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Processing and characterization of ferroelectric thin films obtained by pulsed laser deposition

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Abstract

Ferroelectric thin films with compositions $Pb_{0.67}La_{0.22}(Zr_{0.2}Ti_{0.8})O_3$ (PLZT) and $Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ (PZTN) have been processed by radiofrequency assisted-pulsed laser deposition. The first set of films have relaxor properties and the second are classical ferroelectrics. Film growth was carried out over a wide range of processing parameters and the best conditions of deposition have been selected. The obtained films are polycrystalline, with perovskite structure and almost random orientation. The surface morphology has been investigated by atomic force microscopy. The ferroelectric properties have been obtained by hysteresis loop measurements. From measurements of the dielectric properties as a function of the frequency of driving signal, the amplitude and the rate of change of the bias field, the following characteristics have been found: i) a linear decrease of the capacitance with the frequency logarithm which was attributed to the interaction of pinning centers with moving domain walls; ii) a strong nonlinear decreasing of the capacitance with the increasing of the bias field amplitude, almost without hysteresis for PLZT films; iii) a hysteresis-like dependence, for PZTN films, with maxima corresponding to polarization switching; the separation between these maxima decreases with the decreasing of the rate of change of the bias field. This has been attributed to the accumulation of mobile charged defects (oxygen vacancies) near electrodes which facilitates the nucleation of domains and polarization switching.

Keywords: Films, PLZT, PZT, dielectric properties, ferroelectric properties

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1. Introduction

Ferroelectric thin films have been intensively studied in the last decades, due to their wide range of applications such as microelectromechanical systems, ferroelectric memories, multilayer capacitors, tunable RF devices, electro-optical devices etc [1]. Among the various modern deposition techniques, pulsed laser deposition (PLD) is widely used due to its capabilities for the processing of films with complex compositions [2]. Recently an improvement of this technique by adding a radio frequency (RF) plasma beam source has been reported [3]. This allows the increasing of the reactivity of the species in the deposition chamber thus favoring the formation of complex molecules subsequently organized in crystallites [3]. In previous papers we have reported the employment of RF-assisted PLD for the deposition of various relaxor and ferroelectric thin films [4-6]. In this paper we report on the dielectric and ferroelectric properties of ferroelectric and relaxor lead zirconate titanate-type thin films processed by RF-PLD and discuss especially their behavior in high intensity bias fields. The dielectric properties of ferroelectric and relaxor materials are of interest for many applications [1,7]. Relaxor ferroelectric materials have a broad transition at room temperature, thus a high dielectric constant in a temperature range useful for applications [7]. In the present paper we have investigated the dielectric nonlinearity of the deposited relaxor and ferroelectric thin films by measuring the quasi-static *C-V* characteristics. The dependence of capacitance *C* on a slowly varying bias voltage (rate of change<1V/s), was investigated by applying a small amplitude (1-5 kV/cm) and high frequency electric field to the sample subjected to a slowly varying high intensity field.

2. Experimental

Thin films of PZT-type have been deposited starting from targets with different compositions on Pt/Si substrates. The experimental set-up for deposition is based on a pulsed Nd-YAG laser working at frequency 5-10 Hz, pulse duration 10 ns and different wavelengths (265 nm-1.06 μm). The substrate and target are placed in the deposition chamber in a parallel configuration.

After evacuation the deposition chamber is filled with oxygen gas. During deposition the oxygen ions react with Pb ions thus contributing to the incorporation of Pb in the crystalline structure of the film. For a more reactive oxidant ambient in the chamber, the ionization of the oxygen gas was further increased by the use of a RF plasma beam system which generates a discharge (13.56 MHz, 0-300 W) in flowing oxygen between two electrodes separated by a gap of a few mm [3]. In this way the substrate is simultaneously exposed to the laser plume and oxygen plasma beam. The substrate is heated to the deposition temperature with a ramp of 20 ^{0}C/min and after deposition is cooled with 10 ^{0}C/min in oxygen atmosphere. A first set of films was obtained from La-doped PZT targets (PLZT) with the composition $Pb_{1-3x/2}La_x\boxtimes_{x/2}(Zr_{0.2}Ti_{0.8})O_3$, x = 0.22 (PLZT 22/20/80), prepared by mixed oxide method (calcining at 850 ^{0}C for 4 h and sintering at 1250 ^{0}C for 2 h). La^{3+} ions substitute $Pb^{2+}$and the charge compensation is provided by vacancies (indicated by the symbol ⊠) in the A-sites of the perovskite structure, with one vacancy for 2 La atoms. La ions substitution in the tetragonal PZT 20/80 transform its lattice into a cubic one for x = 0.22, as shown by XRD analysis on the target. The lattice parameter *a* was 3,981 Å and the density of the target was 7.25 g/cm^3 (~93% of the theoretical density). Materials with this composition are relaxor ferroelectrics, characterized by a broad dielectric peak at about 0 ^{0}C [7]. Thin films from these targets have been deposited in the following conditions: target-substrate distance 5.3 cm, oxygen pressure 0.4 mbar, substrate temperature 650 ^{0}C, laser fluence 2 J/cm^2, laser wavelength 265 nm, RF power 200 W. Film thickness was about 0.5 μm.

