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Microstructural investigation of the PZT films prepared from the suspension of nanocrystalline powders

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Abstract

PZT thin films of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ were prepared by a novel method from the suspension of nanocrystalline PZT powders. The powders were obtained by mechanochemical synthesis. Films were deposited on silicon (1 0 0) and platinum covered silicon substrates (Pt (1 1 1) /Ti/SiO_2/Si) using spin-on technique. Substrate type has influence on films crystallinity, orientation and can react with the films changing its phase composition. Films microstructure strongly depends on thermal treatment conditions due to phase and compositional changes of the films.

Keywords: Films; Microstructure-final; PZT; Suspension

1. Introduction

Among large number of different ferroelectric materials, Pb-containing materials, such as PMN, PZT, PLZT, PZN, were proved as very important, because of their excellent dielectric and electrostrictive properties.[1] Most of ferroelectric compositions obtained in bulk form were also produced in thin- or thick-film form by several methods. Coating methods, such as dip-coating, spin-on, and spray-on, showed great advantages, because of excellent compositional control, as well as because of low cost.[1] Spin-on method could be used in the preparation of homogeneous films from the solutions and suspensions.[2–6]

Major concerns in synthesizing Pb-based ferroelectrics are the maintaining of chemical stoichiometry and elimination of the undesirable pyrochlore phases.[7–9] Possible solution of the problem is in the application of mechanochemical synthesis that decreases the temperature of thermal treatment, skip multiple steps of calcination at elevated temperatures and also enables obtaining of nanocrystalline powders, which could be further used to prepare suspension. Mechanochemical synthesis refers to solid–solid reactions initiated by intensive milling in high-energy ball mills. Mechanochemical synthesis increases the area of contact between the reactant powder particles due to reduction in particle size and allows fresh surfaces to come into contact. This allows the reaction to proceed without the necessity for diffusion through the product layer. As a consequence, reactions will occur at lower temperatures during mechanochemical synthesis without any externally applied heat.

In this work we report results of microstructural investigation of the thin PZT films prepared by deposition of the suspension of nanocrystalline powders on different substrates and at different temperatures. The main idea was to prepare films without chemical reaction on the substrate surface. PZT of desired composition was previously synthesized and only deposited on the substrate from the appropriate suspension. The thermal treatment is necessary only to remove solvents and achieve homogeneous microstructure. The proposed preparation method could not be only used in the preparation of PZT films, but also in the preparation of films composed by different materials.

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2. Experimental

The PZT composition selected for this study was $Pb(Zr_{0.52}Ti_{0.48})O_3$, which is near the morphotropic phase boundary. The starting materials were commercially available PbO, ZrO_2 and TiO_2, all of $>99.9\%$ purity. According to the chemical formula of the desired PZT ceramics, appropriate amounts of starting oxides (13.71 g PbO, 3.936 g ZrO_2 and 2.356 g TiO_2) were weighed, mixed and further milled in planetary ball mill (Fritsch). Milling conditions were the following: stainless steel jars (jars volume-$V=500$ cm^3) and balls (balls diameter-$d=13.4$ mm), ball-to-powder weight ratio was 40:1, air atmosphere, basic disc rotation speed was 317 min^{-1}, rotation speed of disc with jars was 396 min^{-1}, milling time was 2 h.

Stable suspension that was used in preparation of thin films was prepared by the following procedure: suspension of 2 wt.% of the mechanochemically synthesized PZT powder was prepared by suspending appropriate amount of the PZT powder in 10 cm^3 of ethylene glycol. The suspension was filtered through the glass filter (ASTM 10-15 M, model: Pyrex No. 36060). Further, appropriate amount of citric acid was dissolved to adjust the suspension viscosity at 20 mPa s (Brookfield viscosimeter). The prepared suspension was precipitate free. The suspension was deposited on silicon (1 0 0) or platinum (Pt (1 1 1) /Ti/SiO_2/Si) substrates using spin-on technique. The spinning rate was 3000 rpm during 60 s. Substrates were coated with five layers. After each coating the films were thermally treated: the films were slowly heated (1 °C/min) up to 300 °C, then heated at 300 °C for 1 h and finally rapidly heated (20 °C/min) up to final temperatures, at which remained for 30 min. Final temperatures of thermal treatment were 600–800 °C. Films were slowly cooled to prevent crack formation. The formation of the PZT films was confirmed by X-ray analysis. Grain size and morphology were examined by AFM analysis (Digital Instruments IIIa). Film thickness was determined with ellipsometer (Rudolph/Auto El Technologies, Inc.)

