Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 34 (2008) 991–995

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Thickness effects on structures and electrical properties of lead zirconate titanate thick films

Peng Lin [*], Wei Ren, Xiaoqing Wu, Peng Shi, Xiaofeng Chen, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

Abstract

$PbZr_{0.52}Ti_{0.48}O_3$ thick films with thickness of 1–6 μm have been prepared by a polymer-assisted MOD process. The polymer, poly(vinyl acetate) (PVAc) was introduced into PZT precursor solutions. The grain size increased from 30 nm to 100 nm with an increase of the additive amount of PVAc. Meanwhile, the grains grew larger (in a range of 100–500 nm) and the surface of the films became rougher with increasing film thickness. This promotes the structural relaxation and prevents cracking formation. The critical thickness at which the film begins to crack increases significantly. The dielectric constant and remanent polarization (P_r) increased from 1070 to 1490 and from 36.1 μC/cm^2 to 52.4 μC/cm^2, respectively, and the coercive field (E_c) decreased from 57.3 kV/cm to 41.3 kV/cm as the film thickness increased from 0.95 μm to 6.02 μm. PZT thick films prepared in this study are promising materials for MEMS applications.

Keywords: C. Electrical properties; D. PZT films; MOD process; MEMS

1. Introduction

In recent years, the demands for miniaturized devices integrated with microelectronics have been increased significantly, which leads to great interest in the design and fabrication of micro-electromechanical systems (MEMS) [1–3]. Lead zirconate titanate (PZT) is an attractive material to be incorporated into MEMS due to its excellent electromechanical properties. Such devices often require crack-free films with thickness of 1–10 μm. But the films prepared by a conventional CSD process often show a low uncracking critical thickness. Recently, a polymer-assisted deposition (PAD) has been investigated to increase the critical thickness [4–7]. The polymers can help to achieve the desired viscosity of precursor solutions and function as binding agents to the metal precursors [8,9]. The reticulate structures in the precursor solutions suppress the condensation reaction and promote the structural and stress relaxation in the films during the thermal treatment, which makes it possible to deposit crack-free thick films.

In this work, we have investigated a metallo-organic compound decomposition (MOD) process modified by poly(vinyl acetate) (PVAc) to obtain 1–6 μm thick PZT films. The films are dense and crack-free, and the single-coating thickness can reach to 0.25 μm. The structure–property relationships of PZT films have been investigated with increasing thickness.

2. Experimental procedure

PZT thick films were prepared by a MOD process. The starting raw materials were lead acetate trihydrate, zirconium *n*-butoxide and titanium *n*-butoxide. 2-Ethoxyethanol was chosen as a solvent. The mole ratio of Zr/Ti was 52/48, and 20 mol% of excess lead was added to compensate lead loss during the thermal processing. PVAc powders with the molecular weight of 30,000–50,000 were dissolved in 2-ethoxyethanol. Then the PVAc solution was added into 1 M PZT precursor solution. The additive amount of PVAc was 2.5 g per 100 ml of PZT precursor solution. The mixed solution was heated to 120 °C for 50 min and then cooled down to room temperature. The 0.5 M PZT precursor solution without addition of PVAc was also prepared to be used as a reference solution.

The precursor solutions were spin-coated on Pt(1 1 1)/Ti/SiO_2/Si(1 1 1) substrates at 3000 rpm for 40 s. The wet films were thermally treated in a rapid thermal annealing (RTA) furnace (East Star RTP-500, China) in air at 500 °C for 10 min,

---

[*] Corresponding author.
E-mail address: linyilong@gmail.com (P. Lin).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2007.09.052

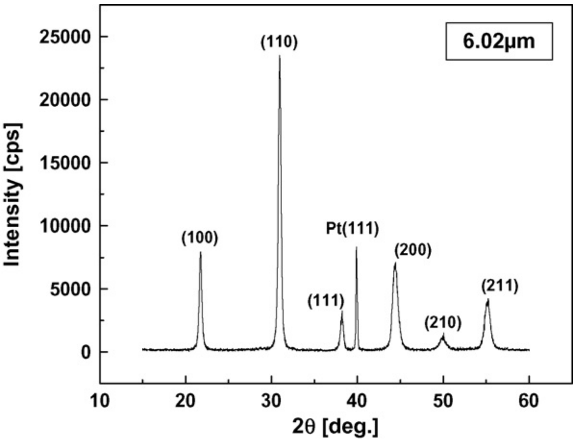

Fig. 1. XRD pattern of 6.02 μm thick PZT film.

and then were annealed at 700 °C for 3 min. The heating rate was kept at 50 °C/s from room temperature to 500 °C and from 500 °C to 700 °C. The coating-thermal treatment process was repeated until the required thickness was achieved. For example, the PZT film with a thickness of 6.02 μm were obtained after repeating the coating-thermal treatment process 24 times. PZT films with different thickness have been prepared and investigated. For electrical measurements, top Au electrodes of 1 mm in diameter were sputtered on the surfaces of the films via a shadow mask to get an Au/PZT/Pt sandwich structure.

