Effect of the heat flux direction on electrical properties of SrBi$_2$Nb$_2$O$_9$ thin films crystallized using a microwave oven

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Abstract

Ferroelectric SrBi$_2$Nb$_2$O$_9$ (SBN) thin films were prepared by the polymeric precursors method and deposited by spin coating onto Pt/Ti/SiO$_2$/Si substrate and crystallized using a domestic microwave oven. It was studied the influence of the heat flux direction and the duration of the thermal treatment on the films crystallization. An element with high dielectric loss, a SiC susceptor, was used to absorb the microwave energy and transfers the heat to the film. Influence of the susceptor position to the sample crystallization was verified, the susceptor was placed or below the substrate or above the film. The SBN perovskite phase was observed after a thermal treatment at 700 °C for 10 min when the susceptor was placed below the substrate and for 30 min when the susceptor was placed above the film. Electrical measurements revealed that the film crystallized at 700 °C for 10 min, with the susceptor placed below the film, presented dielectric constant, dielectric loss, remanent polarization and coercive field of, 67, 0.011, 4.2 mC/cm$^2$ and 27.5 kV/cm, respectively. When the films were crystallized at 700 °C for 30 min, with the susceptor placed above the film, the dielectric constant was 115 and the dissipation factor was around of 0.033, remanent polarization and coercive field were 10.8 mC/cm$^2$ and 170 kV/cm, respectively.

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1. Introduction

Ferroelectric materials have been extensively studied due to their applications mainly as thin films. Thin films have attracted a lot of interest in the last years due to their importance in the development of applied microelectronic and optical-electronic devices [1,2]. The most popular ferroelectric material for nonvolatile memory applications is Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT) [3]. SrBi$_2$Nb$_2$O$_9$ (SBN) and SrBi$_2$Ta$_2$O$_9$ (SBT) have received great attention as an alternative material due to their high dielectric constant, low...
leakage current and the absence of fatigue, besides being environmentally friend [4].

Thin films have been prepared by different deposition methods, such as: chemical vapor deposition (CVD) [5], pulsed laser deposition (PLD) [6], metal-organic chemical vapor deposition (MOCVD) [7], liquid phase epitaxy (LPE) [8], polymeric precursors [9,10] and others. The polymeric precursor method (Pechini method) [11] is attractive due to its advantages, such as high stoichiometric control, good compositional homogeneity, low-temperature processing and low cost [10]. Previous works, have reported the use of this method for the preparation of SBT [9] and SBN [12] besides other oxide powders and thin films such as PZT [13] and ATiO₃ (A = Sr, Ba or Pb) [14].

The electric furnace has been mostly used for the thermal treatment of these ferroelectric materials. Rapid thermal annealing (RTA) has been used in processing of materials, in order to reach the desirable heating temperature in a shorter time. The RTA has advantages such as reduction in surface damage and minimization of the film–substrate interaction [15–17]. Recently the energy in the frequency of the microwave spectrum has been used for the processing of materials at high temperatures. This technology is comparable to RTA and provides the advantages: low investment, rapid and uniform heating, low sintering temperatures and improved product quality and the achievement of unique material properties, which can not be reached using conventional processes [18,19].

Vasconcelos et al. [20] obtained SrBi₂Ta₂O₉ (SBT) films heat treated at 550 °C for 10 min using a domestic microwave oven. The authors used an apparatus in which a susceptor of SiC was placed below of the substrate. The films presented fine and spherical grains, and low roughness and a good adherence between the film and the substrate. The electric properties revealed a dielectric constant and dissipation factor of 77 and 0.04, respectively, at 100 kHz. The remanent polarization (2Pr) and the coercive field (Ec) were of 1.04 μC/cm² and 33 kV/cm. The results showed that it is possible to obtain SBT thin films using a low temperature processing with low costs.

Vasconcelos et al. [21] demonstrated that LiNbO₃ films could be epitaxially grown epitaxially using a microwave oven. The films were deposited on sapphire substrate (0 0 0 1) and heat treated at 550 °C for 10 min. The epitaxial films presented optical and structural quality comparable to those obtained in a conventional oven.

In a previous work [22], it was studied the influence of the direction of the heat flux in the crystallization of SrBi₂Nb₂O₉ (SBN) thin films heat treated at 550 °C for 10 min at different temperatures using a microwave oven. The authors changed the SiC susceptor position (above the film or below the substrate). They observed that the position of the susceptor may lead to changes in the microstructure and orientation of the films. Polycrystalline films are obtained with the susceptor placed above the films and with preferential orientation in the direction (0 0 1) if the substrate is placed directly on the susceptor.

