

Communications

Air-Stable Solutions for the Low-Temperature Crystallization of Strontium Bismuth Tantalate Ferroelectric Films

M. L. Calzada,* R. Jiménez, A. González, and J. Mendiola

Instituto de Ciencia de Materiales de Madrid (C.S.I.C.), Cantoblanco, 28049 Madrid, Spain

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SrBi₂Ta₂O₉ (SBT) has attracted much attention as a capacitor material for ferroelectric nonvolatile random access memories (FERAM) because of its low switching voltage and good fatigue endurance when integrated into silicon devices with common platinum electrodes.¹ Chemical solution deposition (CSD) methods have been used for the preparation of these films because of their low cost, good stoichiometric control, and compatibility with semiconductor technologies.^{2,3} However, these methods still have numerous handicaps when applied to these compositions. Problems are related to the large reactivity toward moisture of the available metal alkoxides and the low affinity among these alkoxides and the solvents used for the preparation of the solution. These solutions are unstable and tend to gel quickly. Film properties change with solution aging prior to film deposition.⁴ Therefore, the replacement or modification of the alkoxides with more stable reagents would simplify the processing of these films and permit the preparation of higher quality films in a more reproducible way. Another major objective is to lower the temperature and time of crystallization as much as possible to permit the process of SBT thin films in conjunction with silicon devices.⁵

For the synthesis of precursor solutions of SBT, tantalum ethoxide is usually used as the precursor alkoxide of Ta(V).^{6–8} This alkoxide is extremely sensitive to moisture and solutions have to be prepared and stored in dry atmospheric conditions. Bradley et al.⁹

reported in the 1970s the reaction between tantalum or niobium ethoxides and glycols. These alkoxides interchange their ethoxide groups with the glycol solvent, yielding a polymeric derivative with a high resistance toward hydrolysis. Similar reactions with glycols have been reported for alkoxides of boron, aluminum, silicon, germanium, tin, antimony, iron, titanium, zirconium, uranium, and lanthanides.⁹ However, titanium and zirconium glycolate derivatives have been the only compounds previously used for the synthesis of air-stable precursor solutions of thin films.^{10,11}

In this work, a tantalum–glycolate sol was synthesized by reflux in air of tantalum ethoxide, Ta(OC₂H₅)₅, and 1,3-propanediol, C₃H₆(OH)₂, in a molar ratio of Ta(V)/diol of 15 at a temperature of ~110 °C for 8 h.^{12,13} A Sr(II) sol was prepared by reflux in air at ~185 °C for 8 h of strontium 2-ethylhexanoate, Sr(C₇H₁₅COO)₂, in a solvent mixture of 1,3-propanediol and 2-ethylhexanoic acid, C₇H₁₅COOH. Molar ratios of Sr(II)/diol and Sr(II)/acid were 15 and 5, respectively. A Bi(III) solution was prepared by dissolving bismuth 2-ethylhexanoate, Bi(C₇H₁₅COO)₃, in 2-ethylhexanoic acid in a molar ratio of Bi(III)/acid of 15. This mixture was maintained under reflux in air for 3 h. The concentrations and densities of the solutions were as follows: ~0.5 mol/L and ~1.4 g/cm³ for the Ta(V) solution, ~0.3 mol/L and ~1.1 g/cm³ for the Sr(II) solution, and ~0.3 mol/L and ~1.2 g/cm³ for the Bi(III) solution. Appropriate aliquots of these solutions were mixed with 2-ethyl-1-hexanol, C₇H₁₅CH₂-OH, to obtain a solution with a nominal composition of Sr_{0.8}Bi_{2.2}Ta₂O₉¹⁴ and a concentration of ~0.05 M. This SBT precursor solution was maintained under stirring for 12 h and then deposited by spin-coating at 2000 rpm for 45 s onto Pt/TiO₂/SiO₂/(100)Si substrates. Wet films were dried on a hot plate at 225 °C for 900 s. Deposition and drying was repeated 10 times. Crystallization of the films was carried out through the formation of a fluorite phase that evolves to the layered perovskite at temperatures ≥ 600 °C.¹⁵ Fluorite films were prepared by their insertion into a tubular furnace preheated at 550 °C in an oxygen flow. Ferroelectric SBT thin films were obtained at 650 °C in an oxygen atmosphere, by rapid thermal processing (RTP), using a heating rate of 200 °C/s. Soaking times ≤ 3600 s were used in these treatments (Figure 1). Thicknesses of the films were ~180 nm. Figure 2 shows the X-ray pattern of these films.

