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Relationship Between Processing and Electrical Behavior of BST Films Deposited by Spin Coating

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Abstract

The present work concerns the preparation of $Ba_{0.67}Sr_{0.33}TiO_3$ ceramic under thin film form, using a chemical route, for infrared detection applications. Dielectric behavior of the deposits as a function of temperature and their structural properties, through electron microscopy investigations, were studied for films prepared with various firing treatments. Relation between the Rapid Thermal Processing (RTP) used, during the firing stage, and the physical characteristics of the obtained layers is discussed. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: barium strontium titanates, films, grain size, interface, dielectric properties.

1 Introduction

$Ba_{0.67}Sr_{0.33}TiO_3$ (BST 67/33) bulk ceramics, characterized by a high sensitivity of their dielectric constant with respect to temperature around 20°C, are interesting candidates for applications such as dielectric bolometers for infrared detection.[1] Because of higher thermal sensitivity, low material thickness are required. In this regard, integrated arrays, where direct deposition on the readout IC is performed, are preferred to hybrid systems, based on the thinning of bulk ceramics. In this report, thin film processing via a sol–gel route has been tested for BST material.

2 Experimental Procedure

A BST 67/33 starting solution is prepared by mixing barium and strontium acetates in acetic acid with titanium isopropoxide in 2-propanol. Details on synthesis conditions have been reported in a previous paper.[2] The obtained sol is deposited on $Pt/Ti/SiO_2/Si$ substrates by spin-coating. Thermal treatments of the deposits consist of a pyrolysis stage on a hot plate at 550°C for 15 min (for each deposited layer), followed by a firing stage. Various film thickness were obtained by repeating the deposition/thermal treatment cycles. Firing conditions with short exposure to heat treatment (heating and cooling rate: 5°C s^{-1}, dwell: 800°C/180 s per cycle) were carried out to crystallize the films. This treatment is applied either for each layer (process A) or after the deposition of five layers (process B). Prior to electrical characterization, the films were coated with sputtered gold electrodes (0·33 μm in diameter). Dielectric measurements were performed with an impedance analyzer SI1260, at 1 kHz under 1 V μm^{-1} and between −150 and +350°C. Morphological and structural properties of the deposits were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3 Electrical and Morphological Characterization of the BST Thin Films

Figures 1(a) and (b) present the dielectric constant (ε_r) as a function of temperature for A and B series, respectively. In both cases, a diffuse transition is observed around a maximum of permittivity near −50°C. Besides, whatever the series or temperature, the dielectric constant increases with film thickness. According to the literature, this effect might result from the existence of a low permittivity interface layer between the bottom electrode and the deposit.[3] For the B type samples, the presence of such a layer has been illustrated through dielectric data analysis based on two capacitive layers in series.[2,3] Linear relationships between the

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inverse of the dielectric constant ($1/\varepsilon_r$) and the inverse of the thickness ($1/t$) have been obtained (Fig. 2). Concerning the A samples, such a correlation is not as obvious as for B films. SEM investigations, carried out on films of various thickness, have revealed a significant influence of the firing process on the microstructure. For A samples, the successive firing cycles lead to a notable evolution of the film morphology so that a 20 layers film (A20, corresponding to 20 RTP treatments) exhibits a well defined microstructure with grain size up to 100 nm [Fig. 3(a)]. In contrast, morphological properties of B samples are not function of the thickness: the microstructure is made up of agglomerates with crystallites ranging from 20 to 70 nm in diameter [Fig. 3(b)]. In both cases, microstructure of the ceramic film near the platinum is not well defined. However, TEM investigations carried out on films with various heating treatments have proved the existence of an interfacial area. Sample with 20 firing cycles (A20) presents a titanium rich and poorly crystallized 80 nm thick layer, near the bottom Pt electrode [Fig. 4(a)]. In contrast, the upper ceramic block exhibits good crystallinity and a composition close to the stoichiometric one (Ba/Sr/Ti: 0·67/0·33/1), identified through EDXS nanoanalysis by TEM. Such an increase in titanium content just above the platinum is also valid for a sample with two firing cycles (B10), while structural defects are not so distinct for the interface region [Fig. 4(b)]. Diffusion through the platinum layer and oxidation of the titanium, from the substrate, during successive firing cycles could explain this phenomenon.[4] In