Crystallizations of PZT films were investigated by a Rigaku D/MAX-2400 X-ray diffractometer (XRD). Surface and cross-section morphologies of the films were observed using a JEOL JSM-6700F field emission scanning electron microscope (FESEM). Dielectric properties were measured by an Agilent 4294A precision impedance analyzer. *P–E* hysteresis loops were determined by a Radiant WS0603-242 precision work-station with a HVI0702-228 precision high voltage interface.

3. Results and discussion

The PZT films prepared are all crystallized with the pure perovskite phase. XRD pattern of the sample with thickness of 6.02 μm is shown in Fig. 1. PZT thick films with PVAc modification have shown a random orientation with the strongest peak at <1 1 0> direction. This indicates that the influence of Pt(1 1 1) bottom electrode is weak in PZT thick films.

Fig. 2 shows the FESEM micrographs of the surfaces of PZT films. The thin film (0.41 μm in thickness) derived from the solution without PVAc is dense and the grain size is less than 30 nm, as shown in Fig. 2(a). The thick film (0.95 μm in thickness) derived from the PVAc-modified solution is dense and crack-free. The average grain size is around 100 nm, as shown in Fig. 2(b). The addition of PVAc in PZT precursor solutions leads to larger grain size of PZT films. It could be noted that when PVAc is introduced into PZT precursor solutions, it is hybridized with metalloxane polymers through the strong hydrogen bonding between C=O groups of PVAc and OH groups of the metalloxane polymers [10,11]. The reticulate structures suppress the condensation reaction and promote the structural relaxation in the PZT thick films during the thermal treatment. When PVAc-related organic compounds are decomposed, there is enough space for PZT to re-crystallize. So the grains grow larger in the PZT thick films with PVAc modification.

In order to investigate the effect of the film thickness on the structures and electrical properties, several film samples with thickness between 1–6 μm have been prepared. The thickness of single-coating layer can reach to 0.25 μm. The FESEM micrographs of the surfaces and cross-sections of PZT films are given in Fig. 3. The four film samples are 0.95 μm, 2.03 μm, 4.03 μm and 6.02 μm in thickness, respectively. From the surface micrographs, it can be seen that the grain sizes of PZT films become larger with film thickness. The grain size of PZT films increases from 100 nm to 500 nm as the film thickness increases from 0.95 μm to 6.02 μm. It indicates that the lower layers of PZT films may have a significant effect on the nucleation and crystallization of the topper layers. Since the PZT films were annealed at 700 °C to crystallize with a pure perovskite phase after each coating. The grains in the lower layers may be acted as the seed layers to promote the nucleation and crystallization of the topper layers. As a result, the grains grow larger with film thickness. At the same time, the surface of the films becomes rougher with increasing thickness, which is caused by the decomposition of the PVAc-related organic compounds during the thermal treatment. This promotes the structural relaxation and prevents the cracking formation. The critical thickness at which the film begins to crack increases significantly.

Dielectric and ferroelectric properties of the PZT films have been investigated as a function of thickness. Dielectric

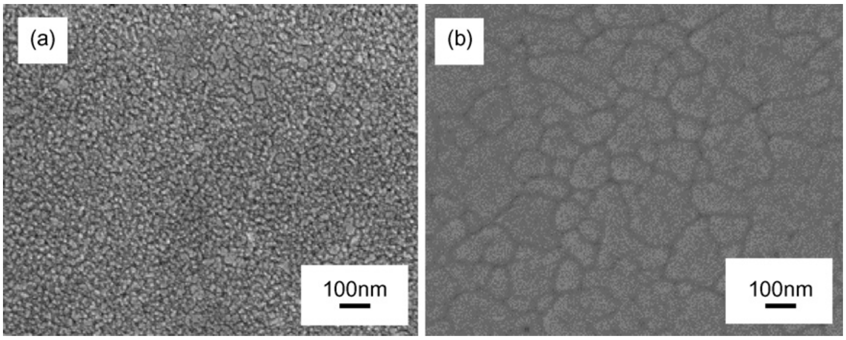

Fig. 2. FESEM micrographs of the surfaces of PZT films: (a) without PVAc modification; (b) with PVAc modification.

