JOURNAL OF MATERIALS SCIENCE **39** (2004) 2937–2940

Temperature induced growth away from the (*00l*) orientation in $SrBi_2Ta_2O_9$ films deposited by PLD

MA. DE LA PAZ CRUZ-JÁUREGUI
Centro de Ciencias de la Materia Condensada, UNAM
E-mail: mcruz@ccmc.unam.mx

J. J. PORTELLES
Facultad de Física-IMRE, Universidad de la Habana, Cuba

J. M. SIQUEIROS
Centro de Ciencias de la Materia Condensada, UNAM

The research on ferroelectric materials has been largely driven by the possibility of application in non-volatile random access memories (NVFRAM). In particular, thin films of $SrBi_2Ta_2O_9$ (SBT) [1–9] have attracted great interest as good candidates for NVFRAM technology due to the excellent behavior regarding fatigue, retention and leakage current. SBT belongs to a family of Bi layered-structure perovskite oxides [10], with a highly anisotropic pseudotetragonal structure [11] (a = 0.5531 nm, b = 0.5534 nm and c = 2.4984 nm) that leads to highly anisotropic ferroelectric properties. The spontaneous polarization vector in this material is in the *a-b* plane but, in films grown on $Pt/TiO_2/SiO_2/Si(111)$ substrates, a large fraction of the crystallites grow with the *a-b* planes parallel to the plane of the substrate leading to low values of the net polarization [8, 9]. It is therefore desirable to manipulate film growth to enhance the projection of the polar vector in a direction perpendicular to the substrate surface. To achieve this goal, and for the more general purpose of studying the influence of crystal orientation on the ferroelectric properties of the SBT films, deposits have been made on substrates such as $SrLaGaO_4(110)$ [3]; $SrTiO_3(001)$, (011), (111) [4]; MgO(110) [5]; and $SrLaAlO_4(100)$ [6]. It is clear, however, from a technological point of view, that these are not suitable substrates for memory devices because of their silicon-based microelectronic incompatibility. Taking this into account,the results presented in this work are based on deposits made on conventional $Pt/TiO_2/SiO_2/Si(111)$ bottom electrodes that are compatible with silicon microelectronic processes. As a consequence of the deposition conditions and the heat treatment applied, after the deposition, to the SBT films deposited on Pt electrodes, the fraction of crystallites grown with the (*00l*) planes parallel to the plane of the substrate was reduced. This led to an enhancement of the measured polarization, reflected in the maximum values of $2P_r = 9.1\ \mu C/cm^2$ and coercive field, E_c, of 52.0 kV/cm, taken at a voltage of 5 V. As a result, the combination of a higher remnant polarization with lower coercive field obtained is better than that reported in recent works [12, 13] using the same technique and depositing on the same bottom electrodes.

The SBT target used in the PLD process was a stoichiometric $SrBi_2Ta_2O_9$ slab obtained from reagent grade oxides by the conventional ceramic method, sintered at 1250 °C for 3 h. The SBT films were grown by PLD using the 248 nm radiation of a KrF excimer laser (LPX 200 by Lambda Physik). The pulse repetition rate was 10 Hz with a fluence of approximately 1 J/cm^2. The films, grown on $Pt/TiO_2/SiO_2/Si(111)$ substrates, were 200 nm thick. The substrate-target separation was 5 cm and the oxygen pressure was 450 mTorr. The deposits were made at temperatures of 570–715 °C and then were post-annealed at 750 °C in air for 90 min. The resulting films were analyzed in a JSM-5300 scanning electron microscope (SEM), by Jeol, and by X-ray diffraction (XRD) using the Cu K_α line ($\lambda_{k\alpha1} = 1.54056$ Å and $\lambda_{k\alpha2} = 1.54439$ Å) of a Phillips X'pert diffractometer. Argon ion magnetron sputtering was used for

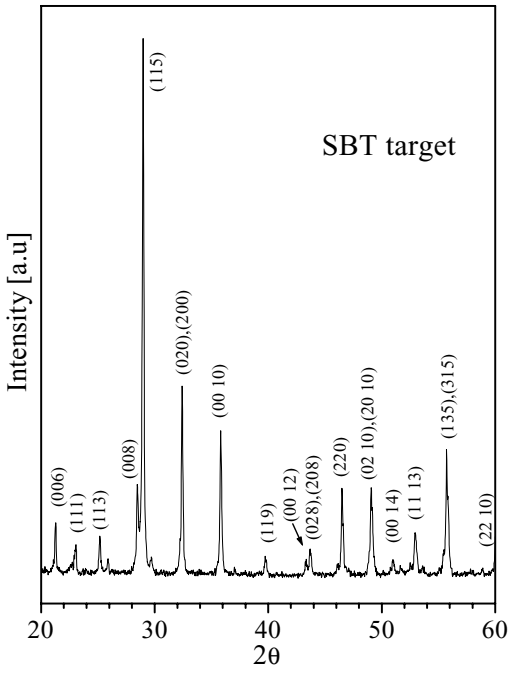

Figure 1 XRD pattern of the $SrBi_2Ta_2O_9$ ceramic sintered at 1250 °C/3 h.