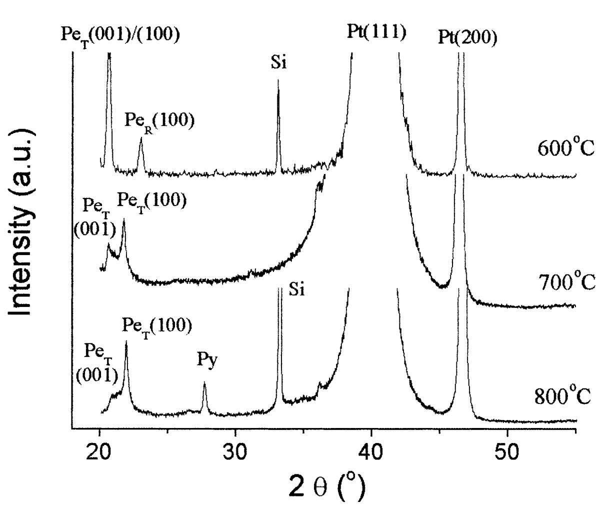

Fig. 1. X-ray diffractograms of the PZT films deposited on Pt substrates and thermally treated at different temperatures (Pe_T—tetragonal perovskite phase, Pe_R—rombohedral perovskite phase, Py—pyrochlore, Si—silicon, Pt—platinum).

3. Results and discussion

3.1. Powder properties

Phase evolution during mechanochemical synthesis of PZT was monitored and explained in our previous investigation.[10] These results, as well as results of powder characterization, will be briefly reviewed here. Powders milled for 2 h contained pure perovskite phase. Obtained PZT powders are agglomerated with wide distribution of agglomerates size ranging from 1 to 10 μm. Inside the agglomerates it is possible to see very small individual particles of submicron size. The mean crystallite size of PZT powder was calculated from

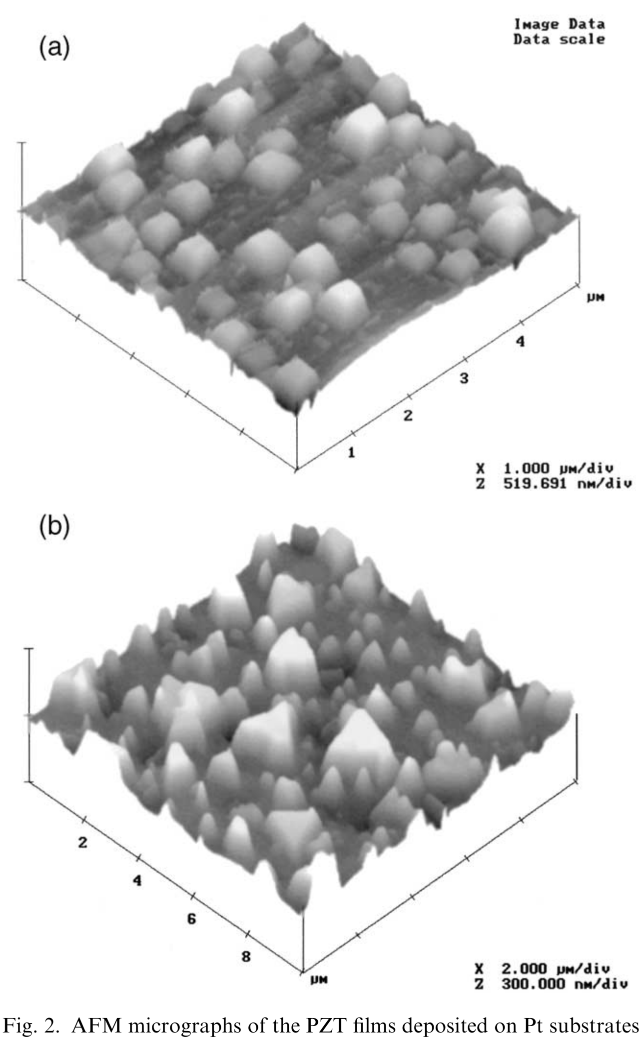

Fig. 2. AFM micrographs of the PZT films deposited on Pt substrates and thermally treated at (a) 600 °C and (b) 800 °C.

