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Journal of the European Ceramic Society 24 (2004) 319–323

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Nanoscale properties of ferroelectric ultrathin SBT films

R. Jiménez[a,*], M.L. Calzada[a], A. González[a], J. Mendiola[a], V.V. Shvartsman[b], A.L. Kholkin[b], P.M. Vilarinho[b]

[a]*Instituto Ciencia de Materiales de Madrid (CSIC). Cantoblanco, 28049 Madrid, Spain*
[b]*Departamento de Engenharia Ceramica e do Vidrio, Universidade de Aveiro, 3180 Aveiro, Portugal*

Abstract

Strontium bismuth tantalate (SBT) ultrathin films with thickness about 40 nm have been prepared by a chemical solution deposition (CSD) method based on the synthesis of a Ta-glycolate derivative. Layers of the precursor solution diluted with 2-ethyl-1-hexanol were spin-coated onto $Pt/TiO_2/SiO_2/(100)Si$ substrates. Crystallisation was carried out in oxygen at 650 °C by Rapid Thermal Processing (RTP). Topography of the films was observed by Scanning Force Microscopy (SFM). The piezoresponse mode of the SFM equipment was used to perform the nanoscale observation of the ferroelectric domain structure of the SBT ultrathin films and to measure piezoelectric hysteresis loops. The macroscopic ferroelectric response was measured on capacitors prepared after the deposition on the film surfaces of top platinum electrodes of ~0.05 mm^2 of area.

Keywords: Ferroelectric properties; Films; SBT; $SrBi_2Ta_2O_9$; Tantalates

1. Introduction

During the last years, the interest on the development of non-volatile ferroelectric random access memories (NVFERAM) has grown very rapidly.[1] It is expected that in a near future dense ultrathin films would be required, thus to get very small memory cells (150×150 μm^2) for high-density memories (>1 Gbit).[2] Strontium bismuth tantalate (SBT) has shown to be an appropriate candidate for these devices. This layered perovskite can be integrated with Si substrates with Pt electrodes, where the material exhibits low fatigue and high retention.[3]

Different deposition techniques have been used for the preparation of these films. Among them, solution deposition processes such as sol-gel are versatile methods that permit to fabricate films inside of a wide range of compositions, with a precise stoichiometric control and at low cost.[4] Besides, the possibility of the control of the solution at molecular level makes possible to obtain films with controlled textures and microstructures and with various thickness (from tens of nm to hundreds of nm). In this way, very thin continuous and dense ferroelectric SBT films have been previously prepared in our laboratory.[5] Here, we show the ferroelectric properties of these films at a macroscopic scale. Also, preliminary results of characterisation of the films at local scale are presented. The local properties were investigated by means of Scanning Force Microscopy (SFM) working in piezoresponse mode. This technique offers a non-destructive high-resolution imaging of domains in ferroelectric films and provides information about the properties of ferroelectric capacitors scaled to the submicrometer range.[6] This method provide to be very useful for development of the high-density ferroelectric memories.

2. Experimental

Strontium bismuth tantalate (SBT) precursor solutions with a nominal composition of $Sr_{0.8}Bi_{2.2}Ta_2O_9$ and with concentrations of 0.9×10^{-2} M, 1.8×10^{-2} M and 3.7×10^{-2} M were prepared using a chemical process published elsewhere.[7] Viscosity of the solutions was measured at 20 °C with a digital viscosimeter Brookfield DV-III+. 20, 10 and 5 successive layers of the solutions were spin-coated onto $Pt/TiO_2/SiO_2/(100)Si$ substrates. Each layer was dried at 225 °C for 15 min and the multilayer stack was subjected to rapid thermal processing (RTP) in O_2 at 650 °C for 1 h, using a heating rate of ~200 °C/s. SBT films derived from the 0.9×10^{-2} M, 1.8×10^{-2} M and 3.7×10^{-2} M solutions are called as UTF1, UTF2 and UTF3, respectively. Thickness of the

* Corresponding author.
E-mail address: riqjim@icmm.csic.es (R. Jiménez).