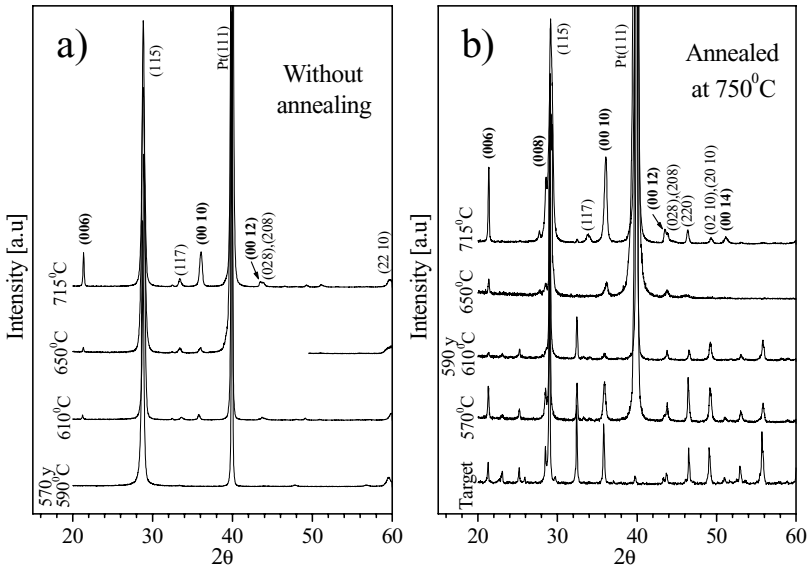

Figure 2 XRD spectra of the $SrBi_2Ta_2O_9$ films deposited on $Pt/TiO_2/SiO_2/Si$ substrates at different temperatures: (a) before annealing and (b) after annealing at 750 °C.

