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Improving the synthesis and properties of SBT thin films by using SBT seeds

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Abstract

Among the different materials studied for ferroelectric applications, $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) have deserved a particular interest for the production of non-volatile random access memories (NVFRAMs) due to their fatigue endurance properties. However, the high temperatures required for obtaining these Aurivillius compounds in a straightforward way make necessary to search alternative procedures to synthesize them. In this work the approach of using SBT seeds to improve the synthesis of SBT thin films by a sol–gel procedure is studied and their effects on the thin film properties are evaluated. XRD and SEM analysis of the obtained seeded and unseeded thin films, annealed at different temperatures, show that the use of SBT seeds lowers the crystallization temperature of the perovskite phase and affects the thin film microstructure inducing the development of well defined and more elongated grains. Dielectric and ferroelectric properties are also improved by the seeding procedure. The characteristics of the seeded films annealed at 720 °C for 20 min show that the present technique has the advantage of requiring smoother annealing conditions than currently reported methods for producing films with comparable characteristics.

Keywords: Thin films; Sol–gel process; Ferroelectric properties; Functional applications

1. Introduction

In the last years bismuth layer structured (BLS) perovskites have been under intensive research as materials for ferroelectric devices. $SrBi_2Ta_2O_9$ (SBT) is a well known member of this family showing promising characteristics, such as fatigue endurance, little tendency to imprint and low leakage current, which raise its effectiveness to be used in memory devices.[1–3] Nevertheless, this compound presents lower values of the remanent polarization (Pr) when compared to other materials such as PZT,[4] which limits its applications and thus justify the interest of new procedures for properties improvement.

The metallorganic chemistry has proved to be an adequate tool to obtain SBT films via sol–gel, with acceptable dielectric and ferroelectric characteristics.[2–8] Although the thermal processing involved in this type of method requires lower temperature than the solid state preparation, it is still high enough to affect both, the properties of the materials employed in the production of such devices and the stoichoimetry of the final compound.[2,3]

Both problems are inherent to thin films fabrication and some methods have been proposed to overcome these drawbacks in different ways for several compounds, including BLS perovskites: rapid thermal annealing,[5] bismuth excess,[6] non-stoichiometric compositions,[2,6] laser irradiation[6] and seeding techniques.[7,8] In the present work an approach based on the utilization of SBT seeds for lowering the processing temperature of SBT thin films is studied. The characteristics of the obtained films are evaluated and processing conditions leading to adequate ferroelectric properties are identified.

2. Experimental

The metallorganic solution was prepared by a modified sol–gel procedure: briefly, bismuth acetate (Aldrich, St. Louis) was dissolved in an organic solvent mixture (1:1) of toluene (Riedel-de Haën, Seelze) and acrylic acid

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(Fluka, Buchs), hereafter TAc mixture. Then strontium acetate (ABCR, Karlsruhe) was added and a clear solution was obtained. This solution was mixed with tantalum ethoxide (Fluka, Buchs) under controlled atmosphere. This final SBT precursor solution remains stable for several days.

SBT seeds were produced by a chemical method described elsewhere.[9] A seed suspension was prepared by adding an appropriate amount of SBT seeds to a TAc mixture kept under ultrasonic stirring for 30 min. The seed suspension was allowed to settle for 30 min and the supernatant suspension was then used for seeding purposes. The solid content of this seeding suspension was approximately 5 wt%. To perform differential thermal analysis (DTA) studies, some portions of the SBT precursor solution, with and without added SBT seeds, were dried at 120 °C for 24 h until obtaining yellow pale gels. The DTA of the gels were carried out at a heating rate of 5 °C/min.

For preparing a seeded substrate several drops of the seed suspension were deposited by spin coating on a Pt/Ti/SiO_2/Si substrate and subsequently dried at 130 °C. The seeded and unseeded films were prepared by spin-coating the precursor solution on seeded and unseeded Pt/Ti/SiO_2/Si substrates at 3000 rpm for 30 s. After each spinning the films were dried at 130 °C and the spinning-drying cycles repeated several times. Then the films were pyrolized at 325 °C and the spinning-drying-pyrolisis cycle repeated once. Finally the films were annealed in a tube furnace for 20 min at temperatures ranging from 700 to 750 °C, in air. The above described procedure was repeated until reaching the desired film thickness.

