Journal of the European Ceramic Society **19** (1999) 1453–1456

PII: S0955-2219(98)00448-8
0955-2219/99/$ - see front matter

Preparation of PZT, PLZT and $Bi_4Ti_3O_{12}$ Thin Films from Oxide Precursors

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Abstract

This work describes a method for preparation of ferroelectric thin films based on a pre-calcination of oxides, to be used as precursor material for a solution preparation. In order to show the viability of the proposed method PZT, PLZT and $Bi_4Ti_3O_{12}$ thin films were prepared. The results were analyzed by X-ray diffraction, scanning electron microscopy and Rutherford backscattering spectroscopy. PZT film shows a coexistence of tetragonal (lattice constant a = *4·02 Å and* c = *4·16 Å) and rhombohedral (*a = *4·13 Å) phases. For PLZT, lattice constant* a *was estimated for pseudocubic phase to be found 4·12 Å. The lattice constant* a, b *and* c *to $Bi_4Ti_3O_{12}$ film (orthorhombic symmetry) obtained were 5·58, 5·53 and 33·67 Å, respectively. The films obtained shown good quality, homogeneity and the desired stoichiometry. Estimated thickness for one layer was approximately 1000 and 1300 Å for BIT and PZT films, respectively.* © *1999 Elsevier Science Limited. All rights reserved*

Keywords: titanates, films, perovskites.

1 Introduction

Several researchers have used solid or solution deposition techniques to produce thin films. Solution depositions are normally cheaper and enable better stoichiometric control of complex mixed oxides than other physical techniques such as RF sputter deposition and laser ablation[1] or chemical vapor deposition (CVD).[2] One of the difficulty of the physical methods, RF sputter or laser ablation for example, is that the film composition does not coincide with that of the target for complex compositions. The most frequently used solution–preparation approaches may be grouped into three categories: sol–gel process that uses alkoxide compounds as starting precursors,[3] hybrid processes that use chelating agents such acetic acid[4] and metalorganic decomposition (MOD) that uses large water insensitive carboxylate compounds.[5] Metalorganic starting reagents such as alkoxide [$M(OR)_n$ where M is a metal and R is an alkyl group] and carboxylate [$M(OOCR)_n$] are employed to prepare the solution for film deposition. As a limitation of these methods can be pointed out the difficulty to obtain the precursor reagents and sometimes the low stability of complex solution.

In recent years, considerable attention has been devoted to the development of thin film technology of ferroelectric materials,[1,6] with a view toward the increasing of applications possibilities in many electronic and optical devices. The ceramic compositions most studied for films preparation are the same as those well established for bulk ferroelectric ceramics, which normally have a complex composition. Large-scale processing of high-quality thin films requires low-temperature synthesis, high reproducibility, simplicity in all processing steps and low cost.

Due to this fact the search for new routes for film preparation remains an interesting and open subject in order to improve the stability of complex solutions, the control of the stoichiometry of the film composition or to reduce the cost of the process.

This work describes an alternative solution method for preparation ferroelectric thin films starting from pre-calcination of oxides or carbonates. The proposed method is applied in the processing of lead zirconate titanate ($PbZr_{0.53}Ti_{0.47}O_3$-PZT), lanthanum lead zirconate titanate [$(Pb_{0.91}La_{0.09})(Zr_{0.65}Ti_{0.35}O_3)$-PLZT], and bismuth titanate ($Bi_4Ti_3O_{12}$-BIT) thin films. The method is based on the fact that not all precursor oxides (PbO, TiO_2, ZrO_2 or Bi_2O_3) are soluble in acid media, but a reacted oxide may be soluble. In a

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very recently paper was verified the viability of this method applied to PZT films.[7]

X-ray diffraction (XRD), scanning electron microscopy (SEM) and infrared (IR) and Rutherford backscattering spectroscopy (RBS) characterization were used to evaluate the efficiency of the method and to compare the film quality to those of films obtained through other methods.