0955-2219/03/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0955-2219(03)00227-9

crystalline films was measured by profilometry and X-ray reflectivity (XRR). Crystalline phases developed in the films were detected by grazing incidence X-ray diffraction (GIXRD). Also, conventional X-ray diffraction in Bragg–Brentano geometry was performed to study the possible preferred orientation in the films.

Top platinum electrodes of ~0.05 mm^2 area were deposited on the film surfaces. The capacitor was treated at 500 °C for 10 min in O_2 by RTP to reduce leakage current. Conventional electric displacement against electric field (continuous sine voltage signal), D–E hysteresis loops were obtained using a HP 8116A function generator, a Keithley 428 current amplifier and a Tektronix TDS520 oscilloscope. The remnant polarisation against electric field, P_r–E loop, was obtained by the method of pulsed hysteresis loops developed by the authors.[8] Retention (3 V) and fatigue (1 MHz, 3 V) measurements have been performed with the RT66A equipment coupled to an external function generator for fatigue measurements. The top electrode was positively biased in all the electrical measurements.

The topography and domain structure of the films were obtained simultaneously by the SFM operating in a piezoresponse mode. A small driving ac voltage with the amplitude of 1 V and frequency of 35 kHz was applied between the conducting tip and bottom electrode for visualisation of the domain structure of the film.[9] To study nanoscale polarization switching, the local piezoelectric loops were acquired. In this measurement, the tip was stopped and short dc pulses of 0.5 s duration were applied. Pulses were separated by time intervals of 5 s, where a small ac voltage of 1V was applied to measure the piezoresponse signal. The dc voltage was stepped cyclic from −9.5 V to + 9.5 V (well above the coercive voltage of the film). In the local measurements, the tip was grounded.

3. Results and discussion

In this work, we have prepared dense ultrathin SBT films with an average thickness of ~40 nm, using the spin-coating deposition of solutions synthesised by sol-gel. 2-Ethyl-1-hexanol was used as a solvent for the dilution of the stock solution. Physico-chemical characteristics of this alcohol allowed us to obtain solutions with suitable viscosity and surface tension for the wetting of the substrate. These properties in combination with the very low concentration of the solutions make possible the fabrication of ultrathin films with a substrate completely covered by the ferroelectric layer, without the formation of islands. Table 1 presents the concentration and viscosity of the solutions related with the thickness of the single layer and the number of coatings needed for the fabrication of 40 nm thick films. As expected, the thickness of a single layer increases as the concentration and the viscosity of the precursor solution increases [Fig. 1(a)]. Thus, smaller number of coatings for more concentrated solutions has to be deposited for the preparation of films of the same thickness [Fig. 1(b)].

The layered SBT perovskite is the only crystalline phase detected in the X-ray patterns of the films (Fig. 2), without remarkable preferred orientation in the Bragg-Brentano X-ray diffraction pattern (not shown). However, SFM

