Thin Solid Films 518 (2010) 4714–4717

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Synthesis of epitaxial $BaZrO_3$ thin films by chemical solution deposition

R.B. Mos [a,*], M.S. Gabor [a], M. Nasui [a], T. Petrisor Jr. [a], C. Badea [a], A Rufoloni [b], L. Ciontea [a], T. Petrisor [a]

[a] Technical University of Cluj, 15, C. Daicoviciu Street, 400020 Cluj-Napoca, Romania
[b] ENEA Frascati, Via Enrico Fermi 45, 00044, Frascati, Roma, Italy

ARTICLE INFO

Available online 24 December 2009

Keywords:
Barium zirconate
Thin films
Chemical solution deposition

ABSTRACT

This work reports on the low temperature preparation and characterization of $BaZrO_3$ (BZO) epitaxial thin films by chemical solution deposition (CSD). The X-ray θ–2θ scan and φ-scan measurements have demonstrated that the BZO films exhibit cube-on-cube epitaxy on (100) MgO substrates, with the full width at half maximum (FWHM) for the ω-scan and φ-scan of 0.35° and 0.46°, respectively. The SEM and AFM analyses revealed that the morphology of the films is strongly correlated with annealing temperature. The root mean square roughness for the film annealed at 600 °C is 3.63 nm, while for the film grown at 1000 °C is 5.25 nm.

1. Introduction

Pure and rare earth oxide doped barium zirconate, $BaZrO_3$ (BZO), with perovskite structure have attracted much attention due to their good chemical and mechanical stability, high protonic conductivity merging into microelectronic device applications such as: ferroelectric memories, IR piezoelectric sensors, micro-electromechanical systems, insulators [1]. Furthermore, BZO can be successfully used as buffer layer in the $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting architectures due to its structural compatibility with YBCO and similar thermal expansion coefficients [2]. At the same time, BZO is the most attractive material to induce artificial pinning centers both in $YBa_2Cu_3O_{7-x}$ (YBCO) bulk melt textured and thin films, in order to increase the critical current density [3,4]. The main reasons for using BZO as artificial pinning centers in YBCO are: (a) BZO has a high melting temperature with respect to YBCO and so the growth kinetics should be slow, leading to small particles, (b) zirconium does not substitute in the YBCO structure and (c) although BZO grows epitaxially, having the same epitaxial relationship as YBCO, due to its relative large lattice mismatch with YBCO (approximately 9%), the strain between the phases could introduce defects for enhanced pinning.

The chemical solution deposition (CSD) is very promising since this technique fulfils the requirements for the fabrication of functional oxide thin films even at industrial level (versatility, low vacuum, inexpensiveness, high deposition rate, easy control of the stoichiometry etc.) [5]. Metal-organic deposition (MOD), as a variant of the CSD method, uses metal alkoxides, carboxylates (acetates, trifluoroacetates, propionates, and naphthenates) and acetylacetonates as precursors [1]. The use of polar solvents with free hydroxyl group (e.g. propionic acid) provides high texture transfer capability, good wetting properties while avoiding the use of toxic solvents, as well as reduced the annealing temperature [6].

In this paper we report on the deposition and characterization of epitaxial oriented BZO thin films obtained by a propionate-based MOD method. The chemistry of the coating solution is also presented.

2. Experimental

2.1. Coating solution synthesis and characterization

The coating solution was prepared starting from barium acetate $Ba(CH_3COO)_2 \cdot xH_2O$ and zirconium acetylacetonate $[Zr(CH_3COCHCOCH_3)_4] \cdot xH_2O$. While the zirconium acetylacetonate was simply dissolved in an excess of propionic acid C_2H_5COOH, the barium acetate was separately dispersed in methanol, an excess of propionic acid was added and further treated with ammonia until the solution became clear. The two solutions were mixed together under stirring and concentrated by distillation under vacuum (42 mbar, bath temperature 75 °C) for the removal of solvents. The nature of the coating solution was investigated by Fourier Transformed Infrared Spectroscopy (FT-IR) using a Perkin Elmer Spectrum BX system. The aging of the coating solution was studied by NMR relaxometry, a completely nondestructive and noninvasive technique [7]. The experiments were performed on a Bruker MINISPEC MQ20 spectrometer operating at a proton resonance frequency of 20 MHz. The data were recorded at 20 °C using the standard Carr–Purcell–Meiboom–Gill (CPMG) technique [8]. The length of one hard 90° pulse was 2.5 μs. The echo time of the experiments was chosen as 300 μs to prevent the appearance of diffusion effects on echo decay.