The films crystal structure was analysed by grazing incidence X-ray diffraction (Philips X'Pert MPD X-ray diffractometer, with Cu Kα radiation) and their microstructure evaluated by scanning electron microscopy (SEM) (Hitachi S-4100). For the electric measurements performed at room temperature, top Au-electrodes were sputtered and the films were annealed at 100 °C for one hour before measurements. The ferroelectric properties were measured with a TFA Meter and the dielectric characteristics in a HP 4248A LCZ bridge.

3. Results and discussion

The DTA results of the gels obtained from seeded and unseeded SBT precursor solution are shown in Fig. 1. Below 200 °C the gels show endothermic features assigned to the final evaporation process of the solvent trapped in the gel structure. After that exothermic effects associated to organics decomposition reactions describe the thermal evolution of the two SBT precursor gels up to 450 °C. When temperature increases beyond 450 °C strong exothermic effects dominate DTA curves of both seeded and unseeded samples. As already reported for a similar temperature range the exothermic effects originated from the burn out of residual organics and from SBT crystallization reaction may overlap and account for such broad and intensive peaks[9,10].

For the seeded sample the reactions are completed at ∼740 °C but extend up to ∼780 °C for the unseeded one. The organics elimination process during thermal treatment interplays with crystallization reactions: organics removal by a prolonged heat treatment carried out at 450 °C (>1 h) gives place to a quite distinct DTA curve (Fig. 1) where a single well defined and small exothermic peak corresponding to SBT perovskite phase crystallization is detected at 840 °C (as confirmed by XRD analysis, not shown). Sung et al.[7] reported different results after pyrolizing $Sr_{0.7}Bi_{2.4}Ta_2O_9$ precursor solution in the same conditions (450 °C, 1 h): the crystallization pathway was described by two exothermic peaks at 650 and 780 °C assigned to fluorite and Aurivillius formation,

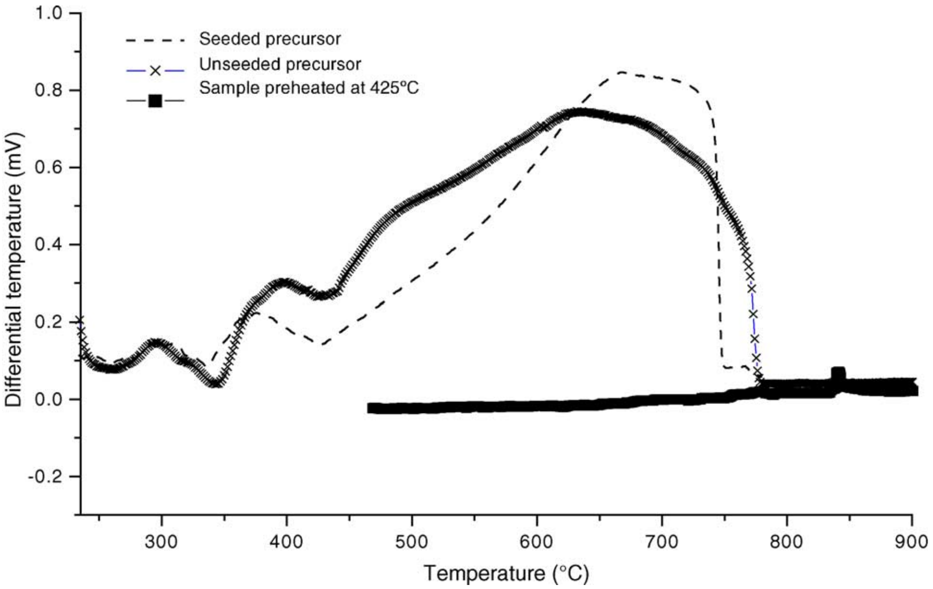

Fig. 1. DTA analysis of seeded and unseeded precursor gel samples.