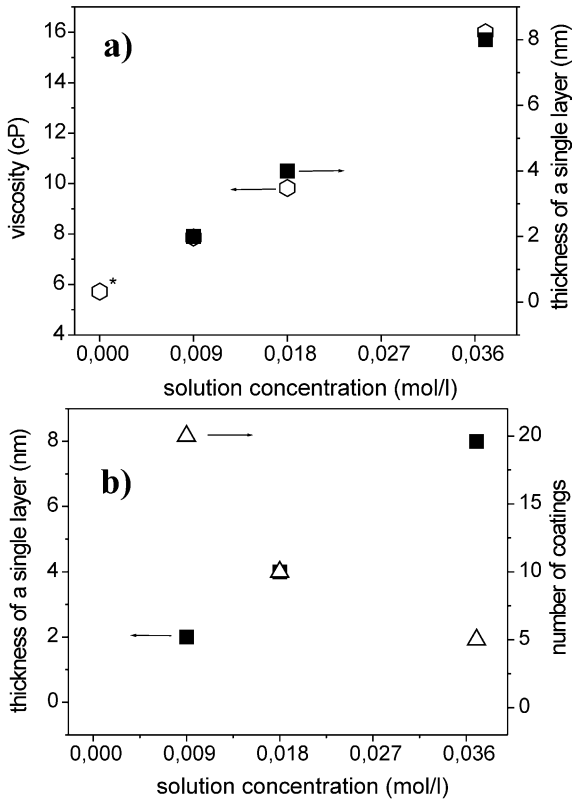

Fig. 1. (a) Viscosity of the precursor solution and thickness of a single layer vs. solution concentration; (b) thickness of a single layer and number of coatings vs. solution concentration.

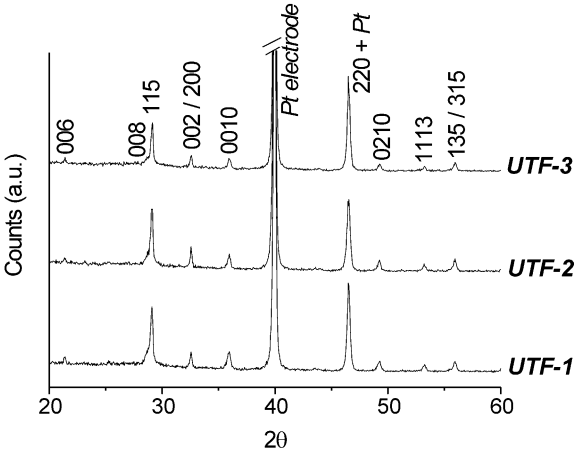

Fig. 2. GIXRD patterns of the films UTF1, UTF2 and UTF3.

studies reveal the coexistence of two phases with different morphology: big SBT grains with size around 100–50 μm and a nano-crystalline phase (grain size ~ 10–50 nm) [Fig. 3(a)].

As explained previously the macroscopic characterisation was carried out on capacitors with top Pt electrodes that cover a film surface containing both the SBT grains and the nanocrystals [see Fig. (3a)]. Well-defined ferroelectric polarization loops are obtained for all the films. Fig. 3b shows the loop corresponding to the UTF2 film. A remnant polarisation of $P_r > 5$ μC/cm^2 is obtained after correction of the non-ferroelectric charge with coercive voltage $V_c = 0.68$ V and a bias voltage (defined as $(V_c^+ - V_c^-)/2$) of −0.22 V [Fig. 3(b)]. This means that high enough charge for memory function is obtained at a very low voltage, which is quite convenient for the use of these materials in CMOS circuits as NVFERAM. Besides, these ultrathin SBT films have good fatigue endurance (10% of reduction of non-volatile polarization at 10^{10} cycles) with a lower retention performance (33% reduction of non-volatile polarization at 10^5 s).

Comparison between simultaneously acquired topographic and piezoresponse images of the UTF2 film [Fig. 4(a) and (b)] reveal correlation between surface morphology and ferroelectric properties. Namely, the piezoelectric contrast indicating the existence of out-of-plane polarization was revealed only in the big grains, which are associated with SBT phase. In our experimental conditions the bright and dark contrast correspond to upward and downward polarization direction, respectively. The nano-crystal phase shows a grey contrast that indicates absence of out-of-plane polarization. Polarization in SBT grains may be switched by local application of opposite dc voltage, while remains zero in nano-crystallites. These observations point to non-ferroelectric character of nano-crystal phase. This conclusion has been confirmed by preliminary selected area electron diffraction (SAED) analysis. More experimental work is needed for the publication of the full data. The SAED results seem to indicate that the nanophase is a

