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Rapid thermal processing of strontium bismuth tantalate ferroelectric thin films prepared by a novel chemical solution deposition method

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Abstract

Strontium bismuth tantalate (SBT) thin films have been deposited on $Pt/TiO_2/(100)Si$ substrates by chemical solution deposition (CSD), using air-stable solutions synthesised by a sol–gel method. Solutions with different Bi/Sr ratios have been tested for the deposition of the films. These ratios and the type of thermal treatment used for the crystallisation of the films have effect on the microstructure. Adequate ferroelectric responses have been measured in films with a Bi/Sr ratio of 2.75 and prepared with a direct thermal treatment that consists of a rapid thermal processing (RTP) at 650°C with a heating rate of ~200°C/s. A coercive field of E_c~60 kV/cm and a remanent polarisation of P_r~11 μC/cm^2 have been measured in these films. They retain their P_r up to ~10^5 s and they are fatigue-free up to ~10^{10} cycles.

Keywords: Ferroelectric properties; Films; Sol–gel processes; Tantalates

1. Introduction

Strontium bismuth tantalate (SBT) thin films have been extensively investigated during the last years for their use in non-volatile memory applications.[1] These films have been prepared by different deposition techniques.[2–4] All of these techniques have to use high temperatures (>750°C) for the fabrication of films with good properties. At these temperatures, the electrode-substrate stack exhibits severe instability and interactions between the SBT film and the substrate occur. Thus, lowering of the processing temperature is one of the major objectives in the preparation of these films.

Among the deposition techniques, chemical solution deposition (CSD) methods have been widely used in the literature for the preparation of SBT films.[5,6] The precursor compounds used in CSD methods for the preparation of these films are difficult to handle due to their toxicity and their sensitivity to moisture. Thus, SBT precursor solutions used in CSD have low stability that decreases the homogeneity and reactivity of the precursors and reproducibility of the process.

Here, we prepare SBT films at low temperatures and with short-time thermal processes by CSD, using air-stable precursor solutions. The films obtained have appropriate properties for their use in non-volatile ferroelectric memories (NVFERAM).

2. Experimental

Solutions of tantalum, strontium and bismuth were prepared separately.[7] Tantalum pentaethoxide, $Ta(OC_2H_5)_5$, was refluxed at ~185°C for 8 h in 1,3-propanediol, $C_3H_6(OH)_2$. Strontium 2-ethyl-hexanoate, $Sr(C_7H_{15}COO)_2$, was refluxed at ~110°C for 8 h in a mixture of $C_3H_6(OH)_2$ and 2-ethyl-hexanoic acid, $C_7H_{15}COOH$. Bismuth 2-ethyl-hexanoate, $Bi(C_7H_{15}COO)_2$ was refluxed at ~70°C for 3 h in $C_7H_{15}COOH$. All the solutions were prepared and stored in air. Aliquots of the three solutions were mixed to obtain SBT precursor solutions with four different nominal compositions: $SrBi_2Ta_2O_9$ (Bi/Sr molar ratio of 2.00), solution I, $SrBi_{2.2}Ta_2O_9$ (Bi/Sr molar ratio of 2.20), solution II, $Sr_{0.8}Bi_2Ta_2O_9$ (Bi/Sr molar ratio of 2.50), solution III, and $Sr_{0.8}Bi_{2.2}Ta_2O_9$ (Bi/Sr molar ratio of

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2.75), solution IV. 2-ethyl-hexanol was the solvent used to dilute these solutions down to ~0.05 mol/l and to make miscible the diol and the carboxylic acid.

Solutions were deposited by spin-coating at 2000 rpm for 45 s onto $Pt/TiO_2/SiO_2/(100)Si$ substrates. Drying of the wet layers was made on a hot plate at 225°C for 15 min. Successive depositions and dryings were carried out previous to the crystallisation of the film. Two thermal schedules were followed for the crystallisation of the films: (1) a two-step thermal process in which formation of intermediate fluorite films is obtained by direct insertion of the amorphous films into a tubular furnace preheated at 550°C for 2 h, in oxygen flow. Further crystallisation of the Aurivillius phase is obtained by a rapid thermal processing (RTP) in oxygen, at 650°C for 1 h with a heating rate of ~200°C/s. (2) A single-step thermal process in which the amorphous films are directly crystallised by the mentioned RTP process. The crystalline SBT films had an average thickness of 300–400 nm.

