Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 989–991

www.elsevier.com/locate/jeurceramsoc

Strontium titanate films prepared by spray pyrolysis

Goran Branković[a,b,*], Zorica Branković[a,c], José Arana Varela[a], Elson Longo[d]

[a]*Instituto de Química, UNESP, PO Box 355, CEF 14.801-970, Araraquara SP, Brazil*
[b]*Center for Multidisciplinary Studies of University of Belgrade, PO Box 33, 11030, Belgrade, Yugoslavia*
[c]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Yugoslavia*
[d]*Departamento de Química-Universidade Federal de São Carlos-UFSCar, CF 676, CEP 13565-905 São Carlos, SP, Brazil*

Abstract

Strontium titanate thin films were prepared by spray pyrolysis technique. Deposition parameters, such as solution concentration, time and temperature of deposition, and flow rate of carrier gas were optimized to obtain dense films without cracks. Films with different thicknesses were prepared through the control of deposition time. Prepared thin films were homogeneous, well crystallized, with uniform grain size.

Keywords: Films; Sol-gel processes; Strontium titanate

1. Introduction

Spray pyrolysis is a versatile technique for producing various materials in a wide range of composition, size and morphology. Powders, films and fibers can be successfully prepared.[1] Thin film is formed by spraying, drying and pyrolytically decomposing onto a heated substrate a solution of precursor salts of the desired constituent ions.[2] This method connects many features of the gas-phase and liquid-phase techniques having the following advantages: (a) one-step, simple, cheap equipment, (b) universal precursors (inorganic, organic or metal-organic compounds), (c) easy and precise composition control, (d) various film morphologies possible, and (e) accurate control of the deposition kinetics.[3] The aerosols may be generated by pneumatic or ultrasonic atomizers.

$SrTiO_3$ is a paraelectric material with cubic perovskite-type crystal structure at room temperature.[4] It has a lot of interesting properties, such as high dielectric constant, good thermal stability, second order phase transformation, stress-induced phase transition, photoactivity, etc.[4,5] According to these properties $SrTiO_3$ has possible applications in dynamic random access memories (DRAM),[5,6] microelectronics,[7] solar and sensor technology.[8]

The aim of this work was to construct equipment set-up that allows preparation of thin films by spray pyrolysis and easy control of deposition parameters, as well as to prepare $SrTiO_3$ thin films. Deposition parameters, such as solution concentration, time and temperature of deposition, flow rate of carrier gas were optimized to obtain dense films without cracks.

2. Experimental

The precursor solutions were prepared from a titanium citrate and strontium acetate. Titanium citrate was formed by dissolution of titanium (IV) isopropoxide in a ethylene glycol solution of citric acid acording to the following molar ratio:

Ti-ion:citric acid:ethylene glycol = 1:4:16.

A stoichiometric amount of strontium acetate was dissolved in water. Further, two solutions were mixed. Water content was changed to obtain the following molar concentrations of the metal ions: 0.2 mol/dm^3, 0.1 mol/dm^3 and 0.05 mol/dm^3.

Prepared solutions were deposited on silicon (1 0 0) substrates. Deposition was performed at different temperatures in the interval: 50–200 °C, and for different flow rates of the carrier gas–oxygen. Deposition time was varied (30, 60 and 120 mm) to obtain films with different thickness. After deposition, the films were heat treated at 650 °C for 2 h. The films were slowly heated (2 °C/min) up to 400 °C, then heated at 400 °C

* Corresponding author. Tel.: +381-11-555258; fax: +381-11-3055289.
E-mail address: milan@drenik.net (G. Branković).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00459-X

for 2 h and finally heated (5 °C/min) up to the temperature 650 °C at which it remained for 30 min. Thermal treatment conditions were chosen from the literature data for the $SrTiO_3$ obtained from the similar precursor solutions.[4] Films were slowly cooled to prevent crack formation. Composition and crystal structure of the films were determined by X-ray diffraction analysis, and microstructure was examined by AFM and SEM.

3. Results and discussions

After equipment construction, great efforts were made to optimize deposition conditions: deposition temperature and oxygen flow rate. It was necessary to adjust oxygen flow rate with the valves 1, 8, and 9 (see Fig. 1) on such a way to obtain dense, quasi-static nebule (extremely low flow rate) above the substrate. This was achieved for the oxygen rate of 500 cm^3/min at valve 1. Several different deposition temperatures were experimented. It was found that deposition at temperatures lower than 70 °C leads to spray condensation on the substrate surface resulting in inhomogeneous films. On the other hand, too high temperatures led to very fast evaporation of the precursor from a substrate surface, and evaporation occurred before the particles were deposited. As a result, films were not formed at temperatures higher than 100 °C. The optimal microstructure and composition were obtained for deposition temperature of 85 °C. Investigated films were deposited under these optimal conditions, but at different times of deposition, to obtain films of different thickness. Also, this equipment construction allowed obtaining of homogeneous thin film on a big substrate area. In our work substrates of different size were used and all obtained films were homogeneous. The biggest substrate which was used was 20×40 mm.