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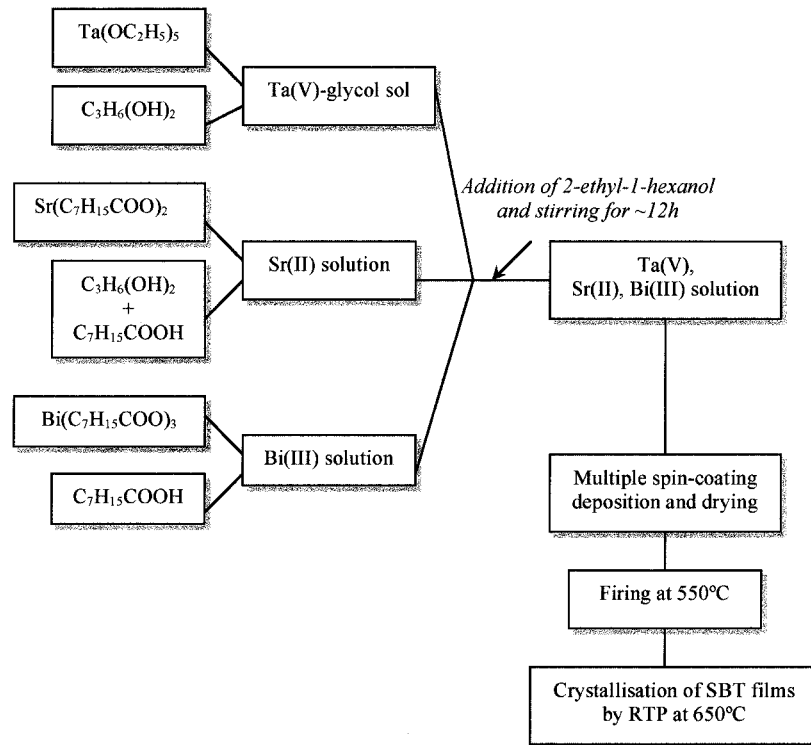


Figure 1. Scheme of the chemical solution deposition method used for the preparation of strontium bismuth tantalate thin films.

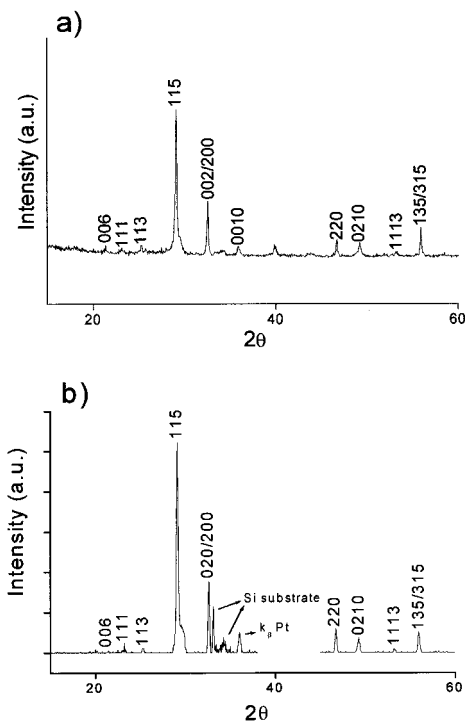


Figure 2. GIXRD pattern of a SBT film.

The pattern of Figure 2a has been obtained by grazing incidence X-ray diffraction (GIXRD), with a grazing angle of 2° . Formation of the layered perovskite phase is observed in the pattern. No second phase is observed. Figure 2b corresponds to the XRD pattern of these films obtained with the conventional Bragg-Brentano geometry. This pattern does not show any preferred orientation. Preliminary results of the texture of these films obtained from pole figures indicate that they are random oriented.

