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Structure and dielectric properties of sol–gel 9/65/35 PLZT thin films

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Abstract

Ferroelectric lead lanthanum zirconate titanate thin films were prepared by a sol–gel method on Pt(1 1 1)/TiO_2/SiO_2/Si substrate. The texture selection was observed to be very sensitive to the preparation routine and samples with different preferred orientation were produced. The large- or fine-grained microstructure was observed depending on film thickness. The dielectric measurements of 360 nm thick film performed in the frequency window 10 Hz÷2 MHz revealed the typical relaxor behaviour. The strong dispersion of dielectric permittivity was observed and the temperature shift of maximum of imaginary part of dielectric permittivity with measured frequency was fitted well with the Vogel-Fulcher law.

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Keywords: PLZT; Films; Sol–gel processes; Dielectric properties; Relaxor behaviour

1. Introduction

Lanthanum-doped lead zirconate titanates $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$ (PLZT) are very interest electroceramic materials because of their excellent electrical, mechanical and optical application potential.[1–3] Among many methods the sol–gel technique has been extensively used for the preparation of thin films due to the advantages of high-purity, ease of composition control, low processing temperature, and cost effectiveness. Due to intrinsic crystalline anisotropy many physical properties of the films depend a lot on film texture. In the case of PZT films on Pt-coated Si substrate the dependence of texture selection on preparation routine was observed to be very complicated. The formation of interfacial PbO or Pt_xPb layers was suggested to play an important role in preferred orientation of resulted films.[4–6] The intermediate pyrochlore or crystalline fluorite phases were proposed as another reason driving the film texture.[7]

The dielectric properties may provide important information about polarization behaviour of material and they have been much investigated in the case of bulk PLZT due to observed relaxor behaviour.[8–11] However, in the case of PLZT thin films the dielectric properties were seldom studied.

In this work we report about texture selection, structure and dielectric properties of PLZT thin films.

2. Experimental

The PLZT thin films were prepared following the modified sol–gel routine. Lead acetate trihydrate, lanthanum nitrate hexahydrate, zirconium-tetra-butoxide and titanium-tetra-isopropoxide were used as precursors and 2-metoxyethanol as solvent. The reagents were taken in quantities in accordingly with the general formula $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-(x/4)}O_3$ where x was chosen to be 0.09 and 5% excess of lead in solution was assumed. Lead acetate trihydrate and lanthanum nitrate hexahydrate were first dissolved in methoxyetanol at 80 °C and dehydrated at 120 °C. After dehydration the solution was cooled down 70 °C and zirconium-tetra-butoxide and titanium-tetra-isopropoxide were added. Then the solution was refluxed at 135 °C and distilled at 138 °C. The dry nitrogen atmosphere was used during the routine.

Then the films were deposited on Si/SiO_2/TiO_2/Pt(1 1 1) wafers at 2500 rpm for 30 s. The pyrolysis was performed in air in two steps: the deposited films were directly put on the hot plate at 200 ± 5 °C for 2 min and then on the hot plate at 350, 390 or 430 °C for 5 min. The sequence spinning-

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pyrolysis was repeated until the required thickness of the film was obtained. The crystallization was performed by conventional thermal annealing at 650 °C in air with the average heating rate of 20 ± 3 °C/min. The precision of temperature stabilization in the cases of the second step of pyrolysis as well as annealing was ±10 °C.

The surface morphology was studied with help of Philips XL30 scanning electron microscope. The X-ray diffraction data were recorded with Philips analytical X-ray diffractometer of PW1710-type with the step of 0.02° and the counting time 1 s. The dielectric measurements were performed with help of QuadTech 7600b Precision LCR Meter with slow measurement accuracy (±0.05%) at the amplitude of measured field 833 V/cm on cooling at a rate of 0.5 °C/min. The top electrode of 1 mm diameter was painted with silver paste and annealed at 400 °C for 20 min. Before every measurement the sample was refreshed by annealing at 200 °C for half an hour. The measurements were repeated several times with the same top electrode as well as with the top electrode in different places on thin film surface. The results were reproducible within the experimental error.