Crystalline phases developed in the films were monitored by grazing incidence X-ray diffraction (GIXRD) with a Siemens D500 difractometer, using a grazing angle of $\alpha = 2°$. Scanning electron microscopy (SEM) was used to observe the morphology of the top surfaces of the SBT films with a microscopy ISI DS-130C model.

Top platinum electrodes between 5×10^{-4} and 7×10^{-4} cm^2 were deposited by cold sputtering on the film surfaces. Hysteresis loops were traced with a Radiant Technology Inc. testing system, RT66A model. A triangular signal of 100 Hz and 12 V of frequency and amplitude, respectively, was used for the measurements. Remanent polarisation, P_r, of the films was also measured using the same Radiant equipment by the five pulse method.[8] Retain and fatigue were also measured with this equipment joined to an external pulse generator for the fatigue measurements. Pulses of 8 V of amplitude and 500–1000 kHz were used to perform fatigue and retain measurements.

3. Results and discussion

The chemical routes followed in the chemical solution deposition of SBT films give unstable precursor solutions. Synthesis has to be carried out in dry atmospheres to avoid a quick hydrolysis and condensation of the solutions that would damage the rheological properties of the solutions appropriate for the deposition of the films.

In this work, we synthesise SBT precursor solutions by a novel chemical process[7] that provides solutions with a high resistance towards hydrolysis. This low hydrolysis rate increases homogeneity and reactivity of the chemical system, making feasible to bring the crystallisation temperature down.

Fig. 1 shows the GIXRD patterns of the films deposited from the different solutions and obtained with the two thermal processes described above. Fig. 1a corresponds to

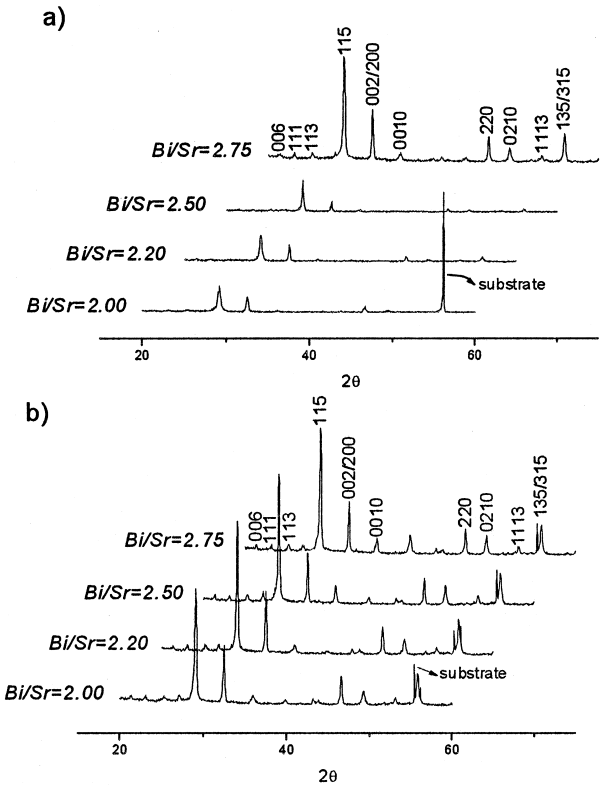

Fig. 1. GIXRD patterns of the SBT films with different Bi/Sr ratios and crystallised by (a) the two-step thermal process and by (b) the single-step thermal process.

the films in which the fluorite phase has been stabilised previous to the formation of the SBT phase. Other authors have reported that fluorite films easily transform into the SBT without the development of undesirable second phases.[9] However, we have not observed appreciable differences among the GIXRD patterns of the films crystallised with the two-steps thermal process (Fig. 1a) and those of the films directly heated at 650°C (Fig. 1b).

The SEM images of the top surfaces of the films prepared with the two-steps and the single-step thermal treatments are shown in Figs. 2 and 3, respectively.

Films prepared with the intermediate fluorite step and with low Bi/Sr ratios have small equi-axed grains and a large number of voids. Rod-shaped grains and a low porosity are developed in the films with a Bi/Sr ratio of 2.75 (Fig. 2). Other authors have reported that this difference in the morphology of SBT films with different compositions is a function of the crystal structure that depends on the amount of Bi occupying Sr-sites.[9] The Bi amount in Sr-sites increases with the Sr-deficiency and this seems to induce fine-equi-axed-grained microstructures. But, this microstructural evolution with composition is not detected in the films directly crystallised by RTP at 650°C (Fig. 3). All of them have rod-shaped grains and the average grain size is substantially larger than that of the corresponding film prepared with the intermediate fluorite step. The SEM images of Fig. 3 seem to indicate

