BaTiO$_3$ thin films obtained by sol–gel spin coating

M. Manso-Silván[a,*], L. Fuentes-Cobas[b], R.J. Martín-Palma[a], M. Hernández-Vélez[a], J.M. Martínez-Duart[a]

[a]*Department Física Aplicada, Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[b]*Laboratorio de Cerámicas Piezoeléctricas, CIMA, S.C., Chihuahua, C.P. 31110, Mexico*

Abstract

BaTiO$_3$ thin film deposition techniques are the subject of many research studies mainly due to their influence on the optical and electrical properties of this material, which are of increasing interest for the processing of opto- and microelectronic devices. In this work, BaTiO$_3$ thin films were grown onto silicon substrates by using a sol–gel spin coating procedure from Ba(OH)$_2$ and tetraisopropyl–orthotitanate (TIPT)-based precursors. The as-grown films were annealed at different temperatures. Both the preparation of the starting solutions through a multi-step process together with an activation energy reached by sintering at approximately 800 °C, were the most important parameters necessary to obtain the ferroelectric phase in these films. The evolution of the network bonds and the structural characterization of the films was studied by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) techniques, respectively. In order to ascertain the suitability of BaTiO$_3$ films for the processing of electronic devices, the electrical behaviour (I–V curves) of different thin films was also determined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ferroelectrics; Sol–gel; BaTiO3; Thin films

1. Introduction

The structural properties of BaTiO$_3$ (BTO) determine their optical and electrical properties that have induced the study of BTO materials in fields such as non-linear-optics, photo refractivity, ferroelectricity and piezoelectricity among others. Previous experimental results suggest that BTO thin films are suitable for the processing of opto- and microelectronic devices such as wave guides, high-*k* gates and non-volatile memories [1–4]. Several techniques have been used to form bare or doped BTO thin films. In that sense molecular beam epitaxy [1,2], plasma sputtering [3], metal organic chemical vapour deposition [4] and pulsed laser deposition [5] are probably the most referenced techniques. Sol–gel BTO coatings have also been previously prepared in order to study their chemical and microstructural properties [6]. However, in this work, the perovskite phase was not reported. The sol–gel method presents several advantages for coatings processing; the control of composition, surface morphology engineering and low tem-

perature processing, which allows the use of thermally fragile substrates, are its principal merits [7]. The aim of this work is to verify that BaTiO$_3$ films can be prepared by sol–gel spin coating and their physicochemical and electrical properties can be improved by sintering at different temperatures.

2. Experimental procedure

2.1. Sample preparation

Silicon wafers (100, polished on one side) were used as substrates for the deposition of BaTiO$_3$ coatings. Before deposition, the Si wafers were treated in air at 500 °C for 2 h to eliminate adsorbed impurities and to form a thermally stable SiO$_2$ surface film. The precursor solution was prepared in a two-step process from tetraisopropyl-orthotitanate (TIPT) and Ba(OH)$_2$ (BOH), both from Fluka chemicals. A 0.2 M TIPT solution diluted in ethanol with a TIPT/water ratio $r_w = 0.82$ and a pH = 1.27 was prepared as described previously [8]. Secondly, a 0.2 M BOH solution in ethanol/acetic acid (50%) was added to an equivalent volume of the TIPT solution, thus obtaining a Ba/Ti molar ratio equal to 1.

* Corresponding author. Tel.: +34-913-974-919; fax: +34-913-973-969.

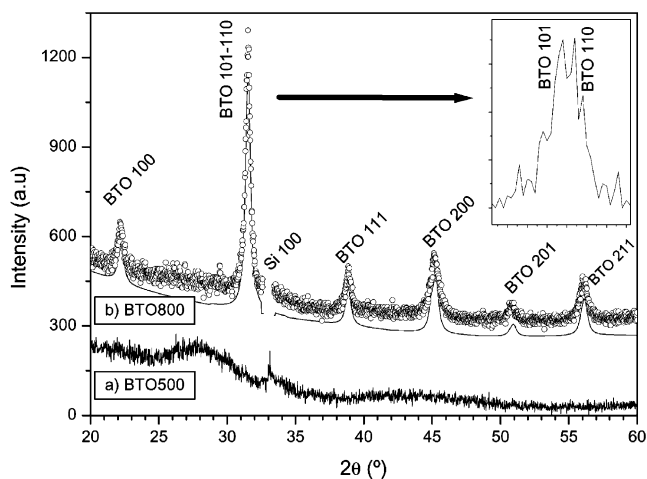*E-mail address:* miguel.manso@uam.es (M. Manso-Silván).