In this work, SBN thin films were prepared by the polymeric precursor method, deposited by spin coating on Pt/Ti/SiO₂/Si substrate and heat treated in a domestic microwave oven, using a SiC susceptor to absorb the microwave energy and transfer the heat to the film. The crystallization temperature is reached with the main advantage of reducing the time of the thermal treatment. The susceptor was placed above the films which were crystallized for 10 and 30 min. For comparison, a film treated for 10 min was placed directly on the susceptor and it was studied the influence of the heat flux direction and the time of the thermal treatment on the crystallization, microstructure and electrical properties of the films.

2. Experimental

The coating solution was prepared by the polymeric precursor method, which is based on the chelation of cations with citric acid in an aqueous solution. Ethylene glycol was added to the metallic citrate formed and the heating of this mixture led to polymerization and resulted in a homogeneous resin [10,12,14]. The viscosity of the coating solution was adjusted to 21 mPa s by the controlled evaporation of water.

The SBN precursor resin was deposited by spin coating on 10 mm × 10 mm Pt/Ti/SiO₂/Si substrates at a rotation speed of 523.6 rad·s⁻¹ for 30 s and heat treated at 400 °C for 2 h in a conventional oven to eliminate organic materials. The desired thickness was obtained by successive depositions followed by pre-treatment. The crystallization was performed in a
microwave oven after all layers had been deposited. A SiC susceptor of 40 mm diameter and 10 mm thickness was used to absorb the microwave energy and transfer the heat to the film, once the volume of the film and substrate are insufficient to couple with the microwave.

The SBN films were crystallized at 700 °C for 10 min with the susceptor placed below the substrate, Fig. 1a. In other experiments, the films were crystallized at 700 °C for 10 and 30 min with the susceptor placed above the film, Fig. 1b. As can be observed the total volume of the apparatus is sufficient to maintain the uniformity of the temperature and of the microwave energy on the sample and susceptor.

A simple domestic microwave oven model (M-301, CCE, 2.45GHz frequency, 900 W power) was used. A 230 °C/min heating rate was applied, using an automatic temperature controller.

The films were characterized by X-ray diffraction (XRD) using Cu Kα radiation (RIGAKU, DM Max 2500 PC), 40 kV and 150 Ma from 20 to 60°. Microstructural characterization was performed by atomic force microscopy (AFM) using a DIGITAL, Nano-scope 3A. Electrical measurements were carried out in a HP4192A impedance analyzer for dielectric properties and the hysteresis loops were measured on a ferroelectric tester (RADIANT, HTV6000S).

3. Results and discussion

Fig. 2 illustrates the XRD patterns for the SBN films heat treated in a microwave oven at 700 °C for 10 min with the susceptor placed below the substrate, and at 700 °C for 10 min and 30 min with the susceptor placed above the film. For comparison, SBN films were also prepared at 700 °C for 2 h in a conventional furnace.

As can be observed in Fig. 2a, intense (0 0 8) and (0 0 1 0) peaks indicate a preferential orientation in the c direction when the susceptor is placed below the substrate. No peak of significant intensity corresponding to a secondary phase was observed.

When the susceptor was placed above the films (Fig. 2b and c), the heat flux downwards induced the surface nucleation and the films presented polycrystalline growth, similarly to the film obtained in a conventional oven (Fig. 2d). However, 10 min is a very short time for the complete crystallization of the perovskite phase. On the other hand, the perovskite phase was obtained when SBN films were heat treated for 30 min.
Changes in the surface morphology of the SBN films obtained using microwave oven were observed by AFM images. Fig. 3a illustrates the AFM micrograph for the SBN films treated using microwave oven with the susceptor placed below the substrate. Plate-like grains with size around 250 nm, typical of $c$-oriented grains are observed. When the films were crystallized for different times (10 and 30 min) with the susceptor placed above the film (Figs. 3b and c), respectively, the morphology were similar to the films obtained using a conventional oven [23]. The grain size to SBN film obtained using the susceptor placed above the film for 10 min (Fig. 3b) is smaller than that film obtained by conventional furnace, probably due to the short time of treatment and also due to the surface nucleation.