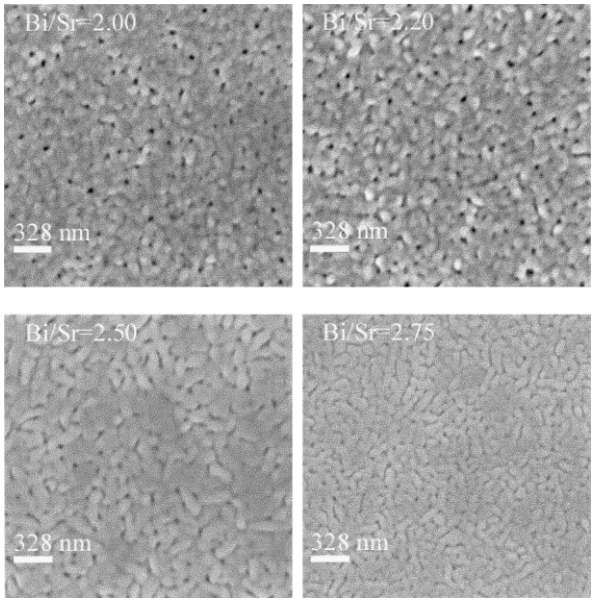

Fig. 2. SEM images of the surfaces of the SBT films with different Bi/Sr ratios and crystallised by the two-step thermal process.

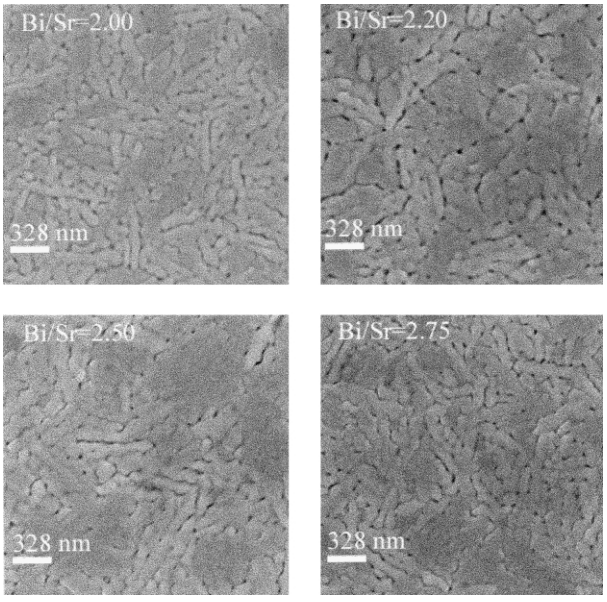

Fig. 3. SEM images of the surfaces of the SBT films with different Bi/Sr ratios and crystallised by the single-step thermal process.

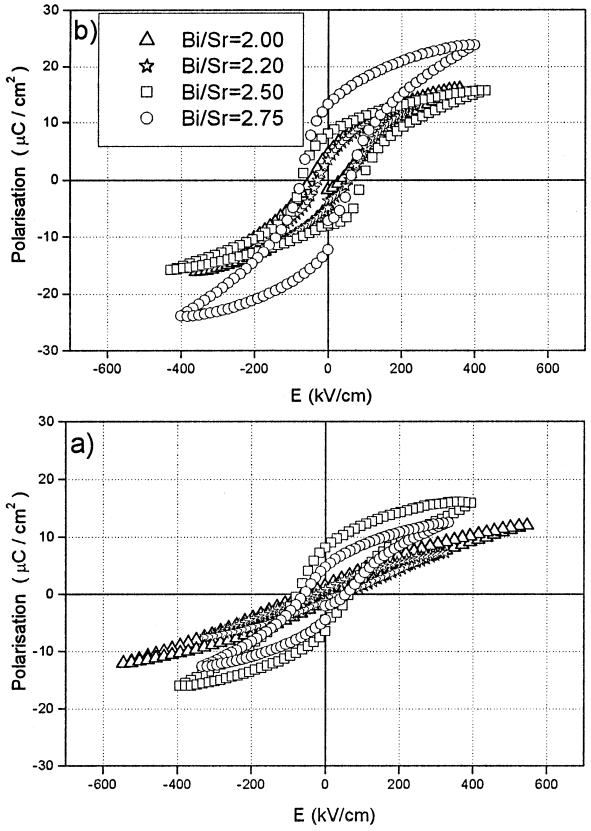

Fig. 4. Hysteresis loops of the SBT films with different Bi/Sr ratios and crystallised by (a) the two-step thermal process and (b) the single-step thermal process.