2 Experimental

It is well know that some oxides and carbonates may be not soluble in acid but a complex oxide, formed by the reaction of these insoluble oxides, may be. For example, while lead oxide (PbO) and bismuth oxide (Bi_2O_3) are soluble, while titanium oxide (TiO_2) and zirconium oxide (ZrO_2) are only slightly soluble in acid media, PZT and BIT are soluble in HNO_3 and HCl acid, respectively. This fact was used in this work to produce the ions solution, instead to use the conventional metalorganic or alkoxide precursors, as starting materials for production of thin films.

To produce the solution containing the desired ions, PZT, PLZT and BIT powders were previously prepared by conventional mixed oxide method. For preparation of the PZT, PLZT and BIT powders were used as precursors lead oxide (PbO), titanium oxide (TiO_2), zirconium oxide (ZrO_2), lanthanum oxide (La_2O_3) and bismuth oxide (Bi_2O_3). These oxides were mixed in appropriate proportion, Zr/Ti = 53/47 for PZT and La/Zr/Ti = 9/65/35 for PLZT, using a ball mill during 4 h. All mixed powders were calcined at 850°C for 3·5 h in an electric furnace using oxidant atmosphere. Under these conditions full reacted PZT, PLZT and BIT powders were obtained. It is interesting to observe that this procedure is the same used to obtain powders to prepare ceramic bodies. Here, these powders were used to produce thin films through the proposed method (described in follow).

2.1 Preparation of the stock solution

Using 2 g of each powder, the stock solution was prepared by dissolution of the powders in acid solution. For dissolution of PZT, powder was used a solution with 10% of nitric acid (HNO_3) and 90% of distilled water while PLZT powder was dissolved in a solution formed by 30% of HNO_3 and 70% of distilled water. BIT powder was dissolved in a solution of the 30% of concentrated chloridric acid (HCl) and 70% of ethanol. Heating the solution up to around 80°C for 1 h the dissolution was optimized.

The final solubility of the PZT, PLZT and BIT was 12·5, 32·3 and 20·5 g l^{-1}, respectively. All ions solutions were clear and transparent, what signify that all elements were dissolved.

2.2 Preparation of the polymeric resin and film deposition

The general idea to deposit a film on a substrate is to distribute the ions atomistically throughout the polymeric resin, whose preparation was based on the Pechini method.[8,9] The process calls for forming a chelate between dissolved ions with a hydroxycarboxylic acid (citric acid). Heating the resin in air causes a breakdown of the polymer. Subsequently, the ions are oxidized to form desired crystalline phases.

To obtain the resin, citric acid and ethylene glycol (citric acid/ethylene glycol = 44/56 in mol%) were mixed with 50 ml from each stock solution. The mixture was heated at 90°C for 1 h, when transparent resins were obtained. Films of the resins (PZT, PLZT or BIT) were deposited at room temperature on fused quartz and Si substrates by dip coating. The as deposited films were previously heated on a hot plate before they were submitted to a heat treatment for crystallization. Deposited films were crack-free, uniform and well adhered on mentioned substrates.

2.3 Characterization of the films

The structure of the annealed film was examined by X-ray diffraction (XRD) analysis, using a Rigaku X-ray diffractometer with CuK_α radiation. Scanning electron microscopy (SEM–JEOL 5800LV) was used to study the surface morphology of the films. The stoichoimetry and thickness of the films were investigated using Rutherford backscattering (RBS) for an energy of the 2 MeV and a normal angle of incidence of the He^+ beam. All characterizations were carried out at room temperature.