Fig. 4 shows the room temperature dielectric constant ($\varepsilon_r$) and the dissipation factor ($\tan \delta$) as a function of the frequency, ranging from 100 Hz to 10 MHz at room temperature, when the susceptor was placed below the substrate. The dielectric constant at 100 kHz frequency was 67 and the dissipation factor was around 0.011. In spite of $2P_r$ to be lightly lower than the literature as showed in Table 1, $E_c$ is lower than that reported so far which is desirable. The crystallization temperature is also inferior to that reported in the literature.

Fig. 5 illustrates the remanent polarization ($2P_r$) and the coercive field ($E_c$) for SBN films heat treated with the susceptor placed below the substrate. $2P_r$ and $E_c$ were 4.2 $\mu$C/cm$^2$ and 27.5 kV/cm, respectively. These low values are probably due to the preferential
orientation in the $c$ direction as already verified by Kato et al. [15].

Fig. 6 illustrates the variation of $\varepsilon_r$ and $\tan \delta$ as a function of the frequency, ranging from 100 Hz to 10 MHz at room temperature, when the susceptor was placed above the film at 700 °C for 30 min. The dielectric constant at 100 KHz was 115 and the dissipation factor was around 0.033. The increase in $\varepsilon_r$ with 30 min of heat treatment can be attributed to increase in the dielectric polarization due to the presence of the perovskite phase. Dispersion was observed around 13.5% when the applied frequency was increased from 300 Hz to 1 MHz, which can be attributed to charges in the electrode–film interface. The hysteresis loop (Fig. 7), observed at a frequency of 60 Hz, at room temperature, presents a remanent polarization ($2P_r$) of 10.8 $\mu$C/cm$^2$ and the coercive field ($E_c$) of 170 kV/cm. $2P_r$ is comparable to the results obtained for Zanetti et al. [24] to SBN films.

### Table 1

| Furnace   | Temperature (°C) | Time | $2P_r$ (|$\mu$C/cm$^2$) | $E_c$ (kV/cm) | Reference   |
|-----------|------------------|------|------------------------|--------------|-------------|
| MW oven$^a$ | 700, air         | 10 min | 4.2                    | 27.5         | This work   |
| MW oven$^b$ | 700, air         | 30 min | 10.8                   | 170          | This work   |
| RTA       | 700, air         | 10 min | 5.9                    | 79           | [15]        |
| Conv. oven | 700, air         | 2 h   | 11.2                   | 100          | [24]        |

$^a$ SBN film heat treated with the susceptor placed below the substrate.

$^b$ SBN film heat treated with the susceptor placed above the film.

![Fig. 5](image1)

**Fig. 5.** Hysteresis loop for the SBN films heat-treated at 700 °C for 10 min, in microwave oven with the susceptor placed below the substrate.

![Fig. 6](image2)

**Fig. 6.** Dielectric constant and dissipation factor as a function of frequency for SBN films heat-treated at 700 °C for 30 min in microwave oven with the susceptor placed above the film.

![Fig. 7](image3)

**Fig. 7.** Hysteresis loop for the SBN films heat-treated at 700 °C for 30 min in microwave oven with the susceptor placed above the film.
prepared in a conventional furnace. The high coercive field can be related with interaction of lone-pair electrons with the ionic polarization, which can increase the internal field that opposes polarization reverse under an external field [25].

4. Conclusion

SBN thin films were crystallized in a short time of heat treatment using a microwave oven. It was studied the influence of the heat flux direction and the time of the thermal treatment for crystallization of the films. The heat flux direction when the susceptor was placed below the substrate occurred upwards and it occurred downwards when the susceptor was placed above the film. The films heat treated at 700 °C for 10 min using the susceptor placed below the substrate presented a preferential orientation in c direction and dielectric constant of 67 and dissipation factor of 0.011. The values of remanent polarization and coercive field were 4.2 µC/cm² and 27.5 kV/cm, respectively. For the films heat treated at 700 °C for 30 min with susceptor placed above the film, it was observed a dielectric constant of 115 and a dissipation factor of 0.033. Remanent polarization and coercive field were 10.8 µC/cm² and 170 kV/cm, respectively.

In summary, these results demonstrate the versatility of the method using microwave energy, allowing the structure of the film to be modulated according to the conditions of the thermal treatment in the microwave oven. It is possible to obtain dense and homogeneous films with low investment, short time and good electric properties.

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