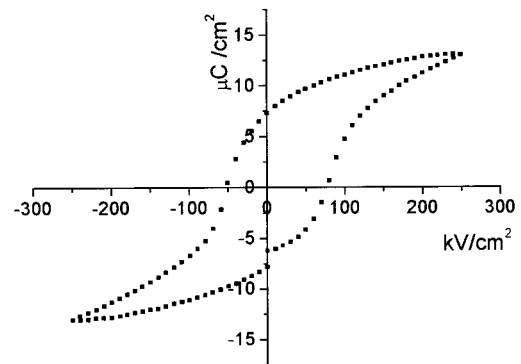


Figure 3. P vs E hysteresis loop measured in the SBT film.

For ferroelectric characterization, platinum electrodes of $5 \times 10^{-4} \text{ cm}^2$ were sputtered, at room temperature, on the top surface of a SBT film crystallized at 650°C for 3600 s with RTP. Figure 3 shows the P - E hysteresis loop obtained in this film with a Radiant Technology Inc. Testing system, RT66A model, and using a triangular wave of 5 V of amplitude and 100 Hz of frequency. Values of the positive remanent polarization, $+P_r$, of $\approx 7.5 \mu\text{C}/\text{cm}^2$ and coercive field, E_c , of $\approx 60 \text{ kV}/\text{cm}$ are deduced from this loop. Figure 4a,b shows the fatigue and retention of the film. Fatigue has been measured at a frequency of 3 MHz and 7 V. Performed switching time measurements with the pulse method¹⁶ allowed us to use this frequency. The switching time was 166 ns. The five pulses method was used with the RT66A ferroelectric tester to measure the retention and the fatigue of Figure 4. Here, P^* and P_r^* are the switched polarization values obtained after the first read pulse, while \hat{P}^* and \hat{P}_r^* correspond to the

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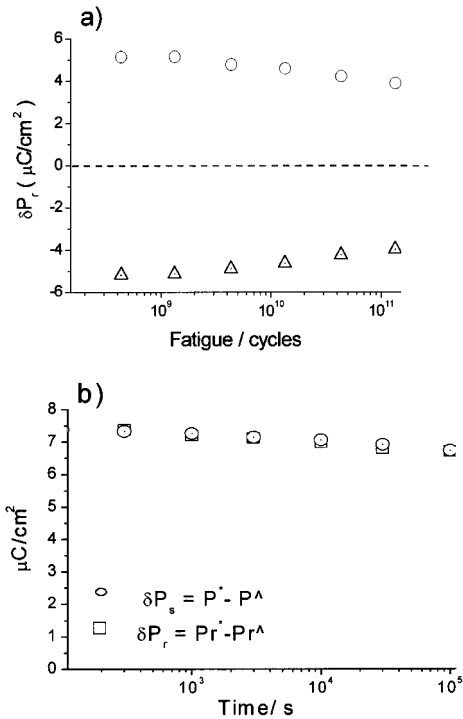


Figure 4. (a) Fatigue, (b) retention of the ferroelectric polarization. Meaning of $\delta P_s = P^* - P^\wedge$ and $\delta P_r = P_r^* - P_r^\wedge$ are explained in the text and can be seen in ref 22.

nonswitched values obtained from the second read pulse when back-switching occurs during the waiting time between the two reading pulses. Thus, $\delta P_s = P^* - P^\wedge$ and $\delta P_r = P_r^* - P_r^\wedge$ are the switched and remaining polarizations, respectively. The films are fatigue-free up to 10^{10} cycles and they retain their polarization up to 10^5 s.

All of these results show that these films have good ferroelectric properties, relatively close to those reported for films obtained by other CSD methods.^{17,18} But the synthesis method used here for the preparation of the solutions uses raw compounds with lower toxicity than those used in methods previously reported,^{2,6,18} simplifies the synthesis of the solutions by processing them in air, and makes possible crystallization of SBT films with appropriate ferroelectric responses using shorter times and lower temperatures than those reported in the literature.^{19,20} Besides, the crystalline films obtained do not need the long-time/high-temperature recovery annealings usually applied to this type of film after the deposition of the top electrodes.²¹

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