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S. M. Zanetti, P. R. Bueno, E. Leite, E. Longo, and J. A. Varela

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Ferroelectric and microstructural characteristics of $SrBi_2Ta_2O_9$ thin films crystallized by the rapid thermal annealing process

S. M. Zanetti,[a] P. R. Bueno, E. Leite, and E. Longo
Departamento de Química-Universidade Federal de São Carlos, P.O. Box 676, 13560-905 São Carlos, SP, Brazil

J. A. Varela
Instituto de Química-Universidade Estadual Paulista, P.O. Box 355, 14801-970 Araraquara, SP, Brazil

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Ferroelectric $SrBi_2Ta_2O_9$ thin films on $Pt/Ti/SiO_2/Si$ were successfully synthesized by the modified polymeric precursor method. The films were deposited by spin coating and crystallized by rapid thermal annealing in a halogen lamp furnace, followed by postannealing at temperatures ranging from 700 °C to 800 °C in an oxygen atmosphere. Microstructural and phase evaluations were followed by x-ray diffraction and atomic force microscopy. The films displayed spherical grain structures with a superficial roughness of approximately 3–6 nm. The dielectric constant values were 121 and 248 for films treated at 700 °C and 800 °C, respectively. The $P-E$ curve showed a voltage shift toward the positive side, which was attributed to crystallization under the halogen illumination. The remanent polarization ($2P_r$) and coercive field (E_c) were 7.1 $\mu C/cm^2$ and 113 kV/cm, and 18.8 $\mu C/cm^2$ and 93 kV/cm for the films treated at 700 °C and 800 °C, respectively.
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I. INTRODUCTION

Bi-layered thin films have attracted much attention in recent years due to their potential application as ferroelectric memory.[1–3] Among the Bi-layered family, $SrBi_2Ta_2O_9$ (SBT) has been the most studied. Many groups have prepared SBT films by several techniques, such as pulsed laser deposition,[4,5] rf sputtering,[6] metalorganic chemical vapor deposition,[7] and by chemical solution, basically metalorganic decomposition[3,8,9] and the sol–gel process.[10,11]

Several crystallization conditions, such as conventional (slow heating rates)[11] and rapid thermal annealing (RTA),[12,13] and pre- and post-annealing treatments[14,15] have been experimented.

RTA is useful for the thermal processing of thin films, mainly for SBT films, since this compound requires high temperatures for good crystallization, i.e., around 800 °C for 2 h. During that time, the wafer may undergo undesirable changes, such as interdiffusion through the stack or through the film. Hence, the possibility of these phenomena occurring decreases the shorter the time that the substrate is subjected to this high temperature.

This article reports on the preparation of SBT films using an alternative chemical route based on the modified precursor method and their precrystallization by a halogen-lamp-RTA treatment.

II. EXPERIMENT

A. Synthesis and characterization of SBT resin

The SBT films were prepared by a chemical solution, the detailed preparation method is published elsewhere.[16] Briefly, the chemistry used for SBT thin film preparation is based on strontium carbonate, bismuth oxide, and tantalum ethoxide as the cation source for the metallic citrate. A polymeric resin was obtained by reaction with ethylenediamine and ethylene glycol was used as solvent. The resin presented no evidence of aging up to 10 months after preparation.

B. Preparation and characterization of the films

The films were deposited onto $Pt/Ti/SiO_2/Si$ substrate by spin coating at a rotation speed of 5000 rpm for 20 s and heat treated at 400 °C for 2 h to eliminate the organic material. Several layers were deposited and treated at 400 °C until the desired thickness was achieved. After all layers had been deposited, the films were treated at 700, 750 and 800 °C for 2 min in a RTA furnace. The RTA furnace provides a fast heating rate (approximately 150 °C s^{-1}) through a halogen lamp (Xe, $\lambda = 800-1000$ nm). Postannealing in a tube furnace at the same temperatures for 1 h in an oxygen atmosphere was carried out to promote full crystallization of the films.

The films were characterized by x-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM), for crystallinity, surface morphology, and thickness measurements, respectively. Film thickness was approximately 250 nm, evaluated by SEM cross section observation.