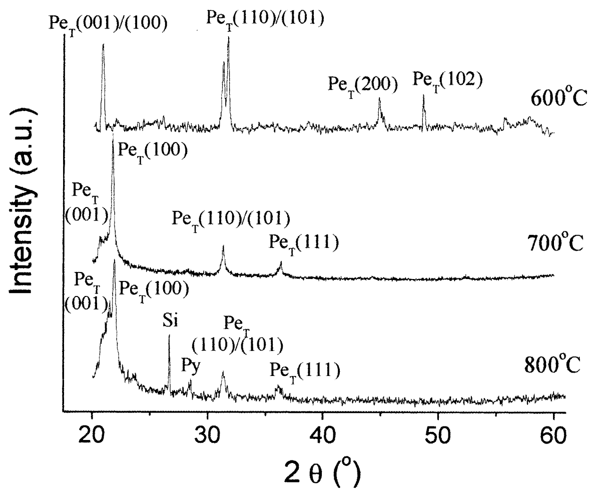

Fig. 3. X-ray diffractograms of the PZT films deposited on Si substrates and thermally treated at different temperatures (Pe_T—tetragonal perovskite phase, Py—pyrochlore, Si—silicon).

HR-TEM photographs and it was found that is in the approximate 15 nm.

3.2. Film properties

It is well known that crystallinity and morphology of the films strongly depend on the conditions of the thermal treatment, as well as on type of substrates. According to X-ray diffraction patterns of the prepared PZT films, the well-crystallized PZT film was formed at 600 °C on Pt substrates (Fig. 1). PZT film deposited at 600 °C showed coexistence of tetragonal and rhombohedral phases. Microstructural analysis showed that the film was made of cubic grains with mean grain size of 250 nm (Fig. 2). Films were very rough (rms roughness was 57 nm). When the temperature of thermal treatment was increased to 700 °C it was not possible to identify rhombohedral phase anymore and only the presence of tetragonal phase was confirmed with well-separated peaks (0 0 1) and (1 0 0). Finally, when the temperature

