Improvement of the ferroelectric properties of ABO_3 (A = Pb, Ca, Ba; B = Ti, Zr) films

M. T. Escote[a], F. M. Ponte[a], G. P. Mambrini[a], E. R. Leite[a], J. A. Varela[b], E. Longo[a]

[a]LIEC – CMDMC, Departamento de Química, Universidade Federal de São Carlos, Via Washington Luiz, km 235, CP 676, 13565-905, São Carlos, SP, Brazil

[b]Instituto de Química, UNESP, CP 353, CEP 14801-970, Araraquara, SP, Brazil

Abstract

High-quality $ABO_3/LaNiO_3$ (A = Pb, Ca, Ba; B = Ti, Zr) heterostructures have been grown on $LaAlO_3$ (100) substrate by the chemical solution deposition method and crystallized by a microwave oven technique. The structural, morphological and electric properties were characterized by means of X-ray diffraction (XRD), atomic force microscope images (AFM), and dielectric and ferroelectric measurements. XRD patterns revealed single-phase polycrystalline and oriented thin films whose feature depends on the composition of the films. The AFM surface morphologies showed a smooth and crack-free surface with the average grain size ranging from 116 to 300nm for both $LaNiO_3$ electrode and the ferroelectric films. Dielectric measurements on these samples revealed dielectric constants as high as 1800 at frequency of 100 KHz. Such results showed that the combination of the chemical solution method with the microwave process provides a promising technique to grow high quality thin films with good dielectric and ferroelectric properties.

Keywords: Films, chemical solution deposition method, ferroelectric properties, perovskites, $BaTiO_3$ and titanates.

INTRODUCTION

The development of ferroelectric thin film technology has been extensively investigated due to the possibility of application in integrated electronic circuits as, for example, ferroelectric random access memories (FeRAMs).[1,2] In order to improve the dielectric constant and to produce fatigue-free ferroelectric thin films, several works reported on the influence of preparation conditions and the conductive electrode on the physical properties of ferroelectric thin films.[4-7]

Into this context, some studies have been performed on ferroelectric films grown on conductive oxides electrodes such as $LaNiO_3$, $SrRuO_3$, $BaPbO_3$, and $Yba_2Cu_3O_{7-\delta}$. These oxides were used to replace the Pt bottom electrode that usually presents serious fatigue problems.[8,9] Between these conductive oxides, the most widely investigated has been the $LaNiO_3$, mainly due its metallic behavior until temperatures close to 4.2 K.[10-12] These study together with growth of epitaxial or high oriented thin films have been successfully to reach ferroelectric films with better properties than the polycrystalline one.[13,14] In addition, attempts have been made to enhance the crystallization ability of ferroelectric thin films and metallic oxide electrode. In this sense, a new way to synthesize these materials have been searched as, for example, the use of microwave frequency source of energy to annealing those ferroelectric films.[15,16] This procedure have produced materials with high degree of crystallinity and at lower annealing processing time. Also it decreases the interfacial reactions between the ferroelectric film and the bottom electrode, which provide a better control of the crystallographic orientation of the thin film.

Another important point regarding the production of ferroelectric thin films concern the method to produce such film. In fact, there are several techniques for synthesizing thin films and the more widely studied are r. f. sputtering, laser ablation deposition and chemical methods (sol-gel, metallorganic chemical vapor deposition, soft chemical deposition). Among those methods, the soft chemical deposition methods have provide the production of high quality oriented films, when the film was controlled annealed in a microwave oven.[15]

In this work, we reported on the preparation of highly (100) oriented $Pb_{1-x}A_xTi_{1-y}B_yO_3$ (A = Ba, Ca; B = Zr) and $LaNiO_3$ thin films by a soft chemical solution deposition method. These films were grown on $LaAlO_3$ (100) substrate and heat-treated in a domestic microwave oven at 700 ° for few minutes.