A second set of films was obtained from ferroelectric PZT targets doped with Nb (PZTN), with the composition $Pb_{0.988}\boxtimes_{0.012}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ (PZTN 52/48). Nb^{5+} ions substitute Zr^{4+} or Ti^{4+} in the octahedral sites and charge compensation is obtained with the formation of A-site vacancies, 2 Nb ions requiring one Pb vacancy. Powders with this composition have been prepared by spray drying the precursor solution, followed by calcination. The composition was exact within the calculated absolute error. The powder was calcined in air at 550^0 C for 4 h then uniaxially pressed (75 MPa) and isostatically pressed at 400 MPa in thin disks. The samples were then sintered

at 1100^0 C for 2h, in a $PbZrO_3$ pack. The sintered density was 7.83 g/cm^3 (97.8% theoretical density). Films from these targets have been deposited in the following conditions: target substrate distance 5 cm, oxygen pressure 0.4 mbar, substrate temperature 650 ^{0}C, laser fluence 2 J/cm^2, laser wavelength 265 nm, RF power 200 W. Film thickness was about 1 μm.

After deposition silver electrodes have been deposited on the film surface for the electrical measurements.

Structural characterization was performed by XRD analysis. Morphology of the film surface was examined by AFM. Ferroelectric measurements have been performed by employing a Radiant Technologies RT66A device in the automatic virtual ground mode. Dielectric measurements have been performed as a function of frequency and bias field intensity by using an HP4194A impedance analyzer. The a.c. driving signal frequency has been varied between 100 Hz and 25 MHz. The dielectric nonlinearity has been investigated by measuring the quasi-static *C-V* characteristics. The dependence of capacitance *C* on a slowly varying bias voltage *V* was investigated by applying a small amplitude (5 kV/cm) a.c. driving signal to the sample subjected to a high intensity bias field. The rate of change of bias field $R = dV/dt$ was varied between 0.01 and 0.1 V/s and its intensity between 0 and 150 kV/cm.

3. Results and discussion

From XRD spectra (not shown here) it has been found that the films are polycrystalline with random orientation. The structure corresponds to perovskite PZT and only small amounts of pyrochlore have been identified.

Fig. 1 a) and b) show two AFM images of the surface of a PZTN (a) and PLZT film (b), taken over a 5 μm x 5 μm area. From fig. 1 (a) it can be observed that PZTN film has larger grains with platelets-like shape and dimensions of about 800 nm. Instead PLZT film (fig. 1b) shows much smaller grains (about 200 nm).

From ferroelectric hysteresis measurements it has been found that PZTN films have a coercive field of about 70 kV/cm and a remanent polarization of about 1 μC/cm^2. The resistivity was approximately 10^{12} Ωcm. The saturation could not be achieved probably due to the influence of an interface layer on the effective applied field and to the limitation of this field by the breakdown value. PLZT films have slim tilted hysteresis loops typical of relaxors with a coercive field of about 20 kV/cm and a remanent polarization of about 0.3 μC/cm^2. The resistivity was ~10^{10} Ωcm.

Fig. 2 plots the variation of the capacitance C with frequency f of the driving signal, for different bias voltage amplitudes, for a PLZT film (a similar dependence was measured on PZTN film but with a smaller slope). It can be observed that the capacitance decreases linearly with frequency logarithm $C(f,E) = C_0(E) - a \ln f$. This behavior can be attributed to interaction of pinning centers with moving domain walls [8]. The dotted line in Fig. 2 corresponds to no applied bias field. It can be observed that up to about 20 kV/cm capacitance increases with increasing the bias field, but below this value it continuously decreases for applied fields down to 150 kV/cm. We plot $C(E)$ variation in Fig. 3 for a PLZT relaxor film measured with an a.c. signal of intensity 5 kV/cm and frequency 20 MHz at room temperature. In these measurements the bias field intensity was swept between –60 kV/cm and +60 kV/cm and back (dotted and full curves, respectively), with different rates of change R varying between 0.01 and 0.03 V/s. A variation of the capacitance by about 17% is obtained when the electric field amplitude is 40 kV/cm. This variation is of interest for tunable devices based on dielectric nonlinearity.