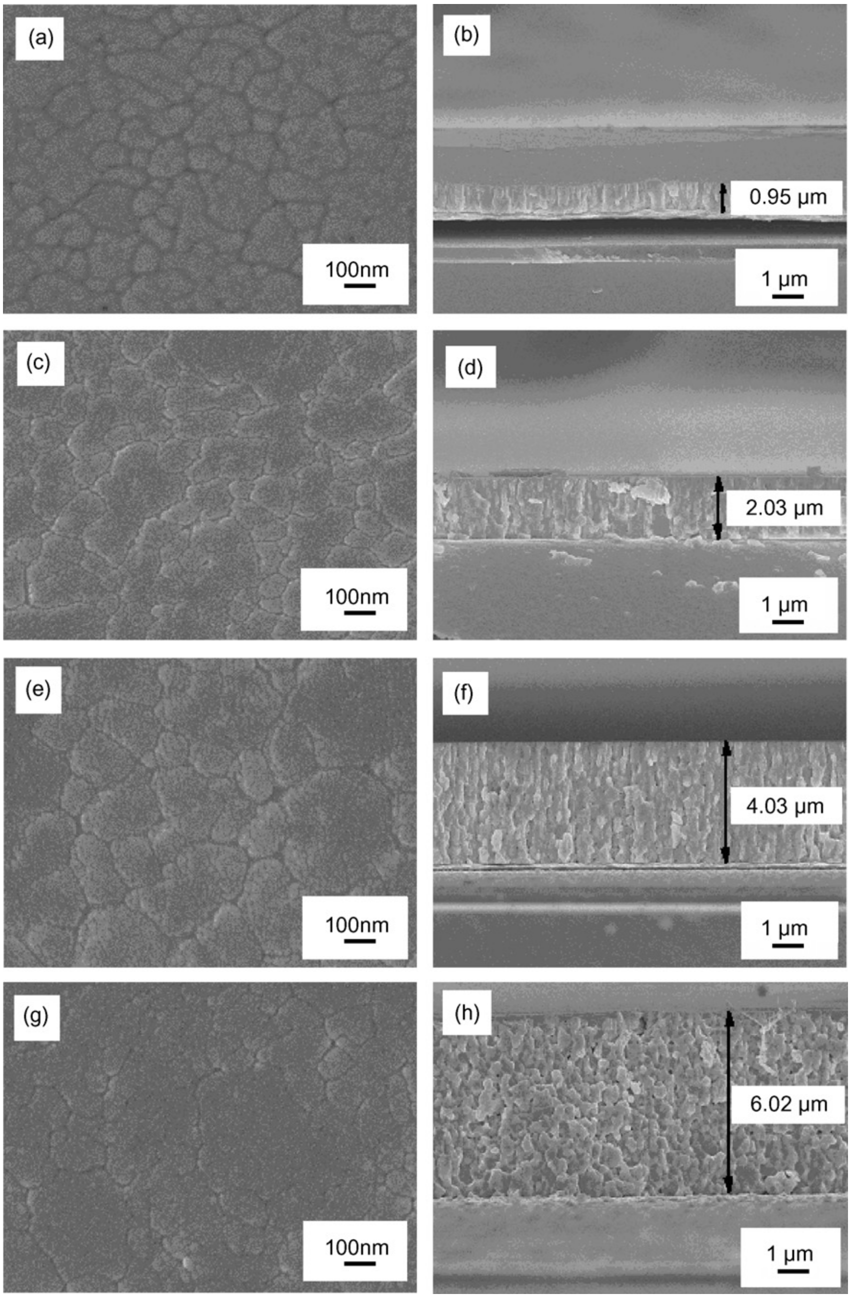

Fig. 3. FESEM micrographs of the surfaces and cross-sections of PZT films.