3 Results and Discussion

The as deposited amorphous films were annealed at temperatures between 600 and 700°C for crystallization. Figure 1 shows the XRD pattern of PZT, PLZT and BIT films, deposited on fused quartz, Si and Pt/Si substrates and annealed at 2·5 h. Figure 1(A) shows the co-existence of a tetragonal and a rhombohedral phases for PZT film, deposited on fused quartz. The lattice constants a and c of PZT were calculated for tetragonal phase using the (101), (111) and (200) peaks and were found to be 4·02 and 4·16 Å ($c/a = 1{\cdot}03$), respectively. For the rhombohedral phase we used the (100), (101) and (111) peaks and obtained $a = 4{\cdot}13$ Å and $90° - \alpha = 0{\cdot}03°$. This result agrees

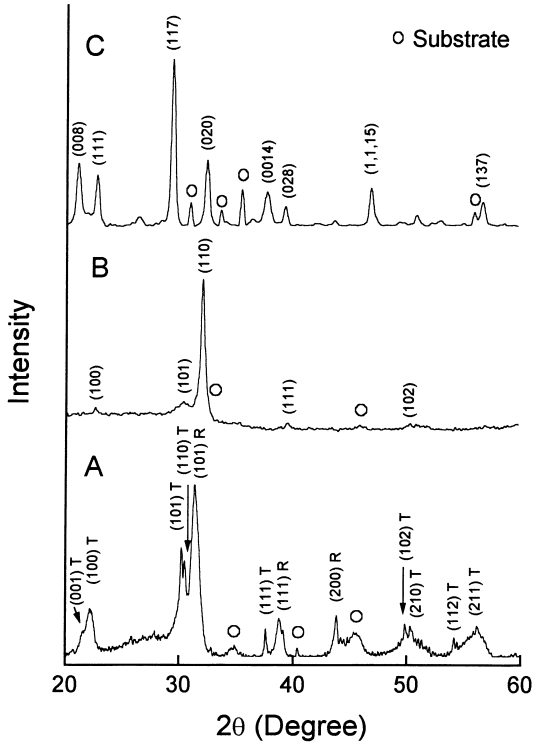

Fig. 1. X-ray diffraction pattern at room temperature for (A): PZT (53/47) film deposited on fused quartz, annealed at 600°C for 2·5 h, (B): PLZT (9/65/35) film deposited on Pt/Si substrate, annealed at 700°C for 2·5 h and (C): BIT film deposited on Si substrate, annealed at 700°C for 2·5 h.

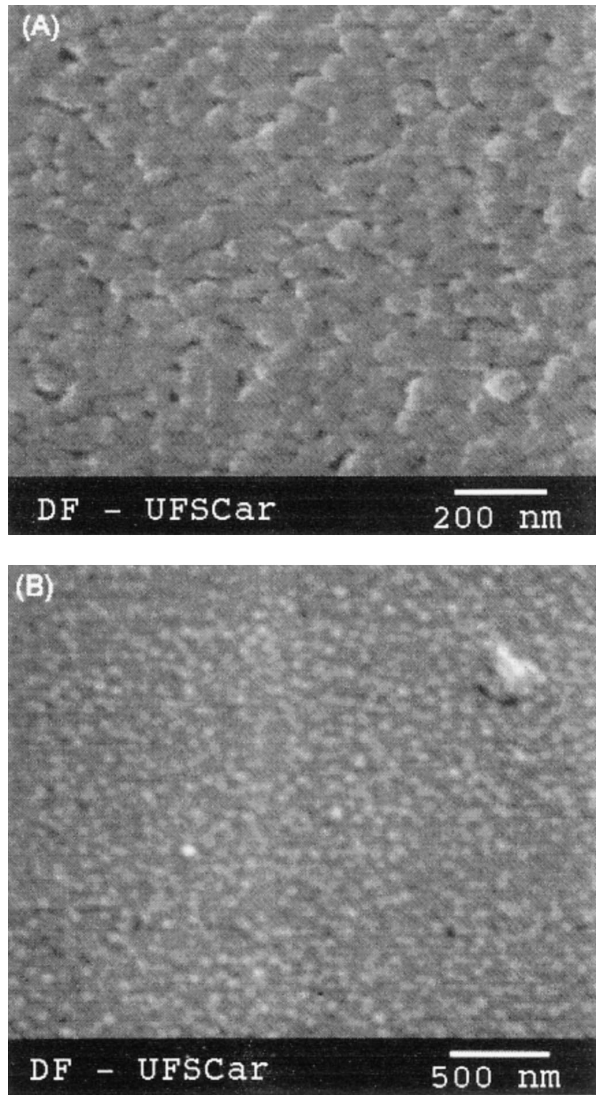

Fig. 2. SEM photography of (A) BIT film deposited on Si and (B) PLZT film (B) deposited on Pt/Si substrate. Both films were annealed in air at 700°C for 2·5 h.