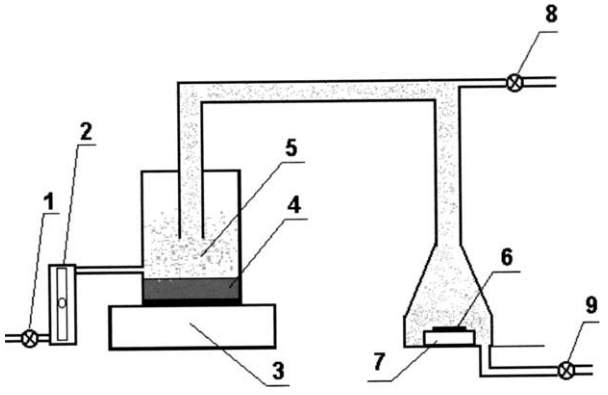

Fig. 1. Schematic representation of the equipment set-up: 1-valve, 2-flowmeter, 3-aerosol generator, 4-solution, 5-aerosol, 6-substrate, 7-heating plate, 8-valve and 9-valve.

According to X-ray diffraction analysis of the prepared films the single phase strontium titanate film was obtained under chosen deposition conditions (Fig. 2). The lattice parameters are given in Table 1. With increase in time of deposition lattice parameters also increased and approximated the lattice parameter of the well-crystalline strontium titanate from the JCPDS card (lattice parameter equal to 3.9050 Å). Also, it was found that the film thickness is approximately a linear function of deposition time (Table 1).

According to AFM analysis the mean Rms roughness was slightly dependent of film thickness and it was in the range 1.68–2.23 nm (Fig. 3). The grains were columnar, with mean size of 30.2–44.1 nm. The films were homogeneous, dense and crack-free.

Since the decomposition of strontium acetate and titanium citrate, as well as formation and crystallization of strontium titanate occurred during additional thermal treatment, it was not expected to obtain great differences in film roughness, mean grain size and lattice parameters. However, small differences in values of these parameters were observed as a function of time of deposition, i.e. film thickness. This could be explained by descending influence of the substrate on the crystal structure of the thicker films. Also, the conglomeration and accumulation of strontium acetate and titanium

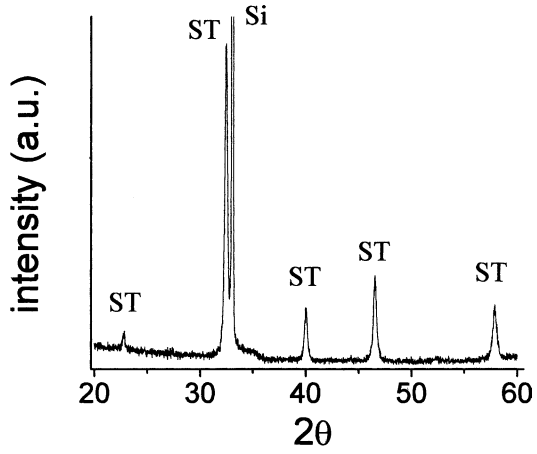

Fig. 2. X-ray diffractogram of $SrTiO_3$ films.

Table 1
The characteristic properties of the strontium titanate films deposited for different times

	Deposition time (min)		
	30	60	120
Thickness (nm)	51	129	212
Mean grain size (nm)	30.2	35.5	44.1
Rms roughness (nm)	1.68	2.13	2.23
Lattice parameters (Å)	3.8885(9)	3.890(3)	3.8970(7)