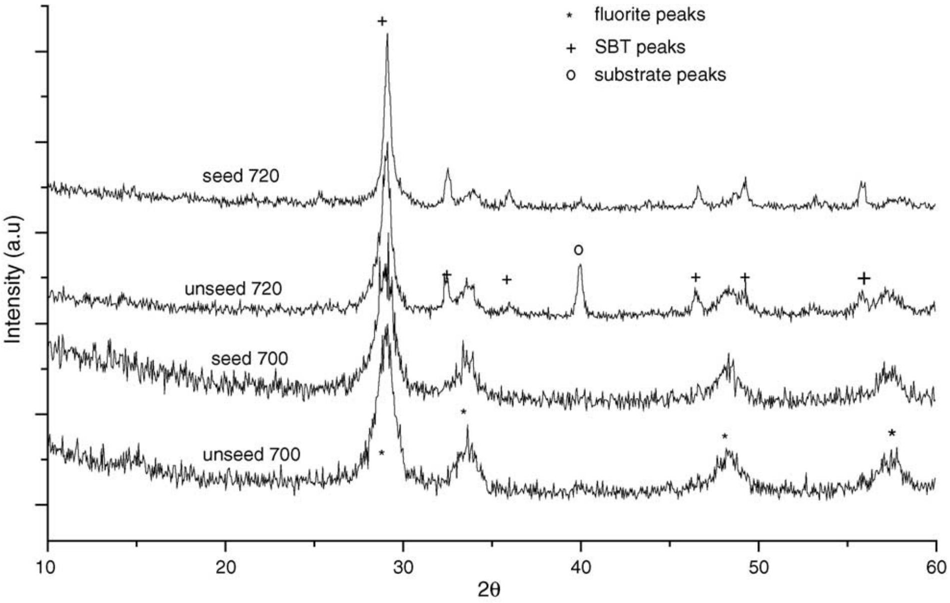

Fig. 2. XRD patterns of seeded and unseeded films annealed at 700 and 720 °C.

respectively. It may be thus concluded that the phase formation mechanism in SBT system is conditioned by the compositional characteristics of the organic precursor solution as well as by the schedule of its components decomposition reaction.

Fig. 2 shows the XRD analysis of the obtained thin films annealed for 20 min at different temperatures. The diffraction patterns of both type of films, seeded and unseeded, prepared at 700 °C may be ascribed to both fluorite and perovskite phase.[3] Increasing the annealing temperature of the films, perovskite peaks are then clearly detected: at 720 °C perovskite coexists with fluorite in the unseeded film but becomes dominant in the seeded film; further temperature increasing (>740 °C) was seen to lead to pure perovskite phase with preferred (115) orientation in both type of films. Similar results showing that SBT may be synthesized at temperatures

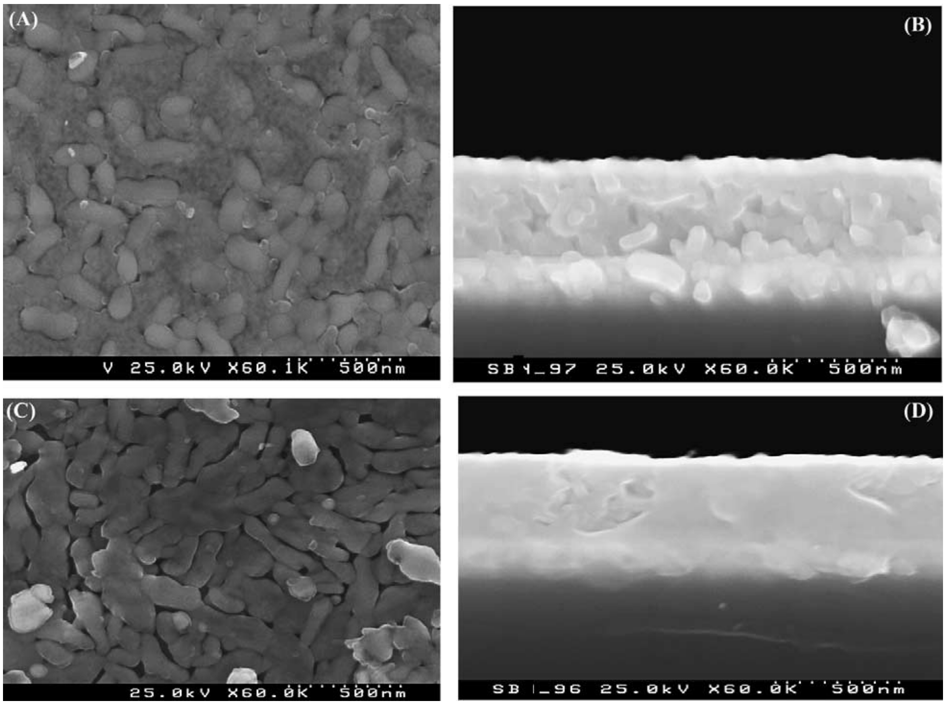

Fig. 3. Surface and cross section SEM images of SBT thin films heat treated at 720 °C: (A) unseeded film surface; (B) unseeded film cross section; (C) seeded film surface; and (D) seeded film cross section.