For the electrical measurements, Au top electrodes, each with a nominal area of 7.07×10^{-4} cm^2, were sputter deposited through a shadow mask. The ferroelectric properties were measured using a RT6000HVS tester under virtual ground conditions. Capacitance and voltage ($C-V$) were measured with a HP 4194A impedance analyzer. Prior to

[a]Author to whom correspondence should be addressed; electronic mail: psmz@iris.ufscar.br

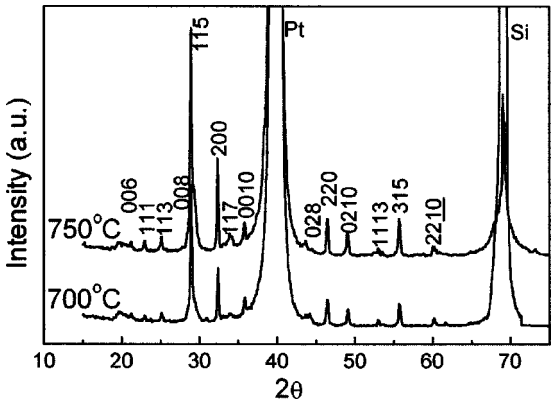

FIG. 1. XRD pattern for SBT films treated by RTA for 2 min and post-annealed for 1 h in oxygen at 700 and 750 °C.

taking the electrical measurements, the Au/SBT/Pt capacitors were annealed at 300 °C for 30 min in a N_2 atmosphere to improve the electrode/film contact.

III. RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns for films treated at 700 and 750 °C for 1 h in an oxygen atmosphere. As can be observed, the SBT perovskite phase crystallized even at 700 °C. The increased temperature led to improved crystallinity. No other secondary phase was observed, even when the films were treated at 800 °C. The films showed a polycrystalline nature with a (115) orientation, which is preferable for ferroelectric properties.

Film surface morphology and topography are illustrated in Fig. 2. It can be observed that the 2 min RTA treatment suffices promote nucleation and an incipient crystallization. Postannealing led to grain growth and complete crystallization of the films. Surface roughness root-mean-square ranged from 3 nm for the film treated at 700 °C to 6 nm for films treated at 750 and 800 °C. The mean grain size for the film treated at 800 °C was around 80–100 nm. The RTA treatment was used to induce crystalline nuclei in the amorphous matrix. With the postannealing treatment, the first nuclei may facilitate complete crystallization, resulting in a dense and uniform structure. On the other hand, nucleation at slow heating rates is relatively reduced and large grains may grow.[17] Figure 2 clearly indicates that the films are dense and devoid of cracks or defects.

The dielectric properties of the SBT films were measured as a function of frequency in a range of 100 Hz–10 MHz, using a HP 4194A impedance analyzer. High dielectric dispersion of around 25%–40% was observed in all the films (Fig. 3), which may be due to electrode/film interface charges. The dielectric constant and dissipation factor values at 100 kHz frequency are summarized in Table I. The values of ε are consistent with the crystallographic and microstructural data.

The $I-V$ measurements were taken using the RT6000HVS tester in the current–voltage mode, with the voltage changing from 0 to +10 V, from +10 to −10 V and back to 0 V. Figure 4 shows the $I-V$ curves for the SBT films heat treated at 700, 750, and 800 °C. A strong asymmetry was observed on the positive and negative sides, which may be attributed to differences in the bottom (Pt) and top (Au) electrodes. Moreover, the hysteresis observed when the voltage changed from +10 to 0 V is due to the filling of the trap sites near the electrode. The linear region extended up to 4 V in the film treated at 800 °C, and the current density at 3 V was 5.4×10^{-10} A/cm^2 in the first measurement, increasing to 1.9×10^{-6} A/cm^2 when the voltage switched from +10 to 0 V, i.e., four orders higher. The same effect was observed in the other films, indicating that filling the traps causes the current to increase. A similar finding was reported by Bhattacharyya *et al.* in SBN ($SrBi_2Nb_2O_9$) films.[18] These results suggest that the films are under space charge limited conduction.[14]