with others observations for PZT thin films, prepared by sol–gel technique,[1] with the same nominal composition.

Figure 1(B) shows the XRD pattern of PLZT film deposited on Pt/Si substrate. In this figure was identified the presence of the PLZT structure. The lattice constant *a* of pseudocubic PLZT film was calculated from (100), (111) and (102) peaks of the XRD to be found 4·12 Å. PLZT film (9/65/35) crystallized on Pt/Si showed a strong (110) preferred orientation in the XRD pattern [Fig. 1(B)]. The preferential orientation of the films depends of the type of substrate used. Similar preferred orientation was obtained recently using $LaNiO_3$/Si and Si_3N_4-coated substrates[10,11] at PLZT films. The result obtained in this work agrees with results for PLZT thin films obtained by others using Pt/Ti/SiO_2/Si substrates.[12] Finally, Fig. 1(C) shows the XRD pattern of BIT film on Si substrate. Full crystallized $Bi_4Ti_3O_{12}$ film without preferential orientation was obtained at 700°C. The calculated lattice constants *a*, *b* and *c* of $Bi_4Ti_3O_{12}$ considering an orthorhombic symmetry and using the (008), (111), (117) and (020) peaks were found to be 5·58, 5·53 and 33·67 Å, respectively.

Figure 2(A) and (B) shows a SEM for BIT and PLZT, respectively. These films were crystallized at 700°C for 2·5 h. The average grain size was estimated to be 76 nm for both films. These micrograph shows good homogeneity and morphology similar with those arising from films prepared by sol–gel technique,[13] for example.

Figure 3 shows a typical RBS spectra for one layer PZT thin film. In this figure, dots represent experimental points while the continuous line represents the simulation for PZT on Si using the RUMP program.[14] The values obtained from the simulation were around 1300 Å for the film thickness and a zirconium to titanium ratio of 53·8/46·2 indicating a value very close to that of the nominal composition. This Zr/Ti ratio confirms that the deposited film had the same nominal composition of the PZT powder, dissolved in acid solution. Similar analysis were made for BIT film (no presented). Through the simulation, estimated thickness was around 1000 Å and a titanium to bismuth ratio of 0·36/0·48 were obtained. Also in this case the Ti/Bi ratio agrees very well with the desired nominal composition.

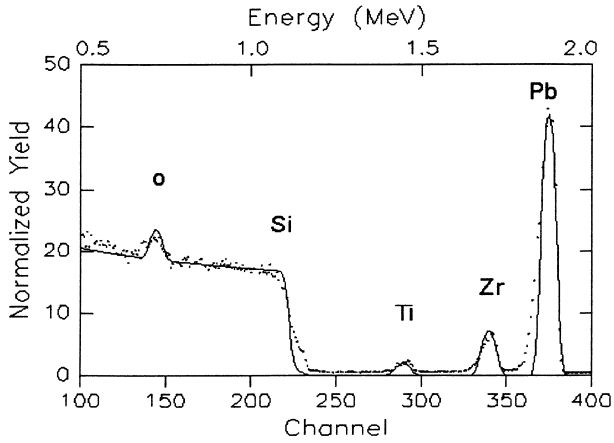

Fig. 3. Rutherford backscattering (RBS) spectra for the PZT thin films deposited on Si and annealed at 600°C for 2·5 h.

The above presented results show that the method enabled us to prepare thin films well crystallized and with the composition of the powders obtained by conventional ceramic method.