Fig. 1. XRD diffractograms of: (a) a BTO500 and (b) a BTO800 coating at higher temperatures.

This solution was dispersed on the substrates and then spin coated at 3000 rev./min for 45 s. The as-synthesised xerogel films were sintered at 300, 500 and 800 °C for 15 min. In order to prepare thicker $BaTiO_3$ films, a multilayer deposition procedure was followed, i.e. the deposition/heat-treatment cycle was repeated up to 10 times. The coatings were finally sintered for 1 h at the corresponding temperature. In this work, the samples were labelled BTO300, BTO500 and BTO800 in correspondence with the sintering temperature.

2.2. Structural and chemical characterisation

The coatings characterisation was carried out using the following techniques. The samples thickness ranged between 0.5 and 1 μm as determined by profilometry. X-Ray diffraction (XRD) was performed in a Siemens diffractometer using θ/2θ configuration with 0.02° scan step and 6 s integration time. The diffractograms were calculated by the Rietveld refinement method by using FULLPROF computing program [9] after deletion of the Si substrate contribution. Fourier transform infrared (FTIR) spectra were recorded in a transmission scheme using a Bio-Rad FTS165 spectrometer (100 scans at 20 Hz, 4 cm^{-1} resolution).

2.3. I–V characteristics

In order to study the electrical properties of barium titanate, Ti/BTO/Si sandwich structures were made. The metal contacts (φ = 3 mm) were deposited on both sides by sputtering. Electrical characterisation of these structures (I–V curves, −1 V to 1 V range) was carried out in the dark, by using a Hewlett-Packard pA meter/DC voltage source, Model 4140B.

3. Results

3.1. Structure and composition

The XRD diffractograms corresponding to BTO300 coatings present no diffraction peaks indicating that the phase grown is amorphous. The film densification was drastically activated by sintering at 500 °C XRD shoulders related to short range order could be observed in the diffractogram of BTO500 in the 2θ range of 25–30° and 42–50° (Fig. 1a). Sintering at 800 °C promoted the crystallisation of the coatings. Multiple peaks appearing in the XRD diffractograms of Fig. 1b confirm the polycrystalline structure of BTO800 samples. The observation of the (110) and (101) peaks is in agreement with the formation of a $BaTiO_3$ perovskite phase (JCPDS 83-1880). The residual peak at 33.3°, corresponds to the Si substrate and was omitted in order to refine the coating structure by the Rietveld method.

The refinement was carried out taking account of 12 reflections. The a and c cell parameters were found to be 4.006 and 4.031 ± 0.001 Å, respectively. The analysis of preferred orientations showed that the relative intensities of the diffraction peaks are in agreement with those obtained from $BaTiO_3$ standards, proving that the substrate does not induce preferential directions in the film growth.

From the FTIR spectra (Fig. 2) it can be observed that in the case of BTO300 coatings, two weak and wide bands are detected at 310 and 460 cm^{-1} which have been previously identified with Ti–O absorptions in a non-developed network. The weak but well-defined band at 630 cm^{-1} appears to be a common feature for BTO300 and BTO500 samples. The band at 820 cm^{-1} may arise from a carbonate trace in the BTO300 coating. Several weak bands associated with titanium–alkoxi
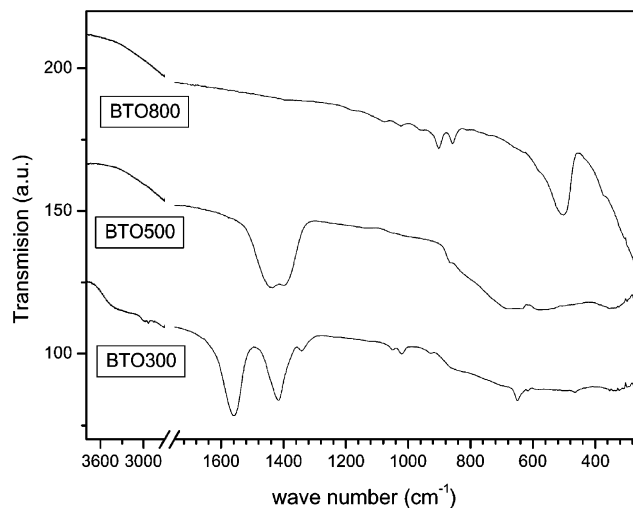

