Thickness on the Ferroelectric Properties of Sol–Gel Prepared Lanthanum Modified Lead Titanate Thin Films

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Abstract

Lanthanum modified lead titanate (PTL) thin films with a thickness ranging between 100 and 650 nm have been prepared by a sol–gel method. Hysteresis loops have been measured in two sets of films: thermally crystallized with 10°C min^{-1} *and more than 500°C min*$^{-1}$*. A thickness dependence of the ferroelectric parameters has been found in both sets. This dependence is related to the presence of a modified layer near the bottom electrode, with a different origin in the two sets of films. In those treated with 10°C min*$^{-1}$*, the layer is a Ti deficient one, most probably with the perovskite structure but La deficient. In those treated with more than 500°C min*$^{-1}$*, it is a layer that bears the ferroelectric-substrate interfacial stress. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: (Pb,La)TiO_3, films, sol–gel processes, ferroelectric properties.

1 Introduction

Among the ferroelectric compositions, lanthanum modified lead titanate (PTL) with small amounts of La has been found to be very suitable for thin film in infrared sensors,[1,2] and it is also under focus for electromechanical applications.

In a previous work,[3] we have shown that PTL films with a 8% of La can be prepared on Si based substrates by a diol based sol–gel method showing good ferroelectric properties, provided that a 20 mol% excess of PbO were added to the precursor solution. It was found that the structure and microstructure of the films can be tailored using different heating rates for the crystallization thermal treatment. In this work, the dependence of the switchable polarization on thickness is studied for the two types of films. A thickness dependence is expected in films when a low dielectric permittivity layer is developed near the electrodes.[4,5] Previous rutherford backscattering spectrometry (RBS) results[6] obtained for the PTL films of this work, suggest that Ti diffusion occurs from the film to the Pt bottom electrode during the thermal treatment depending on the heating rate of crystallization.

2 Experimental Methods

PTL films were prepared as in Ref. 3 from a precursor solution with a 20 mole% excess of PbO with respect to the nominal composition of $Pb_{0.88}La_{0.08}TiO_3$. Films with successive increasing thickness were obtained by repeating solution deposition up to five times.

The average thickness of the PTL films was measured by profilometry. Changes of the structure and microstructure with thickness were monitored by grazing incidence X-ray diffraction (GIXRD) and scanning electron microscopy (SEM), respectively. Electrical characterization was accomplished after 500 μm diameter Pt electrodes were deposited by sputtering on the films. The capacitance and losses at 1 kHz were measured with a HP 4284A precision LCR meter. Ferroelectric hysteresis loops were measured by using a modified Sawyer–Tower circuit and an oscilloscope. A sine wave voltage of variable frequency (between 2 and 200 Hz) was used. To improve the switchable polarization, an electrical treatment consisting in trains of alternating square pulses with a 1 min length, a 200 Hz frequency, and a 250–400 kV cm^{-1} amplitude,[3,7] was applied before measurements.

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3 Results

3.1 Films treated with a 10°C min^{-1} heating rate

GIXRD and SEM show that films of thickness ranging from 110 to 645 nm have the same perovskite structure, characterized by a random orientation, and microstructure, which presents some porosity.[3]

The dependence of the reciprocal average capacitance on thickness for the films treated with 10°C min^{-1}, is shown in Fig. 1. The film with the smallest thickness, i.e. that one prepared by a single deposition, presents such high leakage that the capacitance cannot be measured. The rest of the data fit well to a linear behaviour.

The remanent polarization, P_R, increases with the electrical treatment[3] in the films crystallized with 10°C min^{-1}. The hysteresis loops of a 220 nm thickness film, before and after an electrical treatment with increasing fields, are shown in Fig. 2(a). P_R increases with the measuring field as well as with the one of the electrical treatment in the range between 300 and 400 kV cm^{-1}, and so does slightly the coercive field, E_c. In Fig. 2(b), the hysteresis loops at increasing frequency of a film 485 nm thick, are shown after an electrical treatment with 300 kV cm^{-1}, which in this case, is the maximum field attainable. P_R decreases slightly when the frequency increases, while E_c does not change significantly. P_R values are higher in this case than those obtained for the thinner film. The observed trends on field and frequency strongly suggest that saturation has not been reached in these PTL films.