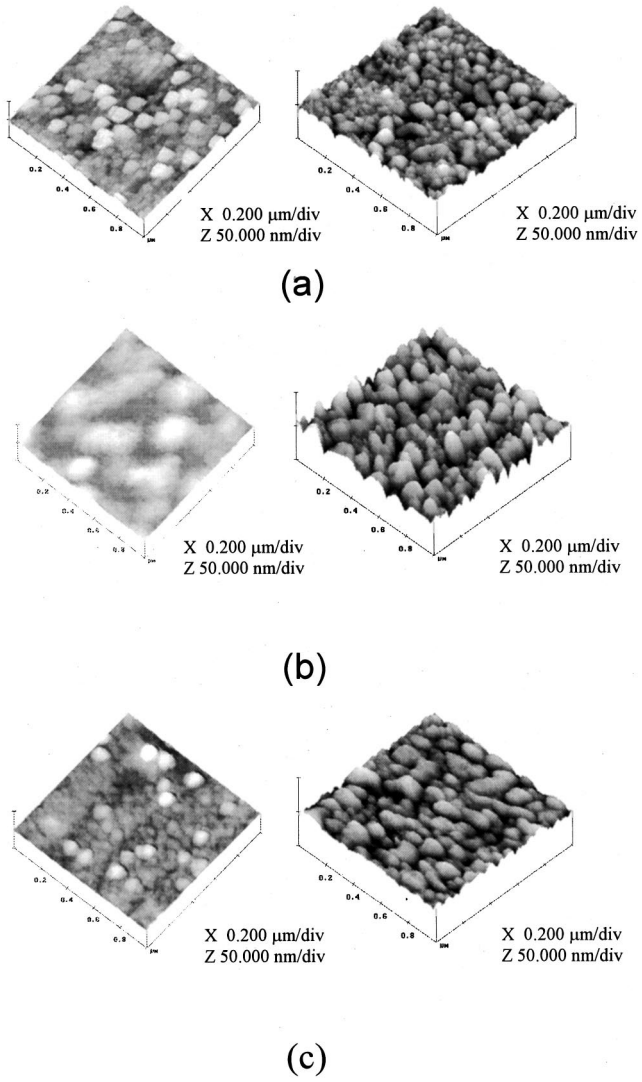

FIG. 2. AFM micrographs of the surface topography of SBT films heat treated by RTA for 2 min and subsequently postannealed for 1 h in an oxygen atmosphere at: (a) 700 °C, (b) 750 °C, and (c) 800 °C. (Area $=1\ \mu\text{m}\times1\ \mu\text{m}$.)

The $C-V$ results are shown in Fig. 5. The butterfly-shape curves that characterize every ferroelectric material are consistent with the other electrical measurements and the microstructural data. The switching voltage took place at different voltages on each side, showing a voltage shift toward

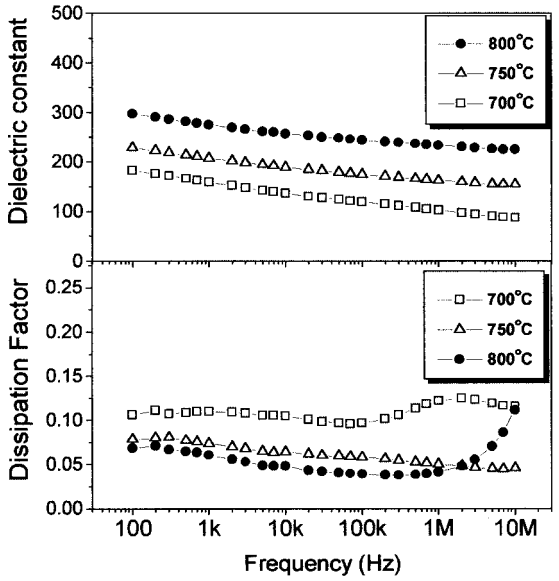

FIG. 3. Dielectric constant and dissipation factor as a function of frequency for SBT films heat treated by RTA for 2 min and subsequently postannealed for 1 h in an oxygen atmosphere at 700, 750, and 800 °C.

the positive side; also, the intersection of the up and down curves lies in the positive voltage.

The ferroelectric hysteresis loops were measured at a 60 Hz frequency under virtual ground conditions. The remanent polarization ($2P_r$) and coercive field (E_c) for the SBT thin films annealed at 700, 750, and 800 °C were 7.1 μC/cm^2 and 113 kV/cm, 15.2 μC/cm^2 and 95 kV/cm, and 18.8 μC/cm^2 and 93 kV/cm, respectively, as shown in Fig. 6. It can be observed that, as the treatment temperature increased, the P_r values improved. These results are in agreement with the microstructural evolution.

It should also be noted that the hysteresis loops show an appreciable shift along the electric field axis toward the positive side, which is defined as imprint. The voltage shifts may lead to the failure of the capacitor due to the apparent loss of polarization in one of the remanent states. Consequently, an increase in the coercive voltage in one direction occurs. These two effects may cause a memory failure. These results are consistent with the $C-V$ measurements.

Warren *et al.*[19] and Dimos *et al.*[20] reported that the voltage shift in piezoelectric transducer films is caused by an asymmetric distribution of trapped charge when the capacitor is heated to 120 °C and that, in optically treated films, the induced voltage shift is originated by trapping charge carriers at the interface, which compensate for the depolarizing field, respectively. According to the electrostatic model proposed by Robels *et al.*,[21] this horizontal shift of the curve represents the internal bias, which is closely connected to the electrode/film interface.

TABLE I. Dielectric constant and dissipation factor values at a 100 kHz frequency.