Table 1
Remanent polarisation, P_r, obtained from the measurements using the five pulse method,[8] for the SBT films with different Bi/Sr ratios and crystallised by the two-step and single-step thermal process

Bi/Sr ratio	P_r (μC/cm^2)	
	Two-step treatment	Single-step treatment
2.00	2.3	4.5
2.20	1.2	5.2
2.50	5.1	8.2
2.75	5.8	11.2

that the major effect on the film microstructure is produced by the type of thermal treatment used for the crystallisation of the SBT films and not by the strontium deficiency and/or bismuth excess.

Better-defined hysteresis loops and higher remanent polarisations, P_r, are obtained for the films directly crystallised by RTP than for those films prepared with the two-steps thermal treatment (Fig. 4 and Table 1). This is probably related with the larger grain size of the first films. Composition seems also to have a considerable effect on the ferroelectric response. The films with Bi/Sr ratios of 2.50 and 2.75 have well-defined loops, whereas the films with a Bi/Sr ratio of 2.00 and 2.20 have a poor ferroelectric response with low values of remanent polarisation, P_r.

Cheon et al.[10] obtained similar results for SBT films with different Bi/Sr ratios. They suggested that the use of large Bi/Sr ratios produced films with good ferroelectric properties due to their low content of impurity phases accompanying to the SBT phase, their good crystallinity and large grain sizes compared with films with a low content of bismuth excess. Here, ferroelectric

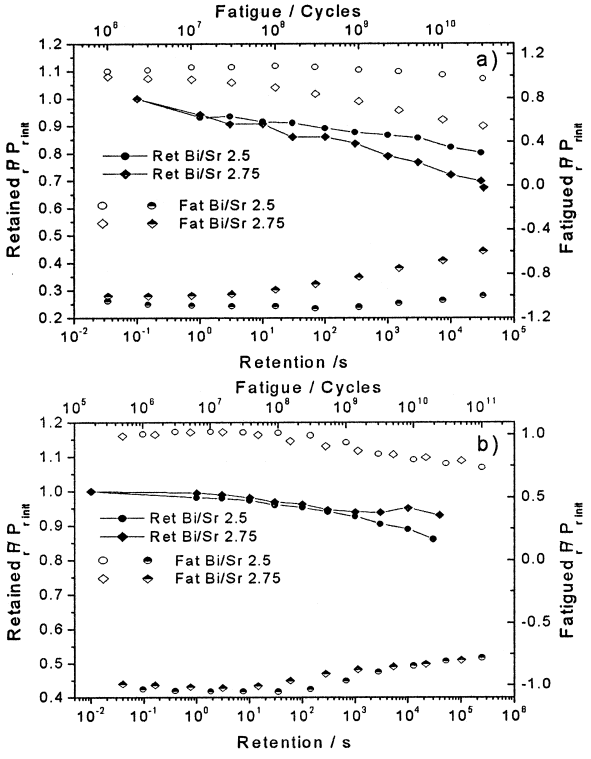

Fig. 5. Retention and fatigue of the SBT films: (a) with Bi/Sr ratios of 2.50 and 2.75, and crystallised by a two-step thermal process and (b) with Bi/Sr ratios of 2.50 and 2.75, and crystallised by a single-step thermal process. Values of retention and fatigue of the figures have been normalised.

properties also improve in the films directly crystallised by RTP, probably due to the increase in the grain size of these films produced by this treatment.

Switching times, retain and fatigue were measured only in the films prepared with the larger ratios of Bi/Sr, because these are the films that have enough values of P_r for their application in memories.

Switching times were ~300 ns for a size of the top electrode between 5×10^{-4} and 7×10^{-4} cm^2.

Fig. 5a and 5b shows the retention and the fatigue of the films with Bi/Sr ratios of 2.50 and 2.75, and crystallised by the two-step and by the single-step thermal processes, respectively. The better values of retain and fatigue have been obtained in the film with the highest Bi/Sr ratio, 2.75, and directly crystallised by RTP. This film has a ~10% of reduction of P_r after ~10^5 s (retention) and ~20% of reduction of P_r, after ~10^{10} cycles (fatigue).

Summarising, the results of this work indicate that the Bi/Sr ratio plays an important role in the fabrication of SBT films with adequate performances. It has to be noted the possibility here shown of obtaining well-crystallised SBT films with short-time and low-temperature treatments, is always provided that the chemical process would be adequately controlled. In this way, SBT films with well-defined ferroelectric responses have been obtained at 650°C with single thermal treatments no longer than 3600 s.

Acknowledgements

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