Fig. 2. FTIR spectra of: (a) a BTO300, (b) a BTO500 and (c) a BTO800 coating.
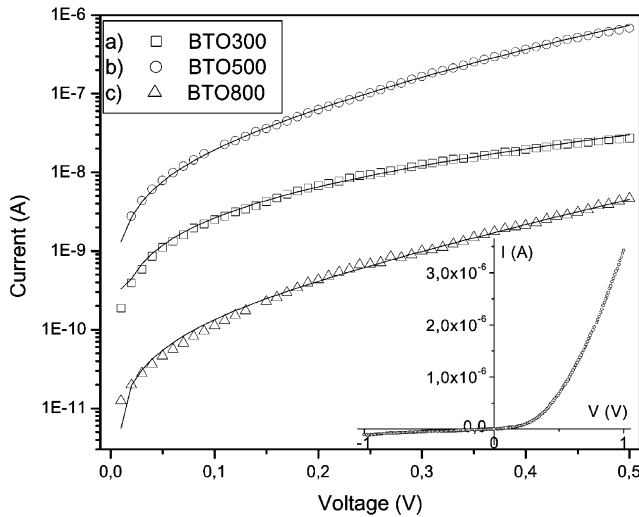
Fig. 3. Experimental I–V curves of the Ti/BTO/Si structures. Inset: general rectifying behaviour in the $-1,1$ V range. Fitted curves of: (a) BTO300, (b) BTO500 and (c) BTO800 structures.

bonds [8] are also detected at 1040, 1070 and 1125 cm^{-1}. The intense bands at 1360 and 1445 cm^{-1} are assigned to carbonate bands partially bonded to barium ions [10]. A high content of carboxyl groups is also detected at 1560 cm^{-1}. The wide band observed at 3600–3100 cm^{-1} is assigned to hydroxyl group asymmetric vibration modes. The spectrum of the BTO500 coating is very similar to the spectrum of BTO300 coatings. It is only worth emphasising the decreasing absorption of some bands, mainly those assigned to carboxyl groups and hydroxyl groups, which are eliminated for increasing sintering temperatures.

The coatings sintered at 800 °C present deeper modifications in their spectra. The intense band at the edge of detection (260 cm^{-1}) is assigned to Ti–O modes in a developed network [11]. Several components appear in the Ti–O–Ti band region. The principal ones are centred at 450 cm^{-1} for these coatings. A broad and strong band at 500 cm^{-1}, characteristic of alkaline titanates [12], appears with a shoulder at 560 cm^{-1} which confirms that TiO$_6$ octahedra have been formed [10]. Several new features can be observed in the spectra of these coatings between 600 and 1500 cm^{-1}. The bands between 600 and 900 cm^{-1} are sharper but weaker than the corresponding bands in the BTO500 film. Furthermore, the BTO500 spectrum presented bands at 1405 and 1450 cm^{-1}, which point out the presence of

a carbonated compound that was not identified in the BTO800 spectrum.

3.2. I–V characteristics

Current–voltage (I–V) measurements of the different Ti/BTO/Si structures were taken in the -1 V to 1 V range. The structures analysed show a rectifying behaviour (Fig. 3, inset). The experimental I–V curves were fitted in the 0–0.5 V range to the following general expression [13]:

$$I = \sum_{i=1}^{N} \left\{ I_{s,i} \left(\exp\left[q(V - IR_s)/n_i kT \right] - 1 \right) \right\} \qquad (1)$$

where $I_{s,i}$ is the saturation current, R_s the series resistance and n_i the ideality coefficient. The aim of the non-linear analysis is to resolve the total current through the various Ti/BTO/Si structures, into several contributions due to different carrier transport mechanisms. In the three cases investigated in the present study, the experimental data could be fitted considering only one contribution (Fig. 3a–c). The non-linear least squares fitting in the 0–0.5 V range was carried out by employing a Levenberg–Marquardt algorithm. Table 1 shows the values of I_s, n_i and R_s of the three structures analysed. It can be observed that they show quite high values of the ideality coefficient, as it is usual when the density of interface states is large. This is supposed to be the case of sol–gel derived thin films. However, it is interesting to note the high values of the series resistance, which is typical of bulk barium titanate.