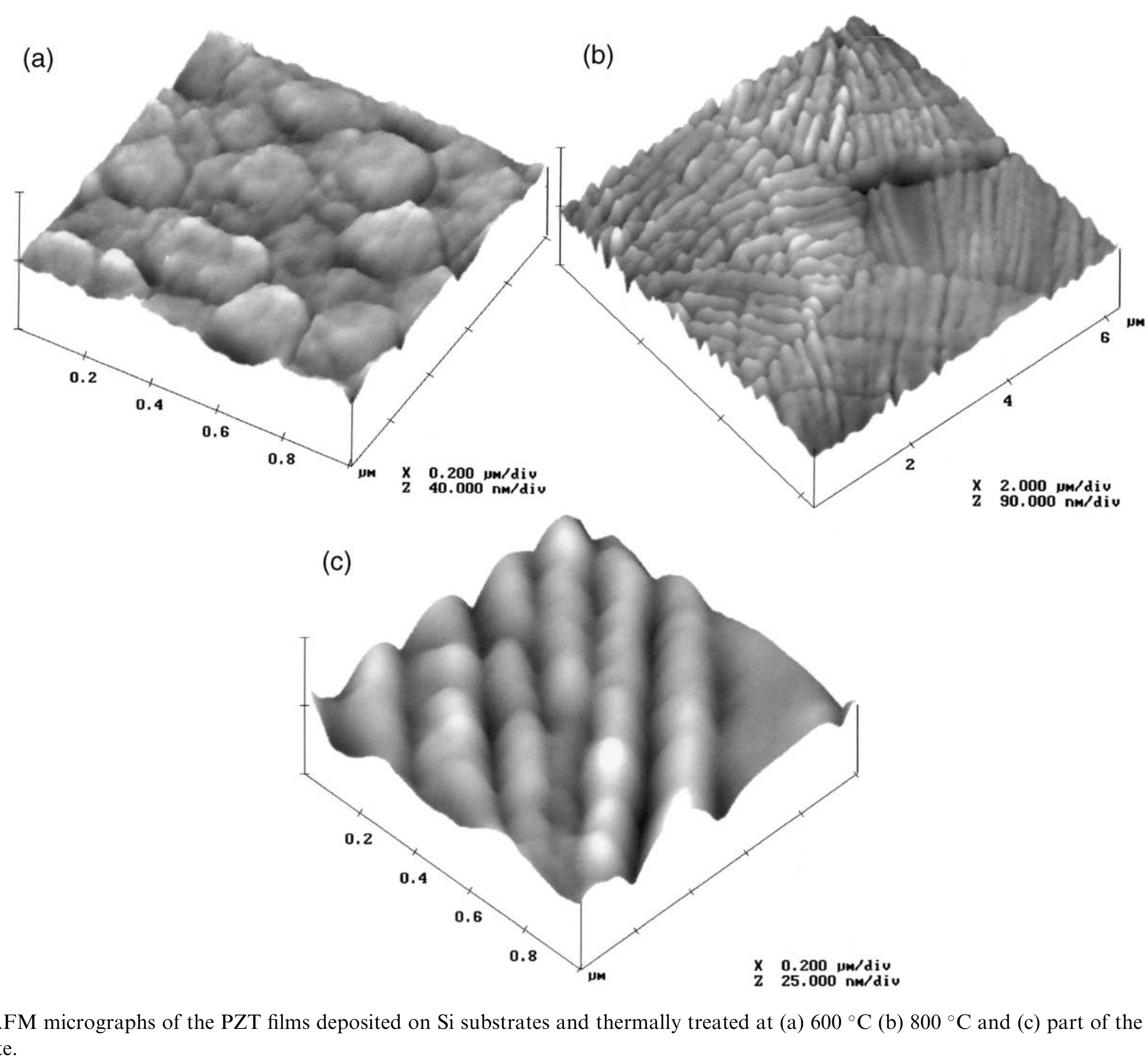

Fig. 4. AFM micrographs of the PZT films deposited on Si substrates and thermally treated at (a) 600 °C (b) 800 °C and (c) part of the film inside the rosette.

was increased to 800 °C X-ray diffraction analysis showed the presence of pyrochlore besides the perovskite phase. Grain morphology was changed again and the coexistence of different grain shapes was found: triangular, cubic and prismatic (Fig. 2). The films are still very rough: rms roughness was 55 nm.

The high roughness of the films, grains of different morphologies, as well as the presence of grain agglomerates, suggested that this method was not successful in preparation of homogeneous, single-phase PZT films on Pt substrates. It was supposed that at higher temperatures chemical interaction between Pt and PZT films led to decomposition of PZT and formation of separate phases with different chemical and structural properties, since there is evidence for existence of such a reaction in literature.[11]

Films deposited at Si substrate at 600 °C showed the existence of the well-crystallized tetragonal perovskite phase (Fig. 3). After increase of temperature to 700 °C the films are single phase and still well-crystallized, but further increase to 800 °C resulted in peak broadening and decrease in peak intensities suggesting decrease in films crystallinity. Also peaks of pyrochlore phase appeared, because of interaction between substrate and PZT films. According to microstructural analysis the films deposited on Si substrates were dense (without pores), with homogeneous grain size, crack-free and very smooth (Fig. 4). The film thickness was about 200 nm for the films containing five layers of PZT. Spherical grains sized about 150–200 nm, observed in the films treated at 600 °C, could be also interpreted as agglomerates of smaller particles sized about 50 nm. There is no significant difference in grains shapes of the films thermally treated at 600 and 700 °C, only lower values of roughness were registered. Films deposited at 700 °C are very smooth with mean roughness of 2 nm, lower in comparison to the films deposited at 600 °C that showed rms roughness of 5 nm. The films treated at 800 °C showed completely different grain morphologies. AFM analysis showed typical rosette structure for PZT films treated at high temperature,[12] containing pyrochlore phase[13] (Fig. 4b). It is possible to recognize separated rosettes that are disoriented one to another. The high magnification of the rosettes could give false picture of highly oriented film (Fig. 4c), but actually, overall microstructure is inhomogeneous and anisotropic because of the presence of rosettes.