* Corresponding author. Tel.: +40 264 599855; fax: +40 264 592055.
E-mail address: Ramona.Mos@chem.utcluj.ro (R.B. Mos).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.12.066

2.2. BZO thin film deposition and characterization

The BZO coating solution was spun on (001) MgO substrates at a spinning rate of 3000 rpm for 60 s. The dried films were heat treated in air in the temperature range from 600 °C to1000 °C for 2 h at a rate of 10 °C/min and cooled down to room temperature at the same rate. The structural properties of the as obtained BZO thin films were investigated by X-Ray Diffraction (XRD) analyses using a Bruker D8 Discover diffractometer with the Cu $K\alpha_1$ radiation. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) using a LEO 1525 field emission-high resolution scanning electron microscope and a Veeco D3100 atomic force microscope, respectively, were used for the investigation of the film morphology. The AFM images were analyzed using the WSxM software [9].

3. Results and discussions

3.1. Coating solution characterization

FT-IR spectroscopy measurements were performed in order to study the nature of the coating solution. The results for the coating solution are presented in Fig.1. Vibration modes corresponding to propionic acid have been identified in the coating solution, the most significant being at 1711, 1466, and 1284 cm^{-1} attributed to the C O asymmetric stretch, CH_3 asymmetric bend and C–O stretch, respectively. This is in good agreement with the initial propionic acid excess. The new vibration modes at 1539 and 1411 cm^{-1} are assigned to the coordination of metals with the propionate ligand. These vibrations have been identified also in the precursor powder as more intense bands, mainly attributed to the asymmetric and symmetric of COO^- stretch in the propionate ligand. The peaks below 660 cm^{-1} are attributed to pure Me–O bond stretching vibrations.

The results of the CPMG transverse relaxation measurements on the coating solution are shown in Fig. 2. The mono-exponential decay of the echo train envelope indicates a good homogeneity of the sample. One can observe that the slope of the CPMG envelope reduces with the aging time. This change in the slope can be associated with the reduction of the paramagnetic centers in the sample as an effect of a crystallization process. Furthermore, it can be observed from the insert that the increase of the transverse relaxation time (T_2) is stronger for the earlier aging times indicating faster crystallization at the beginning of the aging process. Further studies are necessary to determine the correlation between the aging process and the quality of the BZO thin films.

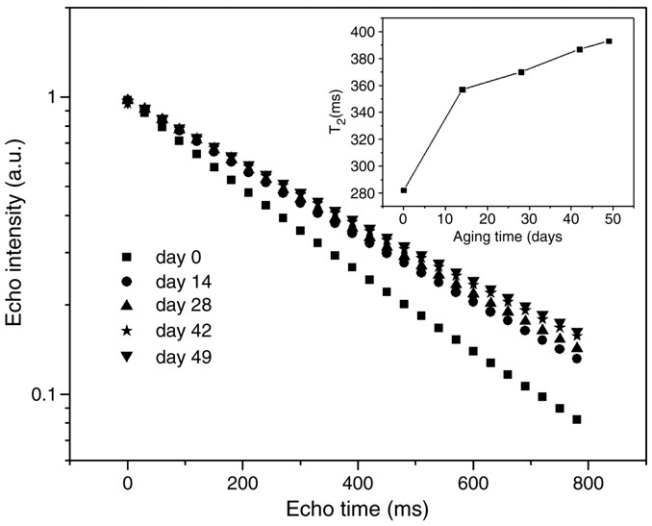

Fig. 2. The echo decays versus evolution time in a CPMG relaxation experiment done on BZO precursor. The observation days are indicated in the legend. The inset shows the extracted transverse relaxation time (T_2) versus aging time.