In Fig. 3, the dependence of P_R on the film thickness, measured with 300 kV cm^{-1} and 200 Hz, after an electrical treatment with the same field, is shown. P_R increases with thickness. Care must be taken when discussing the data marked with *, corresponding to the film with the highest thickness, 645 nm, in which the maximum field attainable was 250 kV cm^{-1}. In the same figure, the dependence of the coercive field on the thickness is also shown, although, in this case, no dependence is observed.

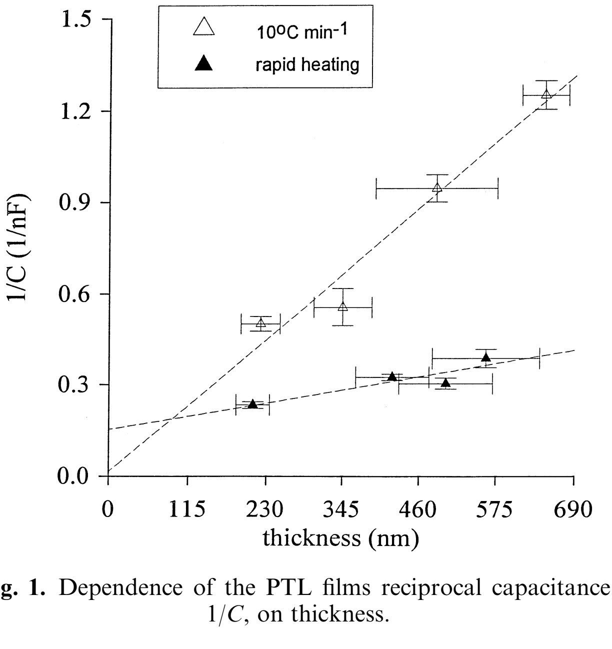

Fig. 1. Dependence of the PTL films reciprocal capacitance, $1/C$, on thickness.

3.2 Films treated with rapid heating

GIXRD and SEM show no changes in films with thickness ranging between 130 and 560 nm. Structure is characterized by a mixed [001] [100] orientation and microstructure is dense.[3]

The dependence of the reciprocal average capacitance on thickness for the films treated with rapid heating, is shown as well in Fig. 1. The single coated films has also such a high leakage that the capacitance cannot be measured.