properties were measured in a frequency range from 100 Hz to 100 kHz, as shown in Fig. 4. With the increase of frequency, the dielectric constant decreases and the dielectric loss increases. Thickness dependence of the dielectric constant and loss tangent at 1 kHz is shown in Fig. 5. The dielectric constant increases from 1070 to 1490 as the film thickness increases from 0.95 μm to 6.02 μm, while the dielectric loss varies little with thickness and is in a range of 0.03–0.04 at 1 kHz. Fig. 6 shows a *P*–*E* hysteresis loop of the PZT film with a thickness of 6.02 μm. Remanent polarization (P_r) and coercive field (E_c) of the sample are 52.4 μC/cm^2 and 41.3 kV/cm, respectively. With the increase of the film thickness from 0.95 μm to 6.02 μm, P_r increases from 36.1 μC/cm^2 to 52.4 μC/cm^2, while E_c decreases from 57.3 kV/cm to 41.3 kV/cm, as shown in Fig. 7. As has been demonstrated by Xu et al. [12], there are both intrinsic and extrinsic contributions to the dielectric and ferroelectric responses in the PZT bulk ceramics. But for the PZT films, there are intrinsic contributions to the dielectric and ferroelectric properties for all films with different thicknesses, grain sizes and preferential orientations. Meanwhile, the extrinsic contributions have been seriously confined in the thin PZT films due to the pinning of the domain walls and begin to increase with thickness after a critical thickness. So we can deduce that the domain wall density becomes larger and the domain wall pinning becomes less with increasing film thickness and grain size in our PZT thick films. As a result,

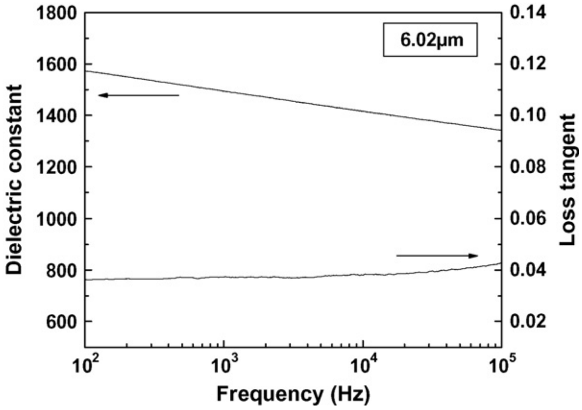

Fig. 4. Frequency dependence of dielectric constant and loss tangent of 6.02 μm thick PZT film.

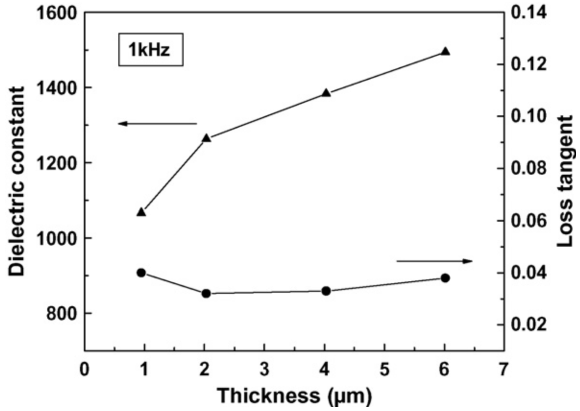

Fig. 5. Thickness dependence of dielectric constant and loss tangent of PZT films.

the domain wall motions become easier, leading to the increase of the dielectric constant and remanent polarization and the decrease of the coercive field. It can be seen from Figs. 4–7 that PZT thick films prepared from PVAc-modified solutions exhibit excellent dielectric and ferroelectric properties, which are promising materials for MEMS applications.

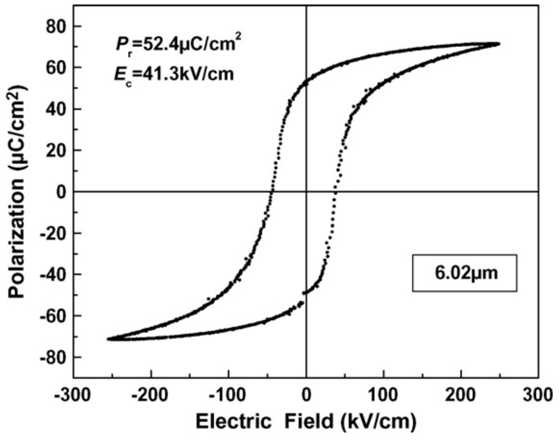

Fig. 6. P–E hysteresis loop of 6.02 μm thick PZT film.

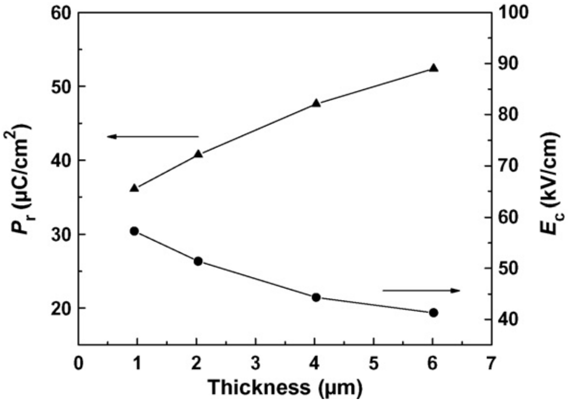

Fig. 7. Thickness dependence of P_r and E_c of PZT films.