Fig. 4 shows the $C(E)$ variation for a PZTN ferroelectric film, measured with an a.c. signal of intensity 5 kV/cm and frequency 1 MHz at room temperature. The bias field intensity was varied between –100 kV/cm and +100 kV/cm and back (dotted and full lines, respectively). The rate of change of the bias voltage was: 0.04 (curve 1), 0.06 (curve 2), 0.08 (curve 3) and 0.1 V/s (curve 4). The hysteresis-like $C(E)$ dependence is typical for ferroelectrics. We recall that $C(E)$ dependence is related to the hysteresis loop $P(E)$ through the relationship $C(E) \sim dP/dE$, thus $C(E)$ characteristic can be also obtained through differentiation of the hysteresis loop. The maxima in the $C(E)$ curves

in Fig. 4 are due to polarization switching, thus their separation ΔE should be related to the switching field values (roughly two times the coercive field E_c) in the polarization hysteresis loop. However ΔE, which varies from about 20 kV/cm to about 40 kV/cm when R changes from 0.04 to about 0.1 V/s, is much smaller than $2E_c$. This difference is due to the fact that polarization hysteresis loop measurement is performed at much higher R (about 100 V/s). The variation of ΔE with R has been attributed to the displacement of mobile charged defects (like e.g. oxygen vacancies) in the near-electrode regions due to the applied quasi-static bias field [9]; the accumulation of the charged defects in these regions is more efficient for slowly varying fields. This facilitates the nucleation of domains and polarization switching which occurs at much weaker external fields [9]. The appearance of a second peak on the positive and negative sweeping *C(E)* curves, more evident for the curves 1 and 2, can be attributed to the 90^0 domains switching [10].

4. Conclusions

Relaxor PLZT 22/20/80 and ferroelectric PZTN 52/48 thin films have been deposited by RF-assisted PLD. Their structure has been examined by XRD and the surface morphology by AFM. The obtained films are polycrystalline, with perovskite structure and almost random orientation. PZTN films have larger grains with platelets-like shape and dimensions of about 800 nm, while PLZT films show much smaller grains (about 200 nm). From ferroelectric hysteresis measurements it has been found that PZTN films have a coercive field of about 70 kV/cm and a remanent polarization of about 1 $\mu C/cm^2$. PLZT films show slim tilted hysteresis loops typical of relaxors with a coercive field of about 20 kV/cm and a remanent polarization of about 0.3 $\mu C/cm^2$. The dielectric properties have been measured as a function of the frequency of the driving signal, the amplitude and the rate of change of the bias field. The linear decrease of the capacitance with the frequency logarithm has been attributed to the interaction of pinning centers with moving domain walls. A nonlinear decreasing of the capacitance with the increasing of the bias field amplitude, almost without hysteresis, was obtained for the relaxor PLZT film. This variation is of interest for

tunable devices based on dielectric nonlinearity. A hysteresis-like *C(E)* dependence typical for ferroelectrics was obtained for the PZTN film, with maxima corresponding to polarization switching. It has been found that the separation ΔE between these maxima decreases with the rate of change of the bias field. This has been attributed to the accumulation of mobile charged defects (oxygen vacancies) near electrodes which facilitates the nucleation of domains and polarization switching.

Acknowledgments

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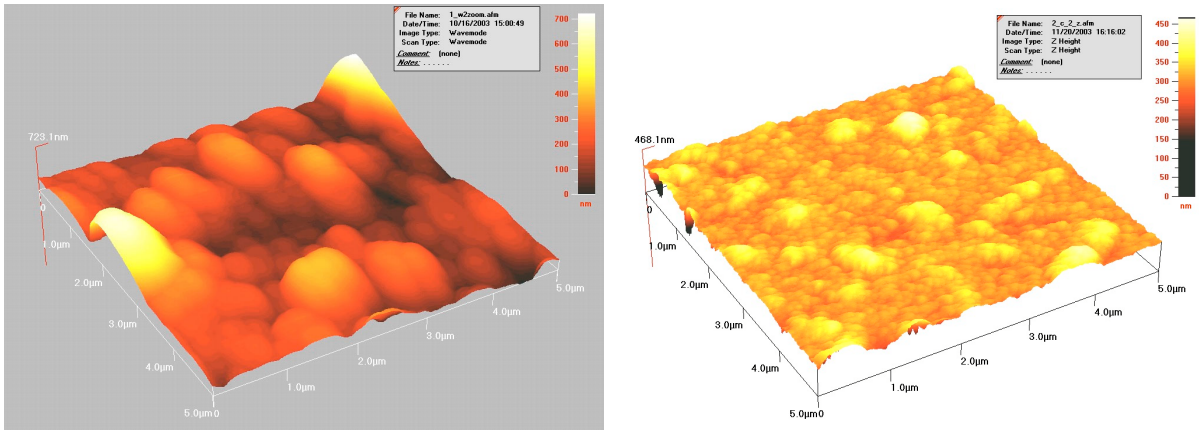
Figure captions

Fig. 1. AFM images taken on a 5 μm x 5 μm surface area of a PZTN film with thickness of about 500 nm (a) and a PLZT film with thickness about 1 μm (b).