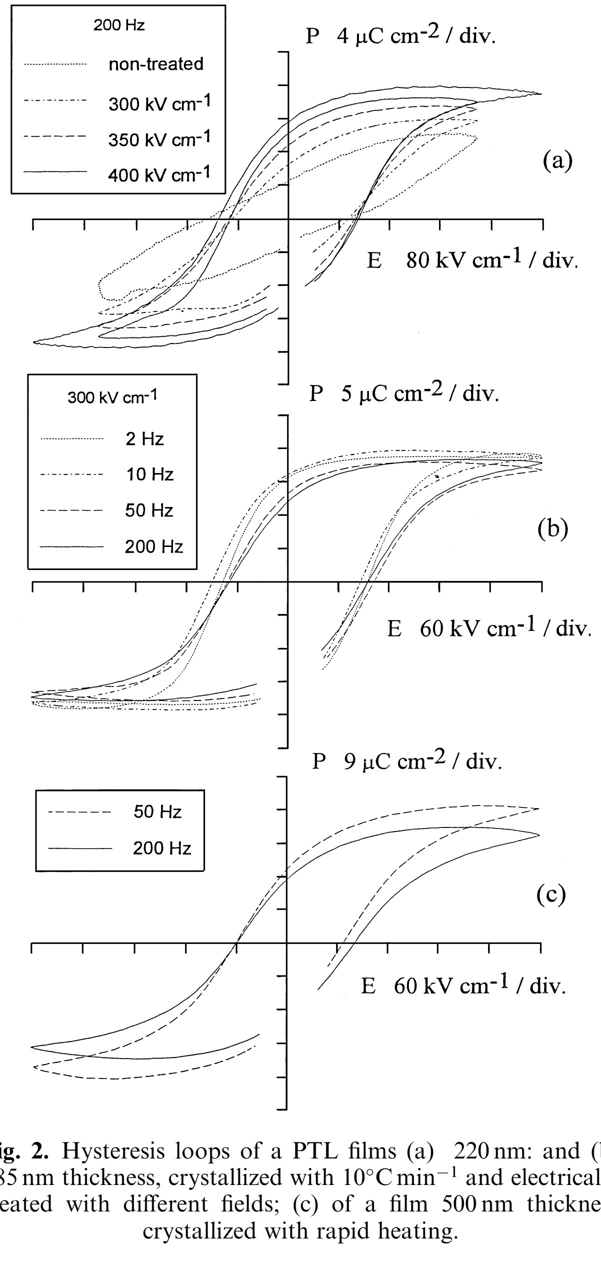

Fig. 2. Hysteresis loops of a PTL films (a) 220 nm: and (b) 485 nm thickness, crystallized with 10°C min^{-1} and electrically treated with different fields; (c) of a film 500 nm thickness crystallized with rapid heating.

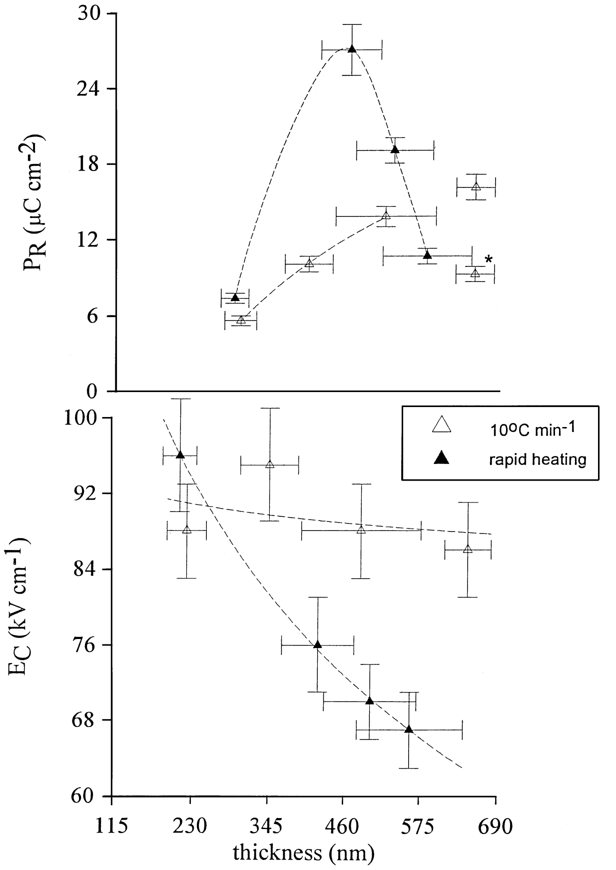

Fig. 3. Thickness dependence of the remanent polarization, P_R, and the coercive field, E_c, in the PTL films 200 Hz, 300 kV cm^{-1} (*at 250 kV cm^{-1}).

Rapidly heated films do not withstand the electrical treatment. The hysteresis loops at two frequencies of a film 500 nm thick, are shown in Fig. 2(c). Similarly to films treated with 10°C min^{-1}, P_R decreases and E_c increases when the frequency is raised, indicating that saturation has not been reached. In Fig. 3, the dependence of P_R and E_c, with an applied field of 300 kV cm^{-1} and a frequency of 200 Hz, on films thickness is shown for films rapidly heated. P_R increases initially up to 27 μC cm^{-2} for films 420 nm thick; and then, it decreases continuously. E_c decreases when the thickness increases in all the range investigated.

4 Discussion and Conclusions

4.1 Films treated with a 10°C min^{-1} heating rate

RBS results have been reported before[6] that provide evidence of the Ti diffusion from the perovskite film to the bottom substrate causing the formation of a Ti deficient area in the film, near the substrate and, therefore, with different electrical properties. A simplified model of the profile of these films is that of two layers system, a first one produced by the interaction between the film and the substrate, with a thickness of t_m and a dielectric permittivity of ε_m (we will refer to it as the modified layer); and a second one, with the nominal composition of the perovskite, with a thickness of t_f and a dielectric permittivity of ε_f (the ferroelectric layer). Previous RBS results[6] indicate that t_m is between 50 and 100 nm. The situation, from an electrical point of view, is that of two capacitors, with capacitances of C_m and C_f, in series. In a system like this, the reciprocal capacitance is given by the following equation:

$$\frac{1}{C}=\frac{1}{S}\left(\frac{1}{\varepsilon_m}-\frac{1}{\varepsilon_f}\right)t_m+\frac{1}{\varepsilon_f S}t \qquad (1)$$

where S is the area of the capacitors and $t = t_m + t_f$ is the whole thickness of the system.