EXPERIMENTAL PROCEDURE

The $ABO_3/LaNiO_3$ (A = Pb, Ca, Ba; B = Ti, Zr) thin films were produced by chemical solution deposition CSD method.[12] Through this method, a polymeric resin of both ABO_3 and $LaNiO_3$ were separated produced by means of the CSD route. The $LaNiO_3$ and ABO_3 films were deposited by spin coated technique on $LaAlO_3$ (100) substrate, as described elsewhere.[15] Then, they are samples were dried, and annealed at ~ 300 °C for 6 h in a conventional furnace and were sintered at 600 and 700 °C in a microwave oven for 10 min. The structural features of these thin films were characterized by X-ray diffraction measurements, which were performed in all samples by using the Cu-K_α radiation on a Rigaku D/Max-2400 diffractometer. Typical 2θ angular scans ranging from 20 to 60° in steps varying of 0.02 ° were used in these experiments. Changes in the morphology of $ABO_3/LaNiO_3$ heterostructures were analyzed by means of Atomic force microscopy (AFM). The images were analyzed using the Digital Instruments Multimode Nanoscope IIIa (Santa Barbara, CA) software. The film thickness was evaluated observing the cross-section of the films using a Zeiss DSM940A scanning electron microscopy (SEM). The dielectric and ferroelectric properties were measured on films in a metal-thin film-metal configuration using a HP4192A impedance/gain phase analyzer. All the measurements were conducted at room temperature.

Discussion and Results

The Fig. 1 displays the X-ray diffraction patterns for: (a) $LaAlO_3$ substrate; (b) conductive oxide $LaNiO_3/LaAlO_3$, also called LNO/LAO; (c) $Pb_{0.8}Ba_{0.2}TiO_3$/LNO/LAO; (d) $Pb_{0.6}Ca_{0.4}TiO_3$/LNO/LAO; and (e) $PbZr_{0.3}Ti_{0.7}O_3$/LNO/LAO. For a better understanding, these films were thereafter called PBT8020; PCT6040, and PZT3070, respectively. It can be seen that the $LaNiO_3$ thin film electrode annealed at 700 °C for 10 min crystallizes in a perovskite and is structure highly (100) oriented, which is feature of the intense peak at $2\theta \sim 23°$. Also, it should be noticed that the low intense reflection at $2\theta \sim 32.7°$ belongs to the polycrystalline $LaNiO_3$ phase. The Fig. 2(c) revealed a highly oriented PBT8020 thin film deposited on LNO/LAO, where the intensities of the (100) and (200) peaks are stronger than those (101) and (110) Bragg reflections, which suggested that this films is highly (100) oriented in the PBT8020 perovskite phase. In the same way, the x-ray pattern of the PCT6040 thin film presents a similar behavior (see Fig.1(d)), which low intense peaks at $2\theta \sim 32.4°$ that are addressed to the (101)/(110) Bragg planes of the polycrystalline phase. The Fig. 1(e) displays a polycrystalline x-ray diffraction pattern for the PZT3070, although it is single-phase. Therefore, we believed that the production of highly oriented (100) $LaNiO_3$ thin films should be a result of the enhanced crystallization and interfacial growth improvement of the thin films, which were influenced by the microwave treatment and by the matching of the lattice parameters of the LNO and ABO_3 thin film.

The surface morphologies for the LNO/LAO, PBT8020, PCT6040, and PZT3070 thin films were observed by AFM images, as are shown in Fig. 2. The films on ALO (100) substrate were found to have smooth surfaces, crack-free, and we have found no evidence of droplet on them. An analysis on these images revealed an average surface roughness R_{rms} value of ~ 9 nm, while the average grains sizes t were evaluated as ~300, 140, and 116 nm for the PBT8020, PCT6040, and PZT3070 thin films, respectively. Meanwhile, AFM images obtained for a PCT6040/ Pt(111)/Ti/SiO_2/Si(100) thin film reported an R_{rms} value of 4 nm and a t value of 70 nm. [17] It is also important to notice that this film was heat-treated in a conventional furnace. In this sense, the sample grown on LNO/LAO structures seems to display a higher R_{rms} and bigger average grain size than those reported for the ABO_3 thin films deposited on Pt-based substrates.

The combined results showed above indicated that the annealing process and the use of high-oriented LNO/LAO structures promoted changes in both size and morphology of the grains, and also allowed the production of highly oriented ABO_3 thin films. As these features have a close relation to the dielectric and ferroelectric properties, the films were characterized by means of the measurements of the constant dielectric and dielectric loss as a function of frequency and through the Polarization-Voltage characteristic curves at room temperature. The dielectric constant (κ) and dielectric loss (tanδ) as a function of frequency characterization obtained for these films on LNO/LAO structures are shown in Fig. 3. These curves show a smooth decrease of the dielectric constant with the increasing of the frequency. The κ values observed for PBT8020 and PCT6040 thin films coated on LNO/LAO are significantly higher than those reported in literature.[15,17-19] In fact, at 1 KHz these films presents κ values close to 2250 and 930, respectively, while films grown on platinum electrodes presents κ values of ~ 118 and 200 observed for similar PBT and PCT films, respectively. However, the PZT3070 deposited on LNO/LAO presents κ values considerably lower than those reported for similar films also grown on LNO/ALO structures.[19] These works reported κ values from 597 to 1250 for PZT50/50 and

