Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 600 (2006) 1780–1786
SURFACE SCIENCE
www.elsevier.com/locate/susc

Diffusion processes in seeded and unseeded SBT thin films with varied stoichiometry

G. González Aguilar [a], A. Wu [a], M.A. Reis [b], A.R. Ramos [b], I.M. Miranda Salvado [a], E. Alves [b], M.E.V. Costa [a,*]

[a] CICECO, Depto. Eng. Cerâmica e do Vidro, Universidade de Aveiro, Campus de Santiago, Aveiro 3810-193, Portugal
[b] Instituto Tecnológico e Nuclear, Estrada Nacional no 10, P-2685 Sacavém, Portugal

Received 4 November 2005; accepted for publication 31 January 2006
Available online 24 February 2006

Abstract

$SrBi_2Ta_2O_9$ (SBT) is a bismuth layered perovskite (BLP) with interesting ferroelectric properties for memories applications. The previous study on the synthesis of seeded and unseeded SBT thin films by the authors [G. González Aguilar, M.E.V. Costa, I.M. Miranda Salvado, J. Eur. Ceram. Soc. 25 (2005) 2331] has shown an increase of the crystallinity of the films and an improvement of the thin film ferroelectric properties when using SBT seeds. However, the detailed role of the seeds as an improver of the thin film properties has not been investigated so far. In the present work we study the role of the seeds, particularly with respect to the reactions between film and (bottom) underlying platinum electrode. The comparison of the results obtained by characterizing the seeded and unseeded thin films via Rutherford backscattering (RBS) and particle induced X-ray emission (PIXE) techniques reveals an effective modification of the substrate–thin film interface by the presence of the seeds. Moreover, the evaluation of the thin film ferroelectric properties by atomic force microscopy (AFM) shows an improvement of the local piezoelectric hysteresis loops by the seeds. These seeding effects as well as those observed in non-stoichiometric SBT thin films with different bismuth contents are used to discuss the barrier-like role of the SBT seeds against reactions between film and the platinum electrode and its contribution to the improvement of the thin film properties.

Keywords: Surface chemical reaction; Surface diffusion; Rutherford backscattering spectrometry (RBS); Thin film structures; Metal–oxide interfaces; Ferroelectric films

1. Introduction

The intensive research focused on $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) thin films revealed these ferroelectric compounds to be competitive candidates for non-volatile ferroelectric random access memories (NV-FRAMs) applications. The structure of these bismuth layered perovskites (BLP) also known as Aurivillius oxides consists of $Bi_2O_2^{2+}$ layers alternating with strontium tantalate ($SrTa_2O_7^{2-}$) (or strontium niobate ($SrNb_2O_7^{2-}$)) perovskite units, respectively. SBT and SBN present several advantages over other ferroelectric compounds, namely $Pb(Zr_{1-x}Ti_x)O_3$, which include a fatigue-free behavior, good retention properties and low leakage currents [2]. In addition the toxicity issues associated to BLP are of lower concern as they are lead free compounds.

As a consequence of such appealing features, great attention has been focused on the improvement of the less attractive characteristics of these materials. For example, several doping studies were reported for improving the value of the remnant polarization (Pr) [3,4], for reducing the perovskite crystallization temperature [5,6] and even for recovering the properties of the films after fatigue [7]. A different approach based on a seeding procedure, either using seeds like SBT seeds [1], Bi and Bi/Ta seeds [8] or Bi_2SiO_5 seeds [5], or using a seeding layer of $Bi_4Ti_3O_{12}$ [8] has also been successful in improving the thin film characteristics.

* Corresponding author. Tel.: +351 234 370 354; fax: +351 234 425 300.
E-mail address: elisabete@cv.ua.pt (M.E.V. Costa).

0039-6028/$ - see front matter
doi:10.1016/j.susc.2006.01.051

The role of SBT seeds in the crystallization of SBT thin films has been described [9] as promoting the perovskite phase formation by two mechanisms: (1) lowering the activation energy for Aurivillius oxide nucleation and crystal growth, hence favoring its growth kinetics with respect to other coexisting phases such as pyrochlore and (2) allowing diffusion of SBT film bismuth ions driven by bismuth concentration gradients which contribute to the transformation of the existing Bi-deficient pyrochlore seeds into perovskite phase.

Due to the high structural anisotropy of BLP, which have spontaneous polarization vector lying perpendicular to *c*-axis, the crystallographic orientation of the film with respect to the substrate has been also of great concern for optimizing its electrical properties. Some studies have shown that the type and orientation of the interface material between the substrate or seeding layer and the thin film may have a strong effect on the growth of the film [9–13]. However, when using a seeding layer, the contribution of the seeds for the interface chemistry has not been investigated yet.