4. Discussion and conclusions

It has been found that the structure of BaTiO$_3$ coatings deposited by the spin sol–gel process strongly depend on post thermal treatments of the as deposited xerogels. FTIR and XRD analysis are very useful to analyse the sequence of processes taking place during sintering. It was shown that a significant activation of the Ti–O–Ba network condensation is produced when a temperature of 500 °C is reached. Further sintering at temperatures of 800 °C provided the activation of a polycrystalline phase. Moreover, a perovskite phase with lattice parameters a = 4.006 and c = 4.031 ± 0.001 Å was found. Although the lattice splitting does not reach the values obtained for bulk samples (a = 3.9945 Å, c = 4.0335 Å) it is shown that BTO ferroelectric coatings

Table 1
Saturation current, series resistance and ideality coefficient of the different Ti/BTO/Si structures, determined from current–voltage measurements

	BTO300	BTO500	BTO800
Saturation current, I_s (A)	$(4.64 \pm 0.07) \times 10^{-9}$	$(1.45 \pm 0.04) \times 10^{-8}$	$(1.25 \pm 0.07) \times 10^{-10}$
Ideality coefficient, n	8.05 ± 0.07	4.5 ± 0.1	5.3 ± 0.2
Series resistance, R_s (Ω)	$(2.81 \pm 0.05) \times 10^{6}$	$(5.3 \pm 0.4) \times 10^{4}$	$(8.8 \pm 0.9) \times 10^{5}$

can be obtained by sol–gel spin coating processing from BOH based precursors. Sol–gel BTO coatings prepared from BOH as a starting precursor and sintered at 800 °C have been previously reported. They were shown to crystallise in the cubic phase so that no ferroelectric properties could be inferred [6]. It is demonstrated in this work that a BTO ferroelectric phase can be obtained by using the same precursor. This result can be attributed to the solution preparation (i.e. two-step preparation influencing composition, viscosity), which determine the evolution of the polycondensation process. Different Ti/BTO/Si structures were elaborated in order to determine the electrical parameters (saturation current, series resistance and ideality coefficient) from the experimental $I–V$ curves. It should be noted that all the structures studied show quite high values of the ideality coefficient (between 4.5 and 8.05), which might be explained by the presence of a large concentration of interface states, specially in the BTO300 structures, which contain a higher OH group density. These structures also show high values of the series resistance, which vary accordingly with the evolution of the sol–gel condensation and densification mechanisms. The BTO300 structure presents the highest series resistance due to a lack of densification and the presence of organic species. Denser BTO500 structures undergo a reduction in the series resistance due to Ba^{2+} mobility in a non-developed network. The crystallisation of the BTO800 film induces Ba fixation in lattice sites and lead to a stable coating with high resistivity values.

The spin coating process combined with an adequate sol preparation has demonstrated the feasibility of depositing $BaTiO_3$ coatings with ferroelectric structure. Further experiments must determine their applicability for the development of opto-electronic devices.

Acknowledgements

References

[1] R.A. McKee, F.J. Walker, J.R. Conner, E.D. Specht, Appl. Phys. Lett. 59 (1991) 782.
[2] T. Zhao, H. Lu, F. Chen, G. Yang, Z. Chen, J. Appl. Phys. 87 (2000) 7448.
[3] N.M. Abuhabda, C.R. Aita, J. Appl. Phys. 71 (1992) 3045.
[4] B. Bihari, J. Kumar, G.T. Stauf, P.C. Van Buskirk, C.S. Hwang, J. Appl. Phys. 76 (1994) 1169.
[5] Y. Liu, Z. Chen, C. Li, D. Cui, Y. Zhou, G. Yang, J. Appl. Phys. 81 (1997) 6328.
[6] N.M. Kamalasanan, N.D. Kumar, S. Chandra, J. Appl. Phys. 76 (1994) 4603.
[7] G.W. Scherrer, C.J. Brinker, Sol–Gel Science: The Physics and Chemistry of Sol–Gel, Academic Press, Boston, MA, 1990.
[8] M. Burgos, M. Langlet, J. Sol–Gel Sci. Technol. 17 (1999) 267.
[9] J. Rodrígez-Carvajal, Physica B 192 (1993) 55.
[10] M.C. Blanco-López, G. Fourlaris, B. Rand, F.L. Riley, J. Am. Ceram. Soc. 82 (1999) 1777.
[11] M. Burgos, M. Langlet, Thin Solid Films 349 (1999) 19.
[12] R.A. Nyquist, R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, San Diego, CA, 1997, pp. 98–99.
[13] J. Pérez-Rigueiro, C. Jiménez, R. Pérez-Casero, J.M. Martínez-Duart, J. Vac. Sci. Technol. B 14 (1996) 2623.