3. Results and discussion

In the XRD pattern of annealed at 650 °C for 45 min L5-1 sample besides perovskite and substrate (Pt and TiO_2) peaks the peaks near 29.7° and 34.3° were visible (Fig. 1). Their position is in a good agreement with the position of pyrochlore peaks.[12] The increase in the annealing time up to 60 min (that was used for all other samples) resulted in the pure perovskite phase without X-ray detectable pyrochlore or other minority phases (Fig. 1b). For a qualitative determination of film orientation the relative intensities were defined as:[4]

$$\frac{I/I^{*}}{(I/I^{*})_{100}+(I/I^{*})_{110}+(I/I^{*})_{111}},$$

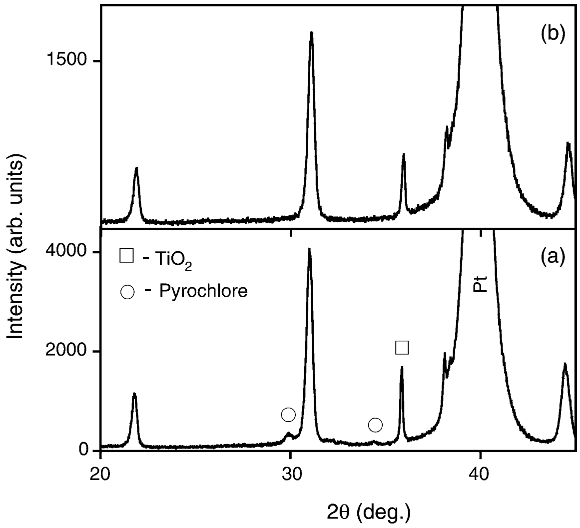

Fig. 1. XRD spectra of L5-1 (a) and L2-1 (b) samples.

Table 1
Dependence of texture selection on pyrolysis conditions

Sample	Number of layers	Relative intensity of psevdocubic reflections (%)			T_{pyr} (°C)
		$(1\,0\,0)_c$	$(1\,1\,0)_c$	$(1\,1\,1)_c$	
L1-7	1	0.070	0.066	0.864	350
L6-1	6	0.076	0.335	0.589	350
L2-1	2	0.220	0.462	0.318	390
L5-1	5	0.224	0.480	0.296	390
L1-1	1	0.445	0.287	0.268	430
L4-1	4	0.603	0.139	0.258	430
L8-1	8	0.829	0.049	0.122	430

where I represents the integrated intensity of a particular psevdocubic reflection $(1\,0\,0)_c$, $(1\,1\,0)_c$ or $(1\,1\,1)_c$ for the films whereas I^* represents its counterpart for the powdered polycrystalline sample.[13,14] The results are summarized in Table 1.

As is seen from the Table 1 the $(1\,0\,0)_c$ oriented samples were grown when high (430 °C) pyrolysis temperature (T_{pyr}) was used, the low T_{pyr} (350 °C) favored in $(1\,1\,1)_c$ orientation and at intermediate T_{pyr} (390 °C) the mixed texture was observed. The L1-1, L4-1 and L8-1 samples were pyrolized and annealed at the same conditions. The only difference is the film thickness. In this case the increase of $(1\,0\,0)_c$ orientation with thickness was observed that was obviously caused by the increased total pyrolysis time. The samples L1-7 and L6-1 were pyrolized at the same temperature (350 °C) but the increased total pyrolized time in the case of six layer L6-1 sample decreased the $(1\,1\,1)_c$ orientation.

These results are in a good agreement with the investigations of texture selection in the case of PZT films on platinized silicon substrate.[4–6] The formation of Pt_xPb buffer layer was suggested to start at 330 °C.[6] This layer favorites in $(1\,1\,1)_c$ film texture because of good lattice match between the intermetallic $a_0 = 4.05$ Å and perovskite $a_0 = 4.035$ Å. The increase in time or temperature of firing leads to the decomposition of Pt_xPb layer due to lead reoxidation that results in decrease of $(1\,1\,1)_c$ orientation. The $(1\,0\,0)_c$ texture was supposed to be caused by formation of PbO interfacial layer that takes place in higher oxidizing conditions. This layer having a layer-like structure and being (0 0 1) textured favors a $(1\,0\,0)_c$ film preferred orientation because of PbO [0 0 1] plane matches well in the lattice arrangement of $[1\,0\,0]_c$ film plane.[4]