Temperature (°C)	Dielectric constant (ε)	Dissipation factor (tan δ)
700	121	0.098
750	174	0.058
800	248	0.040

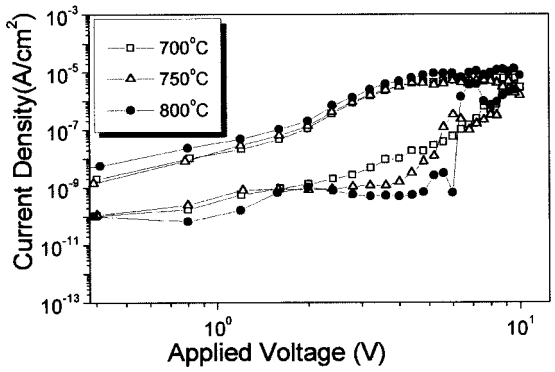

FIG. 4. $I-V$ curves SBT films heat treated by RTA for 2 min and subsequently postannealed for 1 h in an oxygen atmosphere at: (a) 700, (b) 750, and (c) 800 °C.

Al-Shareef *et al.*[22] studied the thermally and optically induced shift of the hysteresis loops in SBT films. They proposed that, in the case of SBT, the voltage shift may also be caused by charge carrier trapping generated at the film/electrode interface by optical or thermal induction. The optical imprint in SBT films is higher than the thermal one.

The internal bias voltage (V_i) values, determined by $V_i = (V_c^+ - |V_c^-|)/2$, were 0.82, 0.70, and 0.65 V for films treated at 800, 750, and 700 °C, respectively. These results are in agreement with those reported in Ref. 22.

An earlier work[16] reported on the preparation and characterization of SBT film by the same method, but crystallization was carried out in a conventional furnace. The films crystallized in the conventional furnace presented a small shift effect toward the positive side, as shown in Fig. 7. The internal bias voltage (V_i) values were 0.14 and 0.23 V for the films treated at 800 and 700 °C, respectively.

These findings suggest that the high voltage shift observed in the films crystallized by RTA resulted from the illumination of the samples during crystallization, since the only difference in the film preparation process is the type of furnace used. In other words, RTA crystallization with a

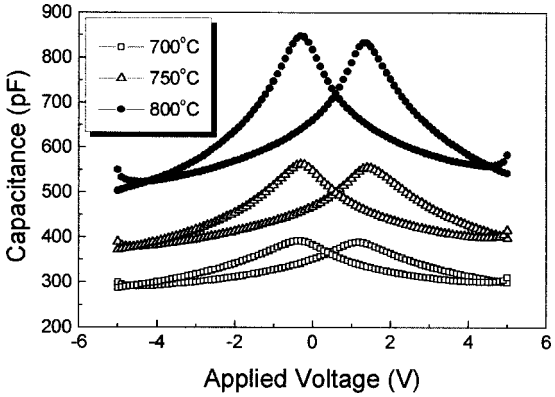

FIG. 5. $C-V$ curves SBT films heat treated by RTA for 2 min and subsequently postannealed for 1 h in an oxygen atmosphere at: (a) 700, (b) 750, and (c) 800 °C.

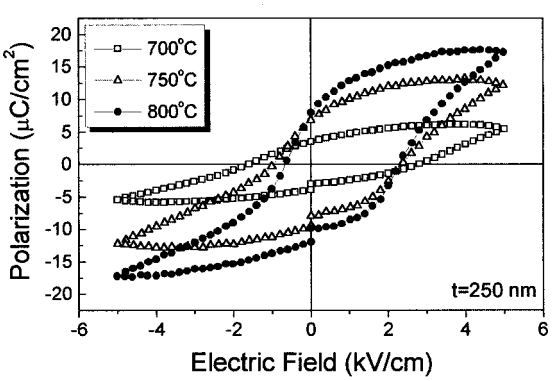

FIG. 6. Hysteresis loop at a 60 Hz frequency, at room temperature, for SBT films heat treated by RTA for 2 min and subsequently postannealed for 1 h in an oxygen atmosphere at 700, 750, and 800 °C.

halogen lamp induces a permanent voltage shift in the hysteresis loops of SBT films due to the generation of trapped charge carriers at defect sites near the electrode/film interface. These results indicate the unsuitability of the films for use as memories owing to the significant difference between $+E_c$ and $-E_c$ (94 and -26 kV/cm, respectively, for the film treated at 800 °C).