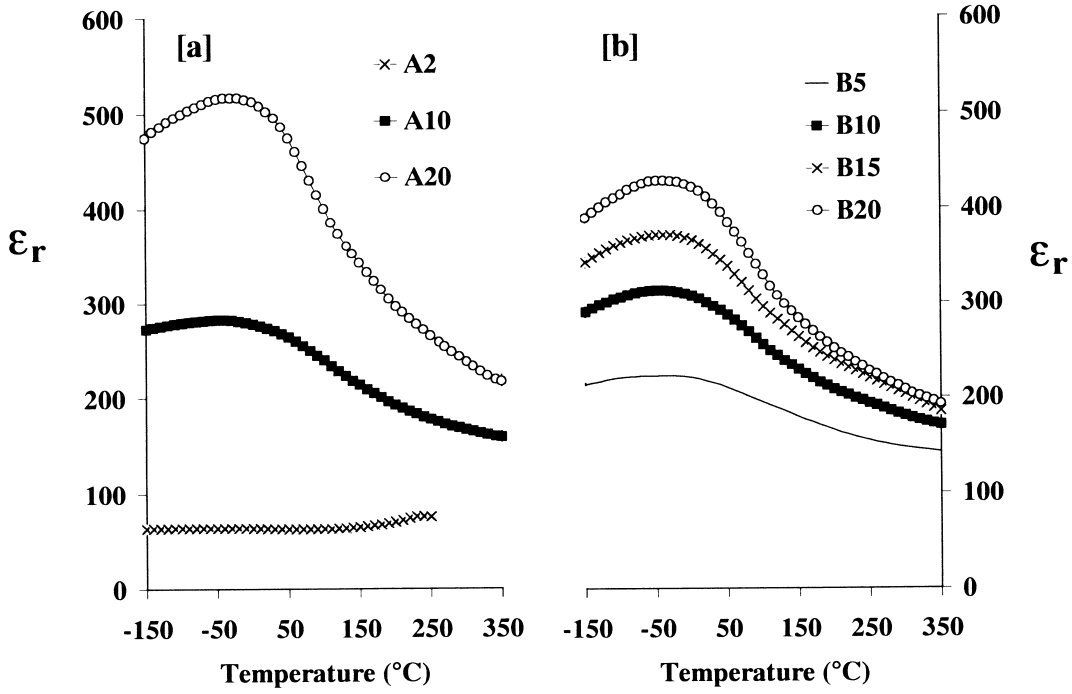

Fig. 1. Temperature dependence of ε_r for $Ba_{0.67}Sr_{0.33}TiO_3$ films prepared according to process (a) A or (b) B. Legends indicate the process used followed by the deposits number. Input signal: 1 kHz, 1 V μm^{-1}.

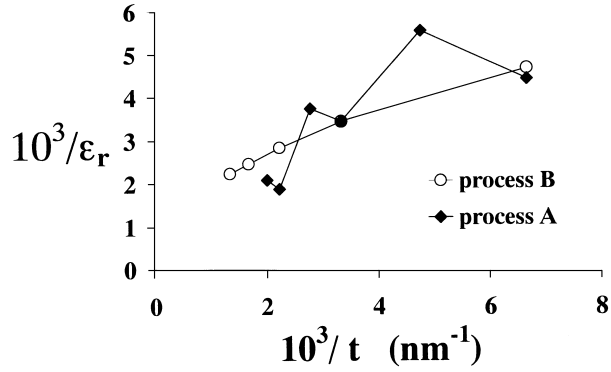

Fig. 2. Relationship between the inverse dielectric constant ($1/\varepsilon_r$) and the inverse layer thickness ($1/t$) for $Ba_{0.67}Sr_{0.33}TiO_3$ films (room temperature, input signal: 1 kHz, 1 V μm^{-1}).