The large-grained structure with the average grain size about 550 nm was observed in the case of L2-1 sample (Fig. 2a). In the case of eight layer L8-1 sample the average grain size was about 200 nm. In both cases the film surface looked flat, smooth and thickness was homogeneous (Fig. 2b and c). The thickness of one layer was estimated to be 60 nm. The decrease in the grain size with increase of film thickness was also observed in the case of sol–gel x/1.5/45/55 PLZT on Pt coated Si substrate.[15]

The dielectric measurements of L6-1 sample revealed the typical relaxor behaviour (Fig. 3). The strong dispersion of

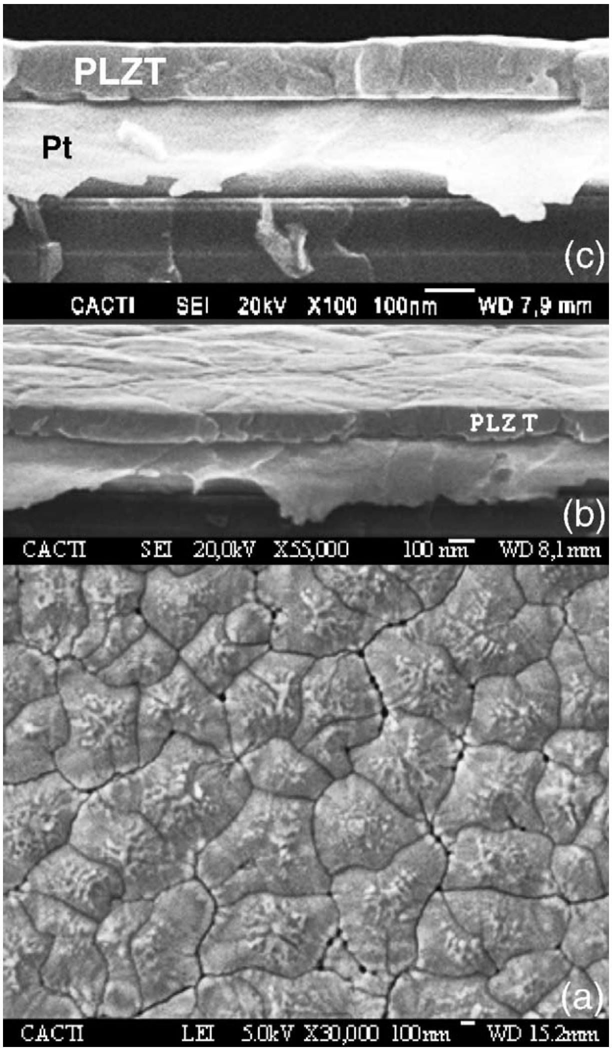

Fig. 2. SEM photos of the surface (a) and cross-section images (b and c) of L2-1 sample.

dielectric permittivity (ε) was observed in the temperature region of peaks. As frequency decreases the values of real part of dielectric permittivity (ε') increase whereas at high temperature slope the values of imaginary part of dielectric permittivity (ε'') decrease and peak position (T_m) shifts towards lower temperatures in both cases. In the case of ε'' the T_m shift was fitted well with the Vogel-Fulcher law with values of $\omega_0 = 9.2 \times 10^{11}$ Hz, $E_a = 0.093$ eV and $T_V = 319$ K (inset in Fig. 3b). As is seen from the Fig. 3 at low frequencies the measurements were influenced by conductivity that is especially seen at high temperatures.