3.2. Structural and morphological characterization BZO thin films

The X-ray θ–2θ scans of the BZO thin films on single crystalline MgO substrates are presented in Fig. 3. The XRD patterns of the BZO thin films present only (h00) reflections, indicating that all the films are c-axis oriented ([001]BZO//[001]MgO). The indexing of the reflections was based on the perovskite lattice cell of $BaZrO_3$ with a lattice parameter of $a_{BZO} = 4.19$ Å. It is to be noted the good crystallinity of the film heat treated as low as 600 °C. This surprising fact can be explained taking into consideration that thin films have a higher surface area to volume ratio and, as a result, the thin films behave quite differently with respect to bulk materials. With the increase of the annealing temperature, the crystallization proceeds and the intensity of the (200) BZO reflection increases. The ω-scans around the (200) BZO peak demonstrates that all the films have a good out-of-plane orientation. The mean value of the full width at half maximum (FWHM) of the rocking curve is about 0.35°. It is to be noted that, in the limit of the experimental accuracy, no clear dependence of the FWHM with temperature has been observed. The X-ray φ-scan of the (110) BZO peak is presented in Fig. 4. The four

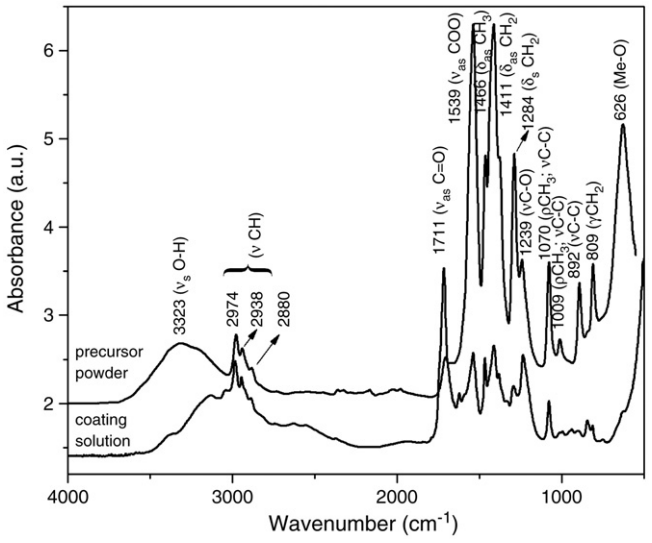

Fig. 1. FT-IR spectra of the BZO coating solution and of the precursor powder.

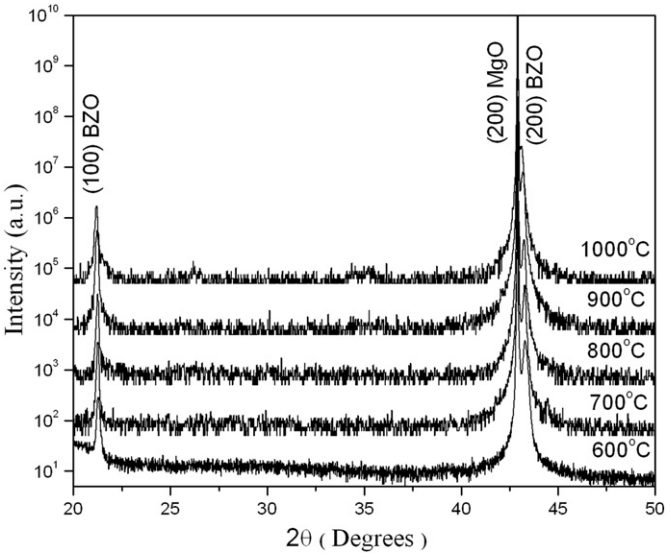

Fig. 3. X-ray diffraction patterns of the BZO thin films annealed at various temperatures.