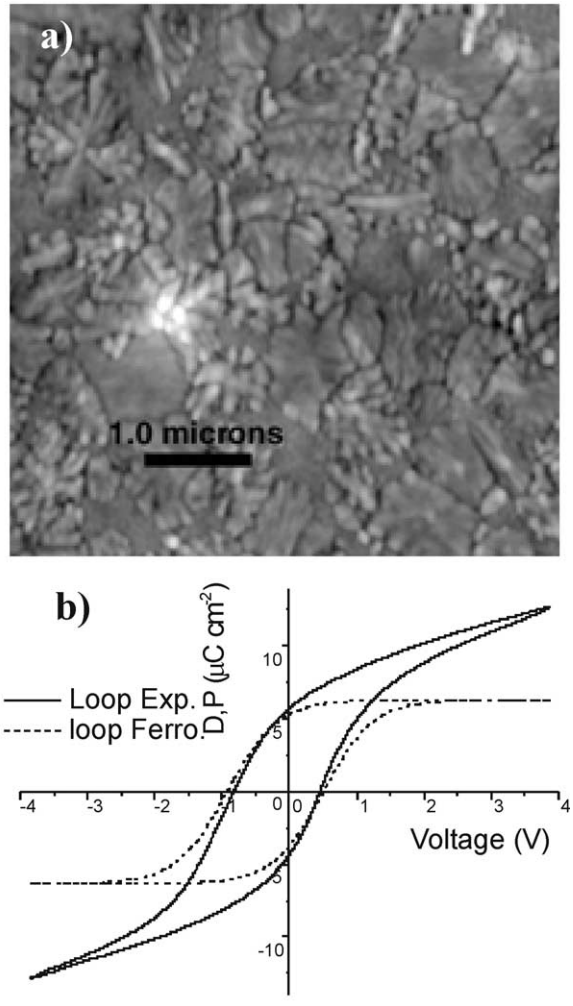

Fig. 3. (a) SFM topography image of the SBT ultrathin films; (b) ferroelectric hysteresis loop of the UTF2 film. The solid line is the experimental loop, the dashed line is the pure ferroelectric polarization loop obtained following the procedure in Ref. 12.

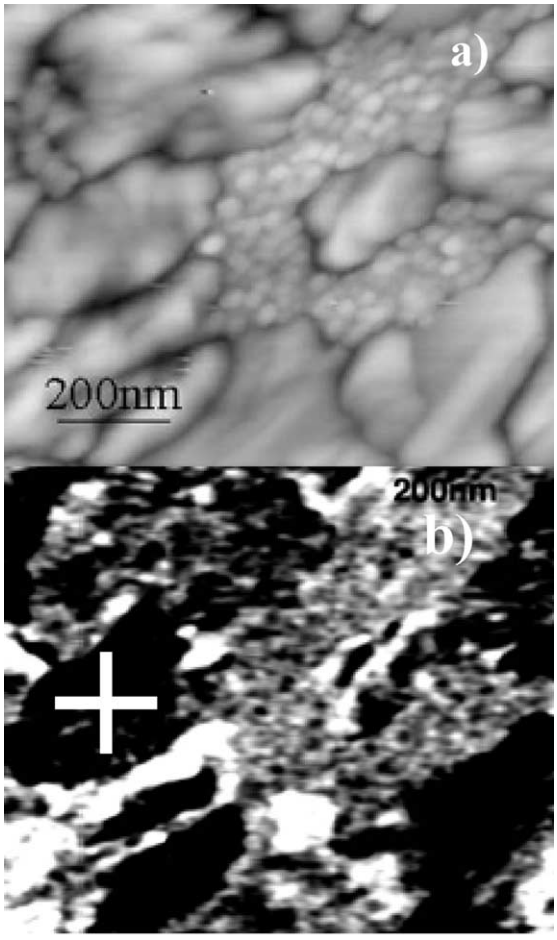

Fig. 4. (a) SFM topography image of the ultrathin films where SBT grains and a second nanocrystal phase are observed; (b) Piezoresponse (domains) image of the SBT ultrathin film.

metastable fluorite that only occurs in the layered SBT perovskite at temperatures over 650 °C.