4 Conclusion

In this work an alternative chemical method to prepare thin films is presented. The method is based on the dissolution in acid media of a ceramic powder, with the same composition as the desired for the film, to obtain a solution containing the metalic ions. The method was successfully applied to produce perovskite (PZT), eletrooptic (PLZT) and bismuth layered ferroelectric (BIT) thin films. The obtained films showed good microstructural homogeneity, the desired composition and a quality similar those prepared by sol–gel processing. Low cost and high stability of the solution in the preparation process are the main advantages compared with other chemical methods. The authors believe that the presented method can be particularly useful to produce doped films.

Acknowledgements

The authors would like thank Dr. N. I. Morimoto and MSc. A. G. Pedrine, LSI-USP, Dr. Manfredo H. Tabacniks and A. F. dos Reis (Tonhão), LAMFI-USP, for facilities and RBS analysis, Dr. Y. P. Mascarenhas, IFSC-USP, for XRD analysis and CNPq (Brazilian agency) for financial support.

References

1. Sayer, M. and Sreenivas, K., Ceramic thin films: fabrication and applications. *Science*, 1990, **247**, 1056.
2. de Keijser, M. and Dormans, G. J. M., Chemical vapor deposition of electroceramic thin films. *MRS Bulletin*, June 1996, **21**(6), 37.
3. Johnson, Jr, D. W., Sol–gel processing of ceramics and glass. *Am. Ceram. Soc. Bull.*, 1985, **64**(12), 1597.
4. Yi, G., Wu, Z. and Sayer, M., Preparation of $Pb(Zr,Ti)O_3$ thin films by sol gel processing: electrical, optical and electro-optic properties. *J. Appl. Phys.,* 1998, **64**(5), 2717.
5. Haertling, G. H., PLZT thin-films prepared from acetate precursors. *Ferroelectrics*, 1991, **116**, 51.
6. Sheppard, L. M., Advances in processing of ferroelectric thin films. *Ceramic Bulletin*, 1992, **71**(1), 85.
7. Araújo, E. B. and Eiras, J. A., PZT thin films obtained from oxide precursors. *J. Mat. Sci. Letters*, 1998, **17**(10), 833.
8. Pechini, M., US Patent No. 3 330 697, 11 July 1967.
9. Lessing, P. A., Mixed-cation oxide powders via polymeric precursors. *Ceramic Bulletin*, 1989, **68**(5), 1002.
10. Tseng, T. F., Liu, K. S., Wu, T. B. and Lin, I. N., Effect of $LaNiO_3$/Pt double layers on the characteristics of $(Pb_xLa_{1-x})(Zr_yTi_{1-y})O_3$ thin films. *Appl. Phys. Lett.,* 1996, **68**(18), 2505.
11. Tseng, T. F., Yang, R. P., Liu, K. S. and Lin, I. N., Ferroelectric properties of $(Pb_{0.97}La_{0.03})(Zr_{0.66}Ti_{0.34})_{0.9875}O_3$ films deposited on Si_3N_4-coated Si substrates by pulsed laser deposition process. *Appl. Phys. Lett.*, 1997, **70**(1), 46.
12. Suu, K., Osawa, A., Tani, N., Ishikawa, M., Nakamura, K., Ozawa, T., Sameshima, K., Kamisawa, A. and Takasu, H., Preparation of $(Pb,Ia)(Zr,Ti)O_3$ ferroelectric films by RF sputtering on large substrate. *Jpn. J. Appl. Phys.*, 1996, **35**(9B), Part 1, 4967.
13. Sedlar, M. and Sayer, M., Structural and electrical properties of ferroelectric bismuth titanate thin films prepared by sol gel method. *Ceramics International*, 1996, **22**, 241.
14. Doolittle, L. R., Algorithms for the rapid simulation of Rutherford backscattering. *Nucl. Instrum. Meth.*, 1985, **B9**(3), 344.