The dependence of $1/C$ on t for the films treated with 10°C min^{-1} is linear, as shown in Fig. 1. This means that t_m and ε_m of the modified layer, and ε_f of the non-modified layer, do not change with the film thickness. This is consistent with the fact that neither the structure nor the microstructure of the film was significantly affected by thickness. From the slope of the fitted line, and using eqn (1), a value of 300 is obtained for ε_f. Similarly, from the intersection with the $1/C$ axis, and using $50 < t_m < 100$ nm estimated from RBS data, ε_m between 260 and 280 is obtained. This dielectric permittivity is only slightly smaller than that of the film, which suggest that the layer originated from the interaction with the substrate is ferroelectric. Thus, it could be formed by a perovskite with less La than the nominal value, since the dielectric permittivity is known to decrease in the PTL system the lower the La content.[8]

The remanent polarization, P_R, of these films presents a dependence on thickness as shown in Fig. 3. It increases with thickness with a decreasing slope. The switchable polarization, P, of the proposed layered structure is given by the following equation:

$$P = P_f + (P_m - P_f)\frac{t_m}{t} \qquad (2)$$

in which P_m and P_f are the switchable polarization of the modified and ferroelectric layers, respectively. Provided that t_m is constant, the increase of P_R with the thickness of Fig. 3 indicates that $P_m < P_f$. It was shown[8] that P_R and the coercive field, E_c, from a saturated loop decrease when the amount of La increases in the PTL system. Being the modified layer of low La content, $P_m < P_f$ results from the lack of saturation.

4.2 Films treated with rapid heating

Previous RBS results[6] do not indicate significant Ti diffusion during rapid heating. However, the dependence of the reciprocal capacitance on thickness shown in Fig. 1 clearly indicates that, from an electrical point of view, the system has to include at least two layers. From the slope of the linear fitting, and using eqn (1), a value of 1525 is obtained for ε_f. ε_m cannot be inferred because t_m is unknown. One possible explanation to this phenomenon is the presence of a layer similar to that discussed in previous section, but thinner, i.e. below the RBS resolution, due to the smaller duration of the treatment with rapid heating. This would lead to a layer with a thickness between 10 and 20 nm, that would be related to a ε_m between 40 and 60. Therefore, the modified layer should have a different origin.

Sol–gel films on Si based substrates are known to be tensile stressed by the substrate.[9] Besides, we have shown[3] that the films shrinkage during the crystallization treatment is higher with rapid heating than with a rate of $10°\mathrm{C\,min}^{-1}$. This indicates that the tensile stress is higher in the former case. Therefore, the modified layer in the rapidly heated films could be a stress induced one, although a question still holds: Why is the stress confined in a thin layer instead of being distributed across the film thickness? The grain size of these films has been studied with transmission electron microscopy (TEM),[10] and found to be between ~50 and ~150 nm. A sharp partial stress relaxation most probably occurs in the grain boundaries, and therefore, the stress is mainly confined in the first row of grains close to the substrate. Assuming that the modified layer is of this type, its thickness can be taken as the grain size, and therefore, ε_m would be ~260, which also suggest that the layer is still ferroelectric, but again with a smaller switchable polarization. Since composition is unchanged, this smaller value is most probably due to 90° domain walls clamping caused by the stress on this layer.

Therefore, this case is the same discussed in the films treated with $10°\mathrm{C\,min}^{-1}$. However, the dependence of P_R on the film thickness is not that expected. The switchable polarization starts to decrease for a thickness above 420 nm. This fact suggests that the characteristics of the layer, either the intensity of the tensile stress or the grain size, change with thickness. Although there is no evidence of grain size changes, the intensity of the tensile stress has been found to increase with thickness in similar Ca modified lead titanate thin films.[11]

In these films a continuous decrease of E_c is observed when the thickness increases. This is due to the significant differences between the dielectric permittivities of the two layers, which causes the field in the ferroelectric not to be constant but to increase with thickness.

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