The distinct local piezoelectric hysteresis loops [Fig. 5(a) and (b)] were acquired in the interior of SBT grains [see the white cross in Fig. 4(b)]. A repeated switching of the grain produces a shift of the loops upward that may indicate a formation of non-switchable layer due to charge trapping at the film/electrode interface during switching.[10] It should be noted that the piezoresponse is likely measured in a single domain, since the thickness of the film is very low, of the order of the grain size (~40 nm). In order to make a comparison between macroscopic and local hysteresis loops, both pulsed polarization loop and local piezoelectric loops were normalized to the maximum value (Fig. 5a). The coercive voltage are $V_c = 1.1$ V and 2.75 V for the ferroelectric and piezoelectric loop, respectively, simultaneously a strong bias voltage is observed in both loops being −0.2 V and −0.93 V, respectively. Difference in parameters of the loops may be attributed to different measured procedures, presence of the second non-ferroelectric phase in the SBT capacitor and the random orientation of grains. Increase in the coercive voltage of the local loop was mainly due to the increase in the negative coercive voltage, which cannot be due only to grain orientation,[11] supporting the charge trapping in the bottom interface. The increase in the coercive field can be related also to the poor contact between the tip and the film surface in comparison to the macroscopic top Pt/ferroelectric interface.

The high asymmetry found in the remnant loops seems to be related to the bottom electrode/ferroelectric interface and is the responsible for the relatively poor retention of the films despite of their excellent fatigue endurance.

Summarising, ultra-thin SBT films with good properties for their use in NVFERAM have been prepared. Ferroelectric domain structure of the films was visualized with nanoscale resolution using SFM. The presence of a second non-ferroelectric nano-crystal phase was revealed. Grains of the layered SBT perovskite phase demonstrated a clear domain structure. They are switchable under application of dc voltage in both macroscopic and nanoscale measurements. Further investigation is needed to correlate the electrical properties of the films at submicron and macroscopic scales.

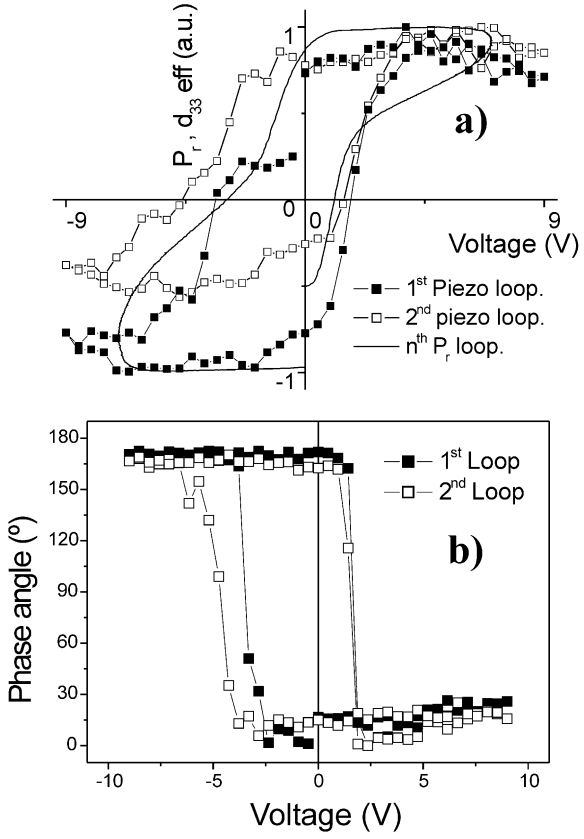

Fig. 5. (a) Normalized remanent Piezoelectric hysteresis loops measured in the domain signed with a cross in the piezoresponse image and the macroscopic remanent ferroelectric loop measured with top Pt electrode; (b) phase of piezoresponse signal measured in the domain signed with a cross in the piezoresponse image showing almost complete switching.

Acknowledgements

This work has been supported by the Spanish–Portuguese project HP2000-0069 and it is in the frame of the EU COST528 action. Dr R. Jiménez acknowledges the "Ramón y Cajal" program of the Spanish MCyT for financial support.

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