PZT53/47, while we observe κ values of ~ 330 at 1 kHz. We believed that such result could be a result of the lack of preferential orientation of this films, as is shown in the x-ray data. Beside, the enhance of the dielectric constant observed for the other films could be due the improvement between the ABO_3 thin film and the $LaNiO_3$ electrode interface, which could promote the formation of a highly oriented $ABO_3/LaNiO_3/LaAlO_3$ structure. In this sense, we believe that the microwave oven treatments suppress the formation of a very low dielectric constant layer at the thin film/electrode interface, which sometimes is the main cause of the lower values of the dielectric constant related to many ferroelectric thin films.[20,21]

Conclusion

In summary, we have produced high-oriented ABO_3/LNO/LAO structures by a wet soft chemical method and using a heat treatment at a microwave oven. This study indicated that the ABO_3 thin film on LNO bottom electrode was shown to have excellent structural, microstructural, and electrical properties. The A with Pb, Ba, and Ca presents a higher dielectric constant, which make them a very attractive candidate to many applications. Moreover, the remarkable improvement in all the properties suggested that the chemical route combined with the annealing by a microwave oven process is an alternative approach to obtaining thin films with a quality comparable to the best thin films, suitable for integrated device applications, and processed by conventional methods.

ACKNOWLEDGEMENTS

This work was financially supported by the Brazilian agencies FAPESP/CEPID, CNPq/PRONEX, and CAPES.

REFERENCES

1. O. Auciello, J. F. Scott, and R. Ramesh, The physics of ferroelectric memories, *Phys. Today*, 1998, **51**, 22-27.

2. J. F. Scott and C. A. Paz de Araujo, Ferroelectric Memories, *Science*, 1989, **246**, 1400-1405.

3. M. Grossmann, D. Bolten, O. Lohse, U. Boettger, R. Waser, and S. Tiedke, Correlation between switching and fatigue in PbZr0.3Ti0.7O3 thin films, *Appl. Phys. Lett.*, 2000, **77**, 1894-1896.

4. See, for example: J. Frantti, S. Ivanov, S. Eriksson, H. Rundlof, V. Lantto, J. Lappalainen, and M. Kakihana, Phase transitions of $Pb(Zr_xTi_{1-x})O_3$ ceramics, *Phys. Rev. B,* 2002, **66**, 064108; D. Sheen, and Jon-Jean Kim, Dielectric and polarization switching anomalies near the morphotropic phase boundary in $Pb(Zr_xTi_{1-x})O_3$ ferroelectric thin films, *Phys. Rev. B*, 2003, **67**, 144102.

5. R. Ramesh, H. Gilchrist, T. Sands, V. G. Keramidas, R. Haakenaasen, and D. K. Fork, Ferroelectric La-Sr-Co-O/Pb-Zr-Ti-O/La-Sr-Co-O Heterostructures on silicon via template growth**,** *Appl. Phys. Lett.,* 1993, **63**, 3592-3594.

6. O. Y. Gorbenko, A. R. Kaul, A. A. Molodyk, V. N. Fuflyigin, M. A. Novozhilov, A. A. Bosak, U. Krause, and G. Wahl, MOCVD of perovskites with metallic conductivity, J. Alloys Compounds, 1997, **251**, 337-341.

7. K. Reichmann, T. Schneller, S. Hoffmann-Eifert, U. Hasenkox, and R. Waser, Morphology and electrical properties of $SrTiO_3$-films on conductive oxide films**,** *J. Eur. Ceram. Soc.*, 2001, **21**, 1597-1600.

8. W. Si, E. M. Cruz, P. D. Johnson, P. W. Barnes, P. Woodward, and A. P. Ramirez, Epitaxial thin films of the giant-dielectric-constant material $CaCu_3Ti_4O_{12}$ grown by pulsed-laser deposition, *Appl. Phys. Lett.*, 2002, **81**, 2056-2058.

9. C. S. Liang, J. M. Wu, and M. C. Chang, Ferroelectric $BaPbO_3/PbZr_{0.53}Ti_{0.47}/BaPbO_3$ heterostructures, *Appl. Phys. Lett.,* 2002, **81**, 3624-3626.