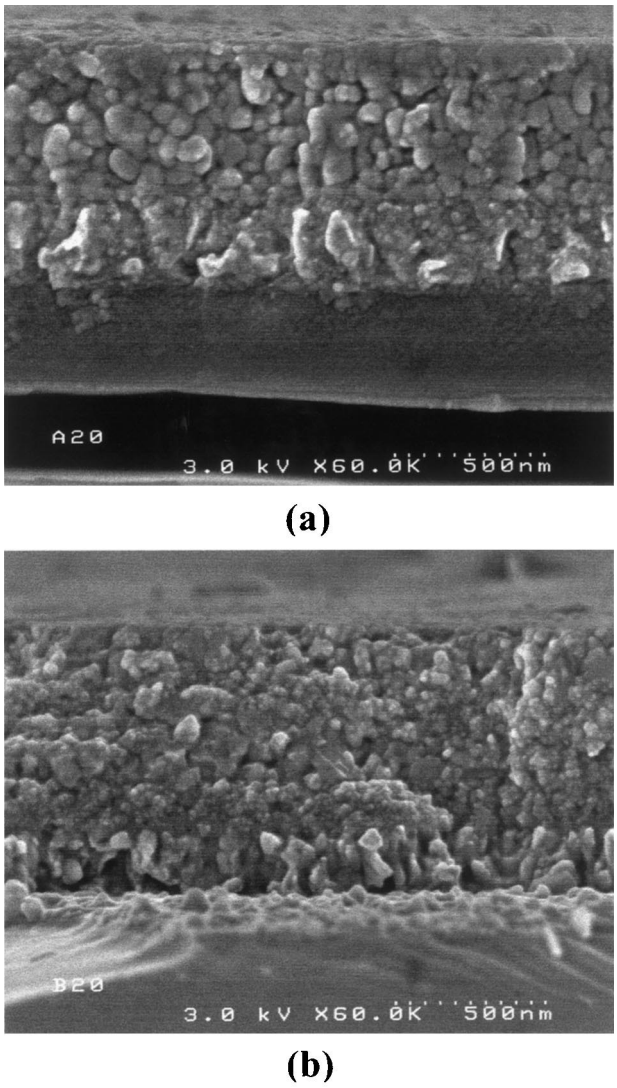

Fig. 3. SEM cross-sections of $Ba_{0.67}Sr_{0.33}TiO_3$ films: (a) samples A20 (process A/20 layers) and (b) B20 (process B/20 layers).

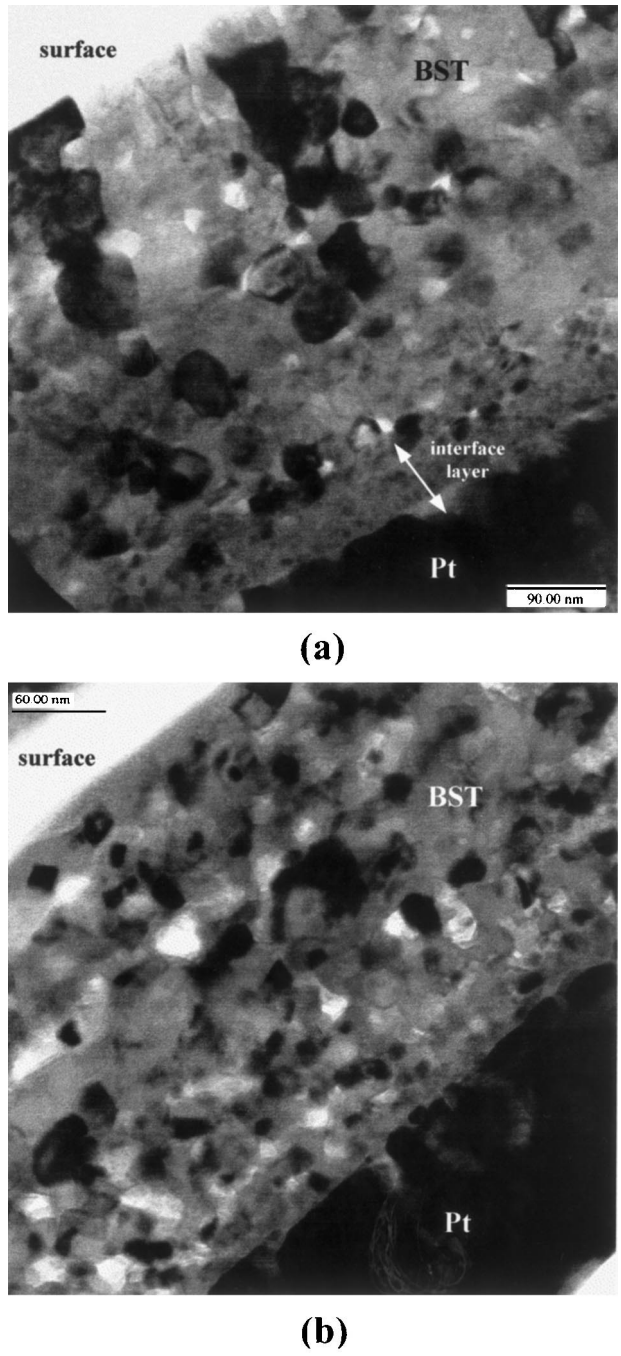

Fig. 4. TEM cross-sections of $Ba_{0.67}Sr_{0.33}TiO_3$ films: (a) samples A20 (process A/20 layers) and (b) B10 (process B/10 layers).

conclusion, these different results illustrate the effects of the firing processes on the physical properties of the films. By using 'soft' firing treatments (process B), the structural properties of the ceramic film (grain size, crystallinity) do not change significantly with the film thickness. The dielectric response of these samples is probably controlled by the contribution of an interface layer in regard to the global film thickness. More severe firing conditions (process A) lead to an increase in the degradation of the interface layer with the deposits number, while the crystallinity of the successive layers improves, giving rise to better dielectric characteristics of the whole material. Consequently, the dielectric response of the thickest films, prepared according to process A, is governed by intrinsic parameters such as grain size, crystallinity degree or chemical homogeneity, rather than the existence of an interface region between the bottom electrode and the film.

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