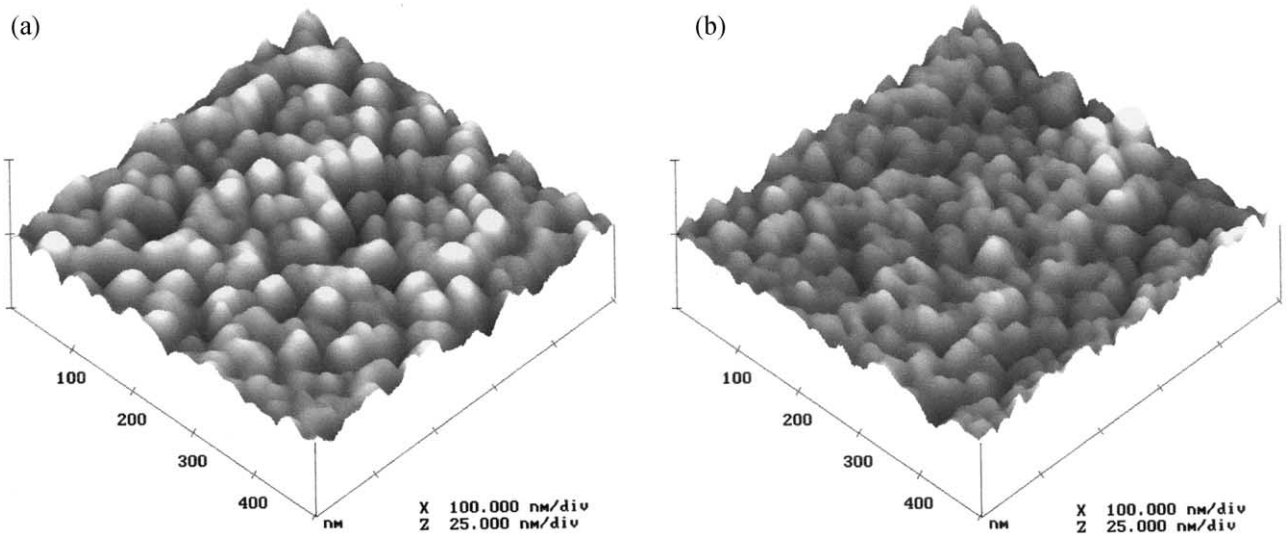

Fig. 3. Atomic force 3D micrographs of $SrTiO_3$ films deposited for (a) 120 min and (b) 60 min.

citrate on the substrate surface, that occurred at relatively low temperatures (85 °C) during deposition, probably influenced the final grain size of the strontium titanate.

4. Conclusion

Strontium titanate thin films were successfully prepared by spray pyrolysis technique. Optimal deposition parameters were the following: carrier gas flow rate: 500 cm^3/min; deposition temperature: 85 °C. Film thickness is approximately a linear function of deposition time and it was in the range 51–212 nm. Obtained films were homogeneous, dense, crack-free and very smooth. Mean roughness was slightly dependent on film thickness and it was in the range 1.68–2.23 nm.

Acknowledgements

This work was financially supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) through the projects number 99/06470-0, 00/09818-6, 02/01403-7 and 98/14324-0 and by the Ministry for Science, Technologies and Development of Serbia through the projects "Synthesis of functional materials in accordance with the synthesis–structure–properties–application relationship" and "Preparation and investigation of oxide and complex systems with catalytic, electrical and bioactive properties".

References

1. Haertling, G. H., Ferroelectric ceramics: history and technology. *J. Am. Ceram. Soc.*, 1999, **82**, 797–818.
2. Delikouras, E. A. and Perlmutter, D. D., Characterization of PLZT films deposited by spray-pyrolysis. *J. Am. Ceram. Soc.*, 1994, **77**, 3142–3144.
3. Wang, H. B., Meng, G. Y. and Peng, D. K., Aerosol and plasma assisted chemical vapor deposition process for multicomponent oxide $La_{0.8}Sr_{0.2}MnO_3$ thin film. *Thin Solids Films*, 2000, **368**, 275–278.
4. Pontes, F. M., Leite, E. R., Lee, E. J. H., Longo, E. and Varela, J. A., Preparation, microstructural and electrical characterization of $SrTiO_3$ thin films prepared by chemical route. *J. Eu. Ceram. Soc.*, 2001, **21**, 419–426.
5. Hübert, T., Beck, U. and Kleinke, H., Amorphous and nanocrystalline $SrTiO_3$ thin films. *Journal of Non-Crystalline Solids*, 1996, **196**, 150–154.
6. Jia, Q. X., Kung, H. H. and Wu, X. D., Microstructure properties of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films on Si with conductive $SrRuO_3$ bottom electrodes. *Thin Solids Films*, 1997, **299**, 115–118.
7. Sakuma, T., Yamamichi, S., Matsubara, S., Yamaguchi, H. and Miyasaka, Y., Barrier layers for realization of high capacitance density in $SrTiO_3$ thin-film capacitor on silicon. *Appl. Phys. Lett.*, 1990, **57**, 2431–2433.
8. Gerblinger, J. and Meixner, H., Fast oxygen sensors based on sputtered strontium-titanate. *Sen. Actuators B*, 1991, **4**, 99–102.