10. See, for example, J. Zhai and H. Chen, Ferroelectric properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films grown on the highly oriented LaNiO3 buffered Pt/Ti/SiO2/Si substrates, *Appl. Phys. Lett.*, 2003, **82**, 442-444; G. D. Hu, I. H. Wilson, J. B. Xu, C. P. Li, and S. P. Wong, Low-temperature preparation and characterization of $SrBi_2Ta_2O_9$ thin films on (100)-oriented $LaNiO_3$ electrodes, *Appl. Phys. Lett.*, 2000, **76**, 1758-1760.

11. K. Sreedhar, J. M. Honing, M. Darwin, M. McElfresh, P. M. Shand, J. Xu, B. C. Crooker, J. Spalek, Electronic-properties of the metallic perovskite $LaNiO_3$ - correlated behavior of 3d electrons, *Phys. Rev. B*, 1992, **46**, 6382-6386; X. Q. Xu, J. L. Peng, Z. Y. Li, H. L. Ju, and R. L. Greene, Resistivity, thermopower, and susceptibility of $RNiO_3$ (R = La,Pr)**,** *Phys. Rev. B*, 1993, **48**, 1112-1118.

12. M. T. Escote, F. M. Pontes, E. R. Leite, J. A. Varela, R. F. Jardim, and E. Longo, Microstructural and transport properties of $LaNiO_{3-\delta}$ films grown on Si (111) by chemical solution deposition, *Thin Solid Films*, 2003, **445**, 54-58.

13. H. N. Lee, D. Hesse, N. Zakharov, and U. Gösele, Ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ films of uniform a-axis orientation on silicon substrates, *Science*, 2002, **296**, 2006-2009 ().

14. R. Ramesh and D. G. Schlom, Materials science - Orienting ferroelectric films, *Science*, 2002, **296**, 1975-1976.

15. F. M. Pontes, E. R. Leite, G. P. Mambrini, M. T. Escote, E. Longo, and J A Varela, Very large dielectric constant of highly oriented $Pb_{1-x}Ba_xTiO_3$ thin films prepared by chemical deposition, *Appl. Phys. Lett.*, 2004, **83**, 248-250.

16. N. S. L. S. Vasconcelos, J. S. Vasconcelos, V. Bouquet, S. M. Zanetti, E. R. Leite, E. Longo, L. E. B. Soledade, F. M. Pontes, M. Guilloux-Viry, A. Perrin, M. I. Bernardi, and J. A Varela, Epitaxial growth of LiNbO3 thin films in a microwave oven**,** *Thin Solid Films*, 2003, **436**, 213-219.

17. F. M. Pontes, D. S. L. Pontes, E. R. Leite, E. Longo, A. J. Chiquito, P. S. Pizani, and J. A Varela, Electrical conduction mechanism and phase transition studies using dielectric properties and Raman spectroscopy in ferroelectric $Pb_{0.76}Ca_{0.24}TiO_3$ thin films, *J. Appl. Phys.*, 2003, **94**, 7256-7260.

18. X. G. Tang, H. L. Chan, and A L. Ding, Electrical properties of $(Pb_{0.76}Ca_{0.24})TiO_3$ thin films on $LaNiO_3$ coated Si and fused quartz substrates prepared by sol-gel process, *Appl. Surf. Sc.*, 2003, **207**, 63-68.

19. See, for example: C. R. Cho, Heteroepitaxial growth and Switching behaviors of PZT(53/47) films on $LaNiO_3$-deposited $LaAlO_3$ and $SrTiO_3$ substrates, *Mat. Sc. Eng,.* 1999, **B64**, 113-117; S. H. Hu, X. J. Meng, G. S. Wang, J. L. Sun, and D. X. Li, Preparation and Characterization of multi-coating PZT thick films by sol-gel process, *J. Crystal Growth*, 2004, **264**, 307-311.

20. D. H. Bao, N. Wakiya, K. Shinozaki, N. Mizutani, and X. Yao, Improved electrical properties of (Pb, La)TiO3 thin films using compositionally and structurally compatible LaNiO3 thin films as bottom electrodes, *Appl. Phys. Lett*. 2001, **78**, 3286-3288.

21. A K. Tagantsev, M. Landivar, E. Colla, and N. Setter, Identification of passive layer in ferroelectric thin-films from their switching parameters, *J. Appl. Phys*., 1995, **78**, 2623-2630.