IV. CONCLUSIONS

Ferroelectric SBT thin films were successfully prepared by the alternative chemical route and crystallized in a RTA halogen lamp furnace. The films showed a high permanent imprint characteristic that was optically induced by the crystallization method. These voltage shifts are caused by the generation of charge carriers that are trapped at defect sites near the electrode/film interface. Our findings demonstrate that these films are unsuitable for memory applications as a consequence of the substantial difference between $+E_c$ and $-E_c$. All the electrical measurements led to the conclusion that crystallization using a halogen lamp RTA furnace is inappropriate for SBT films. This shift effect was not observed in films crystallized by the conventional furnace method.

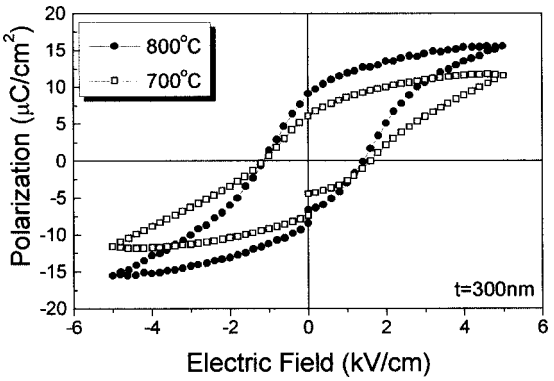

FIG. 7. Hysteresis loop at a 60 Hz frequency, at room temperature, for SBT films heat treated for 2 h in a conventional furnace at 700 and 800 °C.

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[1] P. K. Larsen, R. Cuppens, and G. A. C. M. Spierings, Ferroelectrics **128**, 265 (1992).
[2] J. F. Scott, Integr. Ferroelectr. **19**, 85 (1998).
[3] T. Mihara, H. Yoshimori, H. Watanabe, and C. A. Paz de Araujo, Jpn. J. Appl. Phys., Part 1 **34**, 5233 (1995).
[4] J. J. Lee, C. L. Thio, and S. B. Desu, J. Appl. Phys. **78**, 5073 (1995).
[5] M. Noda, Y. Matsumuro, H. Sugiyama, and M. Okuyama, Jpn. J. Appl. Phys., Part 1 **38**, 2275 (1999).
[6] S.-Y. Chen and V.-C. Lee, J. Appl. Phys. **87**, 3050 (2000).
[7] N. Nukaga, K. Ishikawa, and H. Funakubo, Jpn. J. Appl. Phys., Part 1 **38**, 5428 (1999).
[8] D. J. Taylor, R. E. Jones, P. Zurcher, P. Chu, Y. T. Lii, B. Jiang, and S. J. Gillespie, Appl. Phys. Lett. **68**, 2300 (1996).
[9] J.-P. Han and T. P. Ma, Appl. Phys. Lett. **71**, 1267 (1997).
[10] M. Klee and U. Mackens, Integr. Ferroelectr. **12**, 11 (1996).
[11] T. Osaka, S. Ono, A. Sakakibara, and I. Koiwa, IEICE Trans. Electron. **E81**, 545 (1998).
[12] G. D. Hu, I. H. Wilson, J. B. Xu, C. P. Li, and S. P. Wong, Appl. Phys. Lett. **76**, 1758 (2000).
[13] S.-H. Kim, D. J. Kim, J. Im, C. E. Kim, and A. I. Kingon, J. Sol-Gel Sci. Technol. **16**, 57 (1999).
[14] T. Hase, T. Noguchi, and Y. Miyasaka, Integr. Ferroelectr. **16**, 29 (1997).
[15] C. W. Chung and I. Chung, Thin Solid Films **354**, 111 (1999).
[16] S. M. Zanetti, E. B. Araújo, A. J. Chiquito, E. R. Leite, J. A. Eiras, E. Longo, and J. A. Varela, J. Mater. Res. **15**, 2091 (2000).
[17] R. Pascual, M. Sayer, A. Lo, S. Herbert, L. C. Rolim, and N. Townley, J. Appl. Phys. **79**, 493 (1996).
[18] S. Battacharyya, S. S. N. Bharadwaja, and S. B. Krupanidhi, Appl. Phys. Lett. **75**, 2656 (1999).
[19] W. L. Warren, D. Dimos, G. E. Pike, B. A. Tuttle, M. V. Raymond, R. Ramesh, and J. T. Evans Jr., Appl. Phys. Lett. **67**, 866 (1995).
[20] D. Dimos, H. N. Al-Shareef, W. L. Warren, and B. A. Tuttle, J. Appl. Phys. **80**, 1682 (1996).
[21] U. Robels, J. H. Calderwood, and G. Arlt, J. Appl. Phys. **77**, 4002 (1995).
[22] H. N. Al-Shareef, D. Dimos, W. L. Warren, and B. A. Tuttle, J. Appl. Phys. **80**, 4573 (1996).