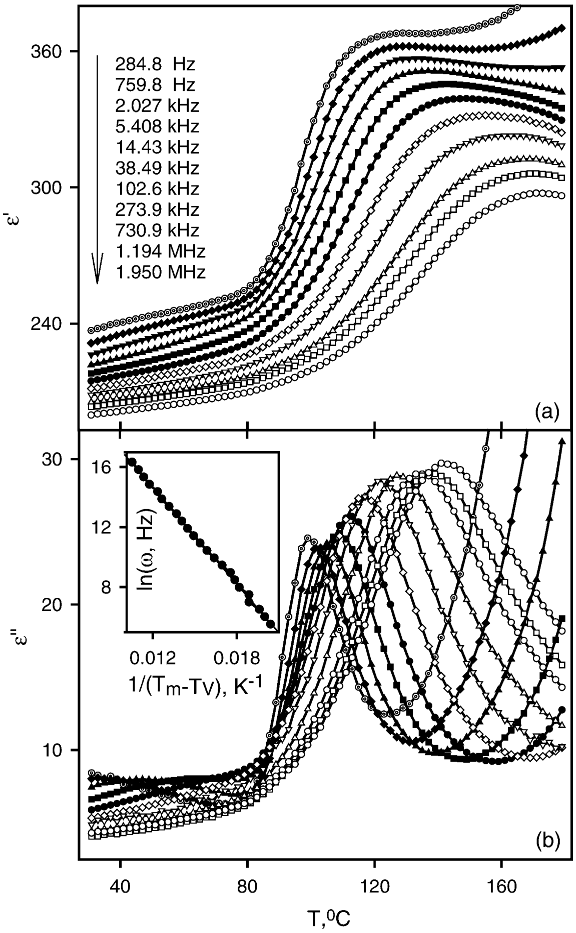

Fig. 3. The real (a) and imaginary (b) parts of dielectric permittivity of L6-1 sample. The results for some selected frequencies are shown. Inset: fitting of ε'' maximum shift with frequency in the range of 40 Hz ÷ 1.95 MHz with the Vogel-Fulcher law: $\omega = \omega_0 \exp(-E_a/(T_m - T_V))$.

The observed relaxor-type behaviour is in a good qualitative agreement with the results obtained in the case of bulk PLZT.[8–11] However, there are several differences. In our case the anomalies of ε happen near the temperatures which are typical for peaks of bulk 8/65/35 PLZT[8,9] and this is nearly 70 °C higher than it takes place in bulk 9/65/35 PLZT.[9–11] The shift of peaks towards higher temperatures was also observed in rf-sputtered[16] as well as in pulsed laser deposited PLZT thin films.[17] One of the possible reason for that might be the lower La content in films than it was expected. However, that cannot explain the considerably lower values of ε' in thin films in compare with bulk 8/65/35 or 9/65/35 PLZT where the values of ε' lie in the region from 1500 up to 3000 below the peaks in the same frequency window.[8–11]

The values of ε' we report are in a good agreement with the results for laser ablated films.[17] The room-temperature values of ε' of sol–gel films were reported nearly three times more with nearly the same tgδ (decreased from 0.032 down to 0.022 compared with 0.035 ÷ 0.020 in our case as frequency increased from 500 Hz up to 1 MHz).[18] However, in that work more the measuring field was more than one order of magnitude higher and the films were higher $(1\,1\,1)_c$ oriented.

Another distinction from bulk PLZT is the much smaller anomalies of ε'. The values of ε' increase less than twice in the peak in compare with values measured away from the peak[16,17] (Fig. 3) whereas it is nearly one order in the case of bulk 8/65/35 or 9/65/35 PLZT.[8–11]

One of the possible reasons for these dielectric properties might be the internal mechanical stresses present in the thin films. They arise from preparation routine, cell parameter mismatch between substrate and film as well as from difference in their thermal expansion coefficients. These stresses may impede the reorientation behaviour of polar nano-regions under external ac electric field which was assumed to produce the main contribution to dielectric polarization in the relaxor ferroelectrics.[10,19,20]

4. Conclusions

PLZT thin films have been grown with help of sol–gel method. SEM showed good surface roughness and thickness homogeneous. The 120 nm thick sample had the large-grained microstructure whereas the average grain size decreased more than twice in the case of 480 nm thick film. The texture selection was observed to be driven by oxidation conditions during the preparation routine. The dielectric measurements showed the low value of dielectric losses and revealed the relaxor behaviour.