Figure Captions

Figure 1 – X-ray patterns of (a) The $LaAlO_3$ substrate; (b) $LaNiO_3$ thin film on the substrate; (c) the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film on $LaNiO_3/LaAlO_3(100)$; $Pb_{0.6}Ca_{0.4}TiO_3$ thin film on $LaNiO_3/LaAlO_3(100)$; and (e) $PbZr_{0.30}Ti_{0.70}O_3$ thin film on $LaNiO_3/LaAlO_3(100)$. S = substrate peak.

Figure 2 – AFM micrographs of the (a) $Pb_{0.8}Ba_{0.2}TiO_3$ thin films; (b) $Pb_{0.6}Ca_{0.4}TiO_3$ thin film; and (c) $PbZr_{0.30}Ti_{0.70}O_3$ thin film.

Figure 3 – Frequency dependence of the dielectric constant and dielectric loss of the (a) $Pb_{0.8}Ba_{0.2}TiO_3$; (b) $Pb_{0.6}Ca_{0.4}TiO_3$; and (c) $PbZr_{0.30}Ti_{0.70}O_3$ thin films.

Figure 1 – Escote et al.

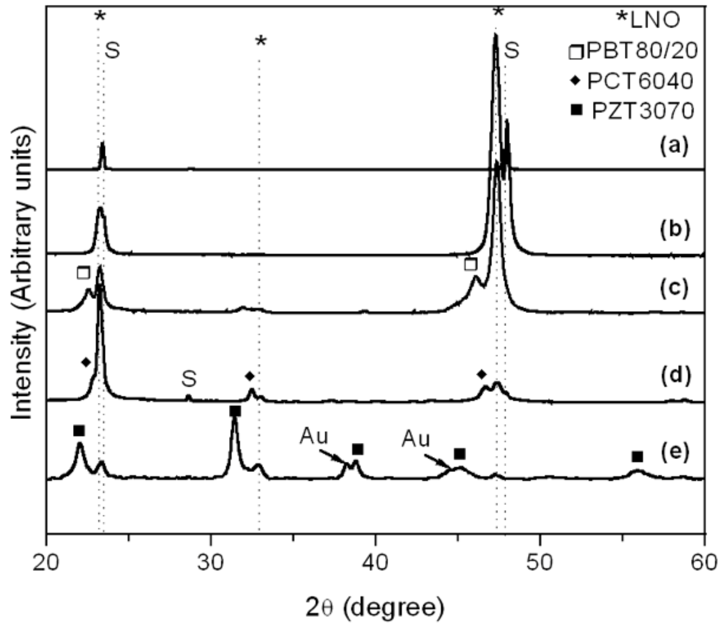

Figure 2 – Escote et al.

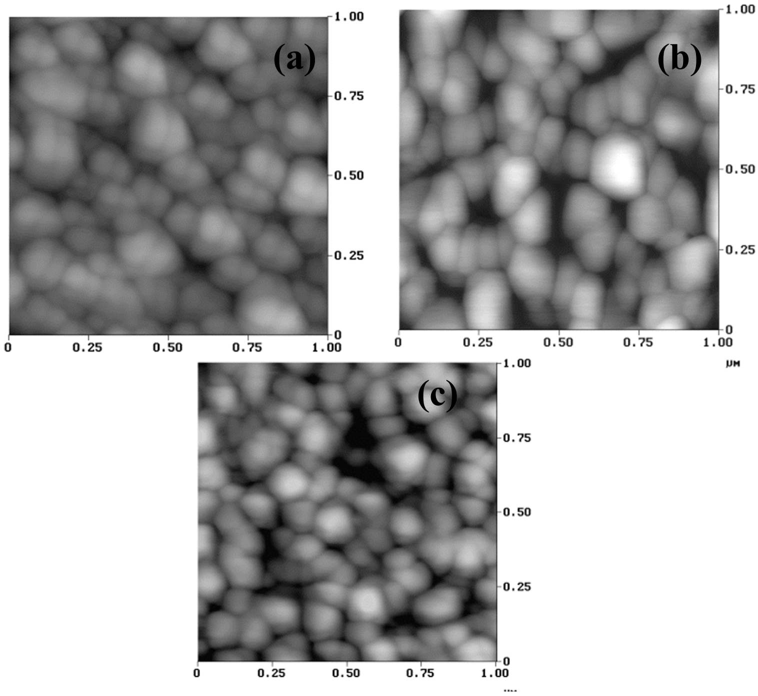

Figure 3 – Escote et al.