4. Conclusions

PZT thick films with thickness of 1–6 μm have been prepared by the repeated deposition via a PVAc-assisted MOD process. The films are dense and crack-free, and the single-coating thickness can reach to 0.25 μm. The grain size increases from 30 nm to 100 nm after the addition of PVAc in PZT precursor solutions. At the same time, the grains grow larger (in a range of 100–500 nm) and the surface of the films becomes rougher with increasing film thickness. This promotes the structural relaxation and prevents the cracking formation. The critical thickness at which the film begins to crack increases significantly. With increasing film thickness and grain size, the dielectric constant and remanent polarization increase from 1070 to 1490 and 6.1 μC/cm^2 to 52.4 μC/cm^2, respectively. The coercive field decreases from 57.3 kV/cm to 41.3 kV/cm.

Acknowledgments

This work is supported by the Natural Science Foundation of China (Grant Nos. 60377035 and 50572086).

References

[1] J.J. Bernstein, S.L. Finberg, K. Houston, L.C. Niles, H.D. Chen, L.E. Cross, K.K. Li, K. Udayakumar, Micromachined high frequency ferroelectric sonar transducers, ieee transactions on ultrasonics, Ferroelectr. Freq. Control 44 (5) (1997) 960–969.

[2] P. Muralt, M. Kohli, T. Maeder, A. Kolkin, K. Brooks, N. Setter, R. Luthier, Fabrication and characterization of PZT thin-film vibrators for micromotors, Sens. Actuators A 48 (1995) 157–165.

[3] Y. Nemirovsky, A. Nemirovsky, P. Muralt, N. Setter, Design of a novel thin-film piezoelectric accelerometer, Sens. Actuators A 56 (1996) 239–249.

[4] G.T. Park, J.J. Choi, C.S. Park, J.W. Lee, H.E. Kim, Piezoelectric and ferroelectric properties of 1-μm-thick lead zirconate titanate film fabricated by a double-spin-coating process, Appl. Phys. Lett. 85 (12) (2004) 2322–2324.

[5] S. Takenaka, H. Kozuka, Sol–gel preparation of single-layer, 0.75 μm thick lead zirconate titanate films from lead nitrate-titanium and zirconium alkoxide solutions containing polyvinylpyrrolidone, Appl. Phys. Lett. 79 (21) (2001) 3485–3487.

[6] H. Kozuka, S. Takenaka, Single-step deposition of gel-derived lead zirconate titanate films: critical thickness and gel film to ceramic film conversion, J. Am. Ceram. Soc. 85 (11) (2002) 2696–2702.

[7] H. Kozuka, S. Takenaka, H. Tokita, M. Okubayashi, PVP-assisted sol–gel deposition of single layer ferroelectric thin films over submicron or micron in thickness, J. Eur. Ceram. Soc. 24 (2004) 1585–1588.

[8] Q.X. Jia, T.M. Mccleskey, A.K. Burrell, Y. Lin, G.E. Collis, H. Wang, A.D.Q. Li, S.R. Foltyn, Polymer-assisted deposition of metal-oxide films, Nat. Mater. 3 (2004) 529–532.

[9] K. Yao, S.H. Yu, F.E.H. Tay, Preparation of perovskite $Pb(Zn_{1/3}Nb_{2/3})O_3$-based thin films from polymer-modified solution precursors, Appl. Phys. Lett. 88 (2006) 052904.

[10] H. Kozuka, M. Kajimura, Single-step dip coating of crack-free $BaTiO_3$ films >1 μm thick: effect of poly(vinylpyrrolidone) on critical thickness, J. Am. Ceram. Soc. 83 (5) (2000) 1056–1062.

[11] H. Kozuka, M. Kajimura, T. Hirano, K. Katayama, Crack-free thick ceramic coating films via non-repetitive dip-coating using polyvinylpyrrolidone as stress-relaxing agent, J. Sol–Gel Sci. Technol. 19 (2000) 205–209.

[12] F. Xu, S. Trolier-McKinstry, W. Ren, B.M. Xu, Z.-L. Xie, K.J. Hemker, Domain wall motion and its contribution to the dielectric and piezoelectric properties of lead zirconate titanate films, J. Appl. Phys. 89 (2) (2001) 1336–1348.