4. Conclusions

PZT thin films of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ were successfully prepared by a novel method from the suspension of nanocrystalline PZT powders. The totally different characteristics, structural and microstructural, were obtained depending on type of substrate. Films deposited on Pt substrates were rough and inhomogeneous, with large grains and grains agglomerates. The films deposited at Si (1 0 0) substrates were homogeneous, dense, smooth and with uniform grain size. Thermal treatment at temperatures higher than 700 °C results in film decomposition and appearance of undesirable pyrochlore phase.

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References

1. Haertling, G. H., Ferroelectric ceramics: history and technology. *J. Am. Ceram. Soc.*, 1999, **82**, 797–818.
2. Wan, D. M., Xue, J. M. and Wang, J., Synthesis of single phase $0.9Pb[(Zn_{0.6}Mg_{0.4})_{1/3}\ Nb_{2/3}O_3]–0.1PbTiO_3$ by mechanically activating mixed oxides. *Acta Mater.*, 1999, **47**, 2283–2291.
3. Xu, B., Cross, L. E. and Ravichandran, D., Synthesis of lead zirconate titanate stannate antiferroelectric thick films by sol-gel processing. *J. Am. Ceram. Soc.*, 1999, **82**, 306–312.
4. Ohya, Y., Saiki, H., Tanaka, T. and Takahashi, Y., Microstructure of TiO_2 and ZnO films fabricated by the sol-gel method. *J. Am. Ceram. Soc.*, 1996, **79**, 825–830.
5. Chen, S. Y. and Chen, I. W., Cracking during pyrolysis of oxide thin-films—phenomenology, mechanisms, and mechanics. *J. Am. Ceram. Soc.*, 1995, **78**, 2929–2939.
6. Abe, R., Ikeda, S., Kondo, J. N., Hara, M. and Domen, K., Novel methods for preparation of ion-exchangeable thin films. *Thin Solid Films*, 1999, **343–344**, 156–159.
7. Lee, S. E., Xue, J. M., Wan, D. M. and Wang, J., Effects of mechanical activation on the sintering and dielectric properties of oxide-derived PZT. *Acta Mater.*, 1999, **47**, 2633–2639.
8. Xue, J. M., Wan, D. M. and Wang, J., Mechanochemical synthesis of nanosized lead titanate powders from mixed oxides. *Mater. Lett.*, 1999, **39**, 364–369.
9. Wang, J., Junmin, X., Dongmei, W. and Beng, Ng Wei, Mechanochemically synthesized lead magnesium niobate. *J. Am. Ceram. Soc.*, 1999, **82**, 1358–1360.
10. Branković, Z., Branković, G., Jovalekić, C., Cilense, M. and Varela, J.A., Mechanochemical synthesis of PZT powders. *Mat. Sci. and Eng. A*, 2003, **345**, 243–248.
11. Fè, L., Vasiliu, F., Norga, G. J., Wouters, D. J. and Van der Biest, O., Effect of crystallization ambient on orientation selection in sol-gel derived $Pb(Zr,Ti)O_3$ thin films on Pt electrode layers. *Key Engineering Materials*, 2002, **206–213**, 1259–1262.
12. Hwang, K. S., Manabe, T., Nagahama, T., Ymaguchi, I., Kumagai, T. and Mizuta, S., Effect of substrate material on the crystallinity and epitaxy of $Pb(Zr,Ti)O_3$ thin films. *Thin Solid Films*, 1999, **347**, 106–111.
13. Song, Z. and Lin, C., Microstructure and electrical properties of $PbZr_{0.48}Ti_{0.52}O_3$ ferroelectric films on different Pt bottom electrodes. *Appl. Surf. Sci.*, 2000, **158**, 21–27.