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References

1. Haertling, G. H., PLZT electrooptic materials and applications – a review. *Ferroelectrics*, 1987, **75**, 25–55.
2. Seth, V. K. and Schulze, W. A., Fabrication and characterization of ferroelectric PLZT 7/65/35 ceramic thin films and fibers. *Ferroelectrics*, 1990, **112**, 283–307.
3. Scott, J. F., The physics of ferroelectric ceramic thin films for memory applications. *Ferroelectr. Rev.*, 1998, **1**, 1–129.
4. Chen, S.-Y. and Chen, I.-W., Texture development, microstructure evolution and crystallization of chemically derived PZT thin films. *J. Am. Ceram. Soc.*, 1998, **81**, 97–105.
5. Impey, S. A., Huang, Z., Patel, A., Beanland, R., Shorrocks, N. M., Watton, R. *et al.*, Microstructural characterization of sol–gel lead-zirconate-titanate thin films. *J. Appl. Phys.*, 1998, **83**, 2202–2208.
6. Huang, Z., Zhang, Q. and Whatmore, R. W., Low temperature crystallization of lead zirconate titanate thin films by a sol–gel method. *J. Appl. Phys.*, 1999, **85**, 7355–7361.
7. Norga, G. J., Fé, L., Vasiliu, F., Fompeyrine, J., Locquet, J.-P. and Van der Biest, O., Orientation selection in functional oxide thin films. *J. Eur. Ceram. Soc.*, 2004, **24**, 969–974.
8. Xi, Y., Zhili, C. and Cross, L. E., Polarization and depolarization behaviour of hot pressed lanthanum zirconate titanate ceramics. *J. Appl. Phys.*, 1983, **54**, 3399–3403.
9. Viehland, D., Dai, X. H., Li, J. F. and Xu, Z., Effects of quenched disorder on La-modified lead zirconate titanate: long- and short-range ordered structurally incommensurate phases, and glassy polar clusters. *J. Appl. Phys.*, 1998, **84**, 458–471.
10. Bobnar, V., Kutnjak, Z., Pirc, R. and Levstik, A., Electric-field-temperature phase diagram of the relaxor ferroelectric lanthanum-modified lead zirconate titanate. *Phys. Rev. B*, 1999, **60**, 6420–6427.
11. Rychetský, I., Kamba, S., Porokhonskyy, V., Pashkin, A., Savinov, M., Bovtun, V. *et al.*, Frequency-independent dielectric losses (1/f noise) in PLZT relaxors at low temperatures. *J. Phys.: Cond. Matt.*, 2003, **15**, 6017–6030.
12. Kwok, C. K. and Desu, S. B., Pyrochlore to perovskite phase transformation in sol–gel derived lead-zirconate-titanate thin films. *Appl. Phys. Lett.*, 1992, **60**, 1430–1432.
13. Keve, E. T. and Bye, K. L., Phase identification and domain structure in PLZT ceramics. *J. Appl. Phys.*, 1975, **46**, 810–818.
14. McClune, W. F., ed., *Powder Diffraction File-Inorganic Phase*. International Centre for Diffraction Data, Swarthmore, 1986, File No. 29-777.
15. Cross, J. S., Fujiki, M., Tsukada, M., Kotaka, Y. and Goto, Y., Microstructure and electrical properties of chemical solution deposition (Pb,La)(Zr,Ti)O_3 thin films on Pt electrodes. *J. Mater. Res.*, 1999, **14**, 4366–4371.
16. Adachi, H., Mitsuyu, T., Yamazaki, O. and Wasa, K., Ferroelectric (Pb,La)(Zr,Ti)O_3 epitaxial thin films on sapphire grown by rf-planar magnetron sputtering. *J. Appl. Phys.*, 1986, **60**, 736–741.
17. Tyunina, M., Levoska, J., Sternberg, A. and Leppävuori, S., Relaxor behaviour of pulsed laser deposited ferroelectric $(Pb_{1-x}La_x)(Zr_{0.65}Ti_{0.35})O_3$ films. *J. Appl. Phys.*, 1998, **84**, 6800–6810.
18. Tang, X. G., Ding, A. L., Ye, Y. and Chen, W. X., Preparation and characterization of highly (111)-oriented (Pb,La)(Zr,Ti)O_3 thin films by sol–gel processing. *Thin solid films*, 2003, **423**, 13–17.
19. Vugmeister, B. E. and Rabitz, H., Dynamics of interacting clusters and dielectric response in relaxor ferroelectrics. *Phys. Rev. B*, 1998, **57**, 7581–7585.
20. Pirc, R. and Blinc, R., Spherical random-bond–random-field model of relaxor ferroelectrics. *Phys. Rev. B*, 1999, **60**, 13470–13478.