The objective of the present work is to get deeper insight into the role of the seeds, in particular regarding the bottom electrode–thin film interface phenomena. For this purpose the results obtained via Rutherford backscattering (RBS) and particle induced X-ray emission (PIXE) on seeded and unseeded SBT thin films with varied stoichiometry are used for evaluating the effects of the SBT seeds on the inter-diffusion between the film and underlying electrode constituents. Combining RBS and PIXE results with ferroelectric and atomic force microscopy (AFM) characterization results, a discussion of the effect of stoichiometry deviation and of the seeding procedure in the thin film properties is presented.

2. Experimental

Seeded and unseeded SBT films were prepared by spin-coating organic solutions of the required cations on Si/SiO2/Ti/Pt substrates followed by drying at 180 °C. After several spinning-drying cycles a heat treatment at 720 °C for 30 min was done. The metallorganic solution was prepared by a modified sol–gel procedure: briefly, bismuth acetate (Aldrich, S. Louis), strontium acetate (ABCR, Karlsruhe) and tantalum ethoxide (Fluka, Buchs) were dissolved in an organic solvent mixture (1:1) of toluene (Riedel-de Haën, Seelze) and acrylic acid (Fluka, Buchs), under controlled atmosphere. Different cation proportions were selected so as to obtain nominal stoichiometric and non-stoichiometric (Bi-deficient) compositions. For seeded films, seeds were previously deposited by spin-coating on the substrate. The details of the experimental procedures are published elsewhere [1]. Table 1 identifies the samples used in the current work. The film crystalline structure was analyzed by grazing incidence X-ray diffraction (Philips X'Pert MPD X-ray diffractometer with CuKα radiation), which confirmed the crystalline perovskite structure of all the prepared films without any second phases. The average thickness of the obtained thin films was around 500 nm as evaluated by scanning electron microscopy measurements.

Table 1
Identification of the studied thin films

Thin film stoichiometry	Sample code*	Heat treatment temperature (°C)	Seeds
$SrBi_{1.5}Ta_2O_9$	U72-1.5	720	No
$SrBi_{1.7}Ta_2O_9$	U72-1.7	720	No
$SrBi_{1.9}Ta_2O_9$	U72-1.9	720	No
$SrBi_{1.9}Ta_2O_9$	S72-1.9	720	Yes
$SrBi_2Ta_2O_9$	U72-2.0	720	No
$SrBi_2Ta_2O_9$	S72-2.0	720	Yes

* S stands for seeded; U stands for unseeded; 7× indicates heat treated at 7 × 0 °C; *y.z* stands for Bi stoichiometry ($Bi_{y.z}$).

Rutherford backscattering spectrometry (RBS) and particle induced X-ray emission (PIXE) analyses were performed using a 2.5 MV Van de Graaff Accelerator. RBS spectra were obtained with 2 Schottky barrier detectors placed in IBM geometry at 140° and 180° scattering angles, with resolutions of 15 and 25 keV, respectively, using a 2.250 and a 2 MeV He^+ beam. Analyses were performed with samples tilted at 0°, 20° or 30° (angle between beam direction and sample normal). PIXE measurements were performed with a 2.15 MeV H^+ beam and the X-rays were detected with a Gresham Scirus detector with 155 eV energy resolution placed at 110° to beam direction and at a distance of 25 mm from the samples. The PIXE spectra were analysed using the AXIL [10] and DATTPIXE codes [11] and RBS spectra with the NDF code [12].

The ferroelectric properties were measured with a TFA analyzer (AIXACCT, Model: TFA-LI). The film surface topography was analyzed by atomic force microscopy (AFM) using commercial AFM equipment (Multimode, Nanoscope IIIA, Digital Instruments). A conductive Pt-coated Si tip-cantilever (NSG01/Pt, NT-MDT Co., Russia) system was used as a top electrode and for vibration detection. Local piezoelectric hysteresis loops were performed via piezoresponse mode (PFM) that relies on a local piezoelectric effect exhibited by film's surface.

3. Results and discussion

In the RBS spectra, the Sr, Bi and Ta backscattering signals appear convoluted, thus impairing a direct determination of the Ta, Sr and Bi concentrations from these spectra. To overcome this inconvenient the samples were analyzed by PIXE. The results obtained showed that, with the exception of sample U72-1.5, the composition of the films does not deviate significantly from the nominal composition. As regards the nominal non-stoichiometric films, which were prepared with specific Bi deficiencies (Table 1), the combined PIXE–RBS results confirmed them to be non-stoichiometric, though with slight variations from the nominal composition. Selected results are shown in Table 2.

The Ta/Sr and Bi/Sr ratios determined by PIXE were used for simulating the experimental RBS spectra, thus