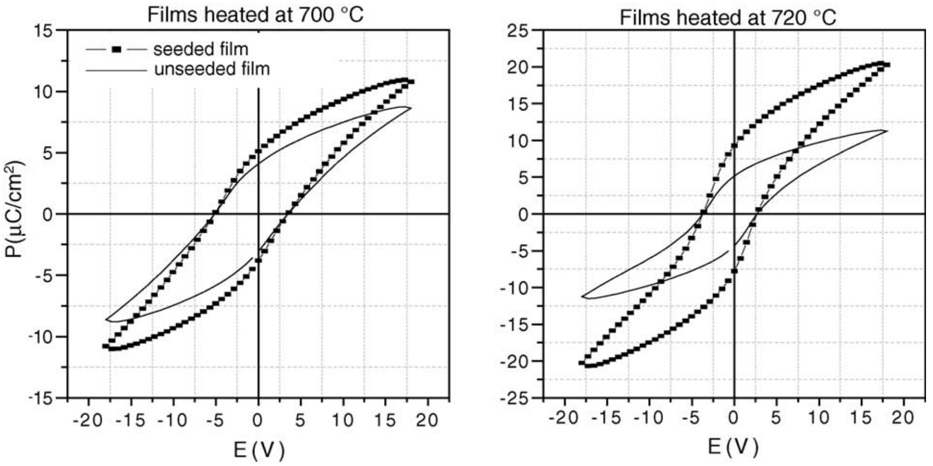

Fig. 4. Hysteresis loops of the unseeded and seeded films annealed at different temperatures.

ranging from 700 °C (when using rapid thermal annealing) and 780–800 °C (when using conventional annealing)[2–8] were reported. In several systems (including this one) fluorite appears as an intermediate phase that easily converts to layered-perovskite as already observed.[3,11] Moreover this conversion is improved by the introduction of seeds. As also shown by the DTA study, perovskite crystallization is completed at lower temperature when seeds are used. Previous studies on seeded SBT thin films reported[7,8] that the use of seeds lowers the incubation time and temperature of the fluorite-to-Aurivillius phase transformation while enhancing the transformation kinetics due to a decrease of the activation energy. The results obtained in this work are insufficient for detailing the role of the seeds in the present system. New studies are being carried out to clarify this issue.

SEM evaluation of the films microstructure showed that seeded films generally present a more dense structure with better-defined morphology and more elongated grains as confirmed by the surface and cross section images presented in Fig. 3. These characteristics are consistent with XRD results that denoted incomplete crystallization of perovskite phase at 720 °C for the unseeded films.

Fig. 4 illustrates the effects of seeds and annealing temperature on the polarization behaviour of the films. After heat treatment at 700 °C, ferroelectric behavior is already displayed by both types of films and becomes improved with further heating: the remnant polarization of unseeded and seeded films has increased from $2P_r = 6.7$ and $2P_r = 8.9$, respectively, at 700 °C to $2P_r = 9$ and $2P_r = 16.2$, respectively, at 720 °C, and a decrease of the coercive field is observed for both films. The properties of seeded films treated at 720 °C for 20 min are thus comparable to published results obtained after longer treatments (∼1 h) at higher temperatures (750–800 °C).[2,11–13] Dielectric properties of seeded films (720 °C/20 min) measured at room temperature and different frequencies revealed a frequency independent behavior of permittivity, $\varepsilon_R \approx 300$ (for the unseeded films, $\varepsilon_R \approx 254$), and of dielectric loss, $\tan\delta < 0.1$; dielectric properties of unseeded films showed some dependence on low frequency values. The reasons underlying this different dielectric behavior are now under study.

4. Conclusions

Chemical and thermal processing conditions for the crystallisation of SBT thin films were identified. The use of seeds in the reaction of SBT formation contributes to lower the temperature of the perovskite phase crystallization. Moreover, seeds benefit the thin film microstructure and ferroelectric and dielectric properties. It was observed that the properties displayed by seeded films treated at 720 °C/20 min are thus comparable to those reported for films submitted to longer treatments (∼1 h) at higher temperature (∼800 °C).

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