Fig. 2. Capacitance *vs*. frequency for different bias field amplitudes, measured on a PLZT film (dotted curve: 0 kV/cm; continuous top curve: 20 kV/cm; continuous bottom curve: 150 kV/cm).

Fig. 3. Dependence of capacitance on the bias field intensity for different rates of change varying between 0.01 (bottom curves) and 0.03 V/s (top curves), measured on a PLZT film, with an a.c. signal of intensity 5 kV/cm and frequency 20 MHz; dotted and continuous curves correspond to positive and negative sweeping, respectively.

Fig. 4. The same as in Fig. 3, measured on a PZTN film with an a.c. signal of intensity 5 kV/cm and frequency 1 MHz. The rate of change of the bias voltage was: 0.04 (curve 1), 0.06 (curve 2), 0.08 (curve 3) and 0.1 V/s (curve 4); dotted and continuous curves correspond to positive and negative sweeping, respectively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100
0
nm
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250
200
150
100
50
0
nm

a) **b)**

Fig. 1.

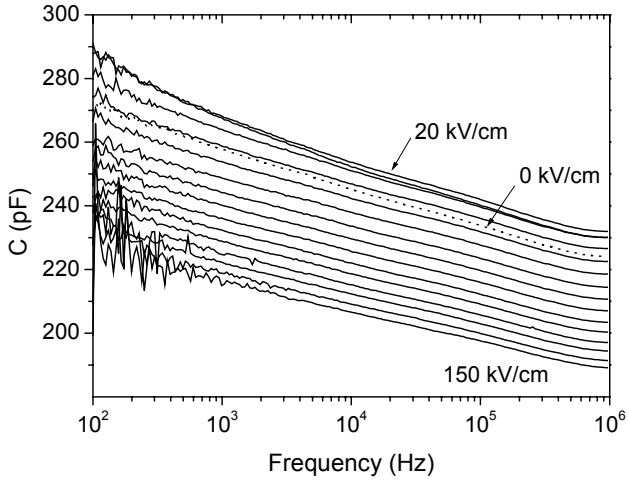
300
280
260
240
220
200
C (pF)
20 kV/cm
0 kV/cm
150 kV/cm
10^2
10^3
10^4
10^5
10^6
Frequency (Hz)

Fig. 2.

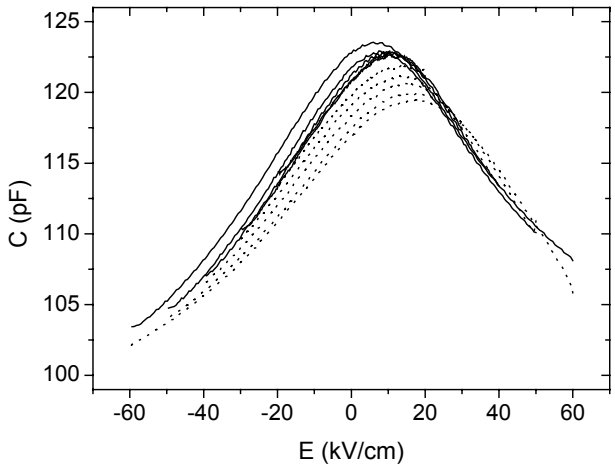
125
120
115
110
105
100
C (pF)
-60
-40
-20
0
20
40
60
E (kV/cm)

Fig. 3.

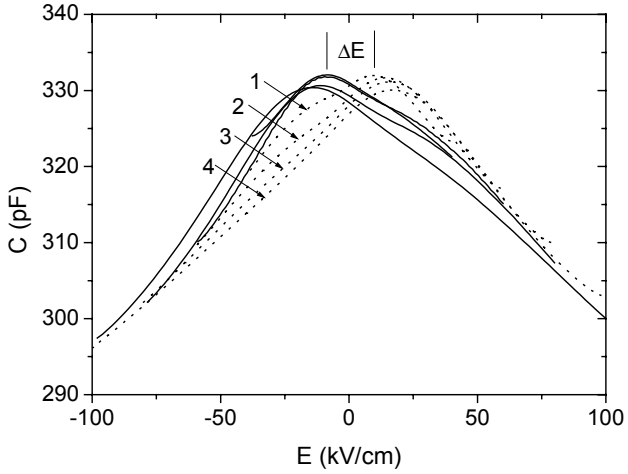
340
330
320
310
300
290
C (pF)
ΔE
1
2
3
4
-100
-50
0
50
100
E (kV/cm)

Fig. 4.