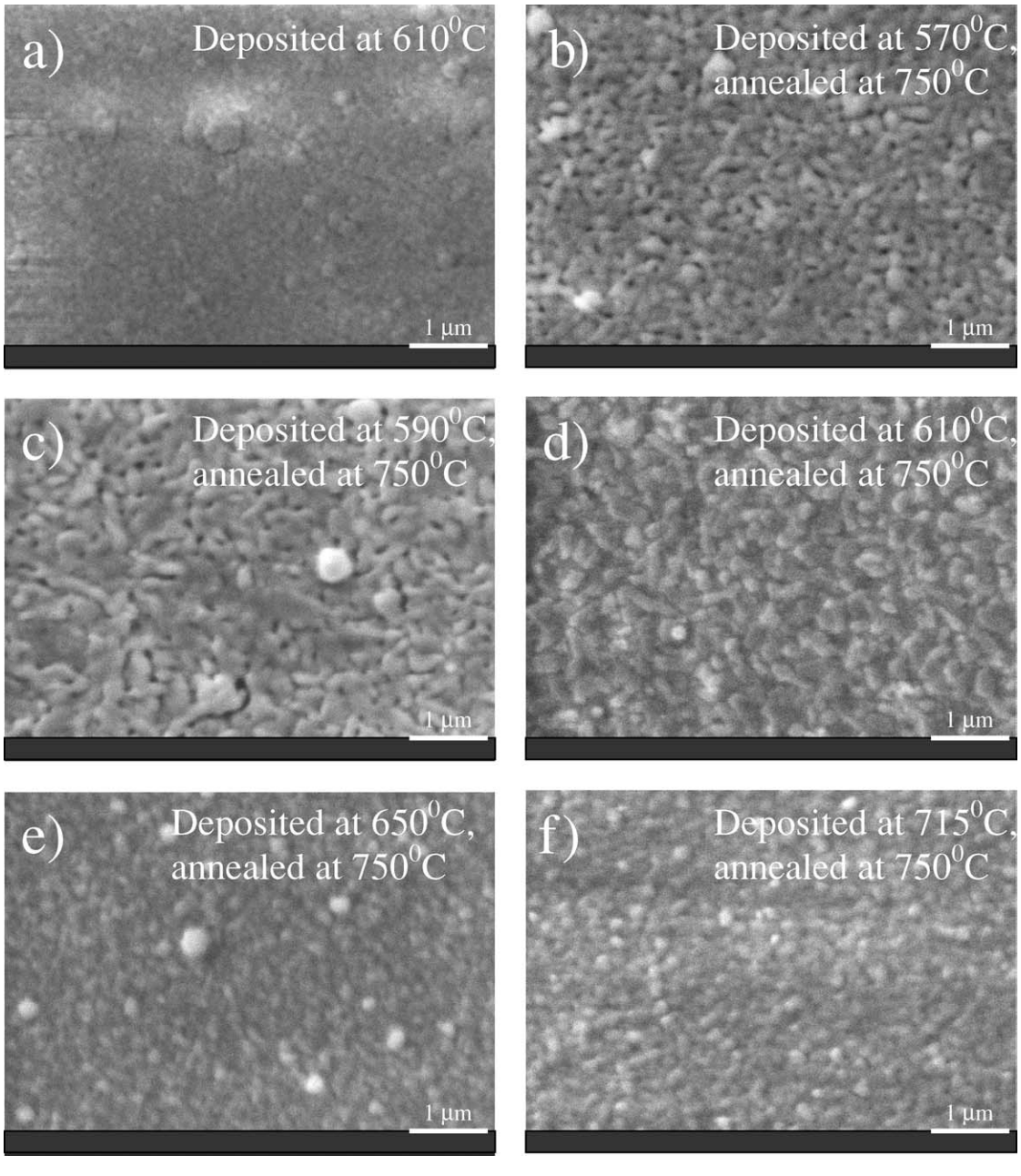

Figure 3 SEM micrographs of $SrBi_2Ta_2O_9$ films deposited over $Pt/TiO_2/SiO_2/Si$ substrates.

the 150 nm thick Pt bottom electrode deposition, and an electron gun for the 30 nm thick TiO_2 films. Pt top electrodes were r.f. sputtered at room temperature on the SBT films. An RT66A tester from Radiant Technologies was used for the electric characterization.

The SBT target used for PLD was a single phase stoichiometric ceramic disk with no secondary phases as shown by XRD (see Fig. 1), and a 305 °C ferroparaelectric transition temperature similar to that reported by other authors [14].

The results of the present report complement those of previous work [7], where it was shown that films deposited at 600 °C were totally formed by SBT crystals with a (115) preferred orientation. The same result was reproduced in this work for films deposited at 570 and 590 °C where no differences were detected in their XRD patterns. For higher deposition temperatures, between 610 and 715 °C, the (115) oriented phase is still dominant but peaks from (00*l*) planes appear in the XRD profiles (see Fig. 2a). These peaks are indicative of crystals grown with their *c*-axis oriented perpendicular to the substrate plane and no contribution to the polarization [8, 9] is expected from them. Wang *et al.* [13] achieved similar results for films grown at 680 °C however their resulting films were highly *c*-oriented.

It was also shown in a previous report that heat treatment at temperatures above 650 °C of films deposited at low temperatures promotes polycrystalline growth [7]. This result is verified in this work where the films deposited at 570 °C turn polycrystalline after a 750 °C annealing in air. However, the same heat treatment applied to films deposited at 590 and 610 °C results in polycrystalline growth with a smaller fraction of the crystallites oriented in the (00*l*) direction (see XRD pattern in Fig. 2b). On the other hand, films deposited at temperatures higher than 610 °C heat-treated at 750 °C produced crystals with an increased intensity of the peaks associated with the (00*l*) direction (see also Fig. 2b) and a topography of regularly shaped grains in contrast to the elongated grains developed in heat-treated films deposited at lower temperatures. Before heat treatment at 750 °C, surface topography is very similar for all films (Fig. 3). Measurements of the ferroelectric properties showed an improvement of the polarization values for the post-annealed films deposited at 610 °C as can be seen in the hysteresis loops of Fig. 4, rendering maximum values for the remnant polarization of $2P_r = 9.1\ \mu C/cm^2$, and 52.0 KV/cm for the coercive field, E_c, at 5 V. More specifically, the highest polarization value and correspondingly the highest coercive field are obtained for a deposition temperature between 590 and 610 °C as can be concluded from the graphs in Fig. 5a and b for films annealed at 750 °C.

It can be concluded that the deposition temperatures of 590 and 610 °C followed by annealing in air at 750 °C of SBT films on $Pt/TiO_2/SiO_2/Si(111)$ substrates produced an increase of the fraction of crystallites with the *c*-axis parallel to the substrate plane. An increase in the value of the remnant polarization results as a consequence. It was found that deposition temperatures above 610 °C increase the amount of film material growing in the unwanted (00*l*) direction. This tendency is increased with the annealing process at 750 °C. The recommended route for higher polarization values is, therefore, to deposit at temperatures between 590 and 610 °C followed by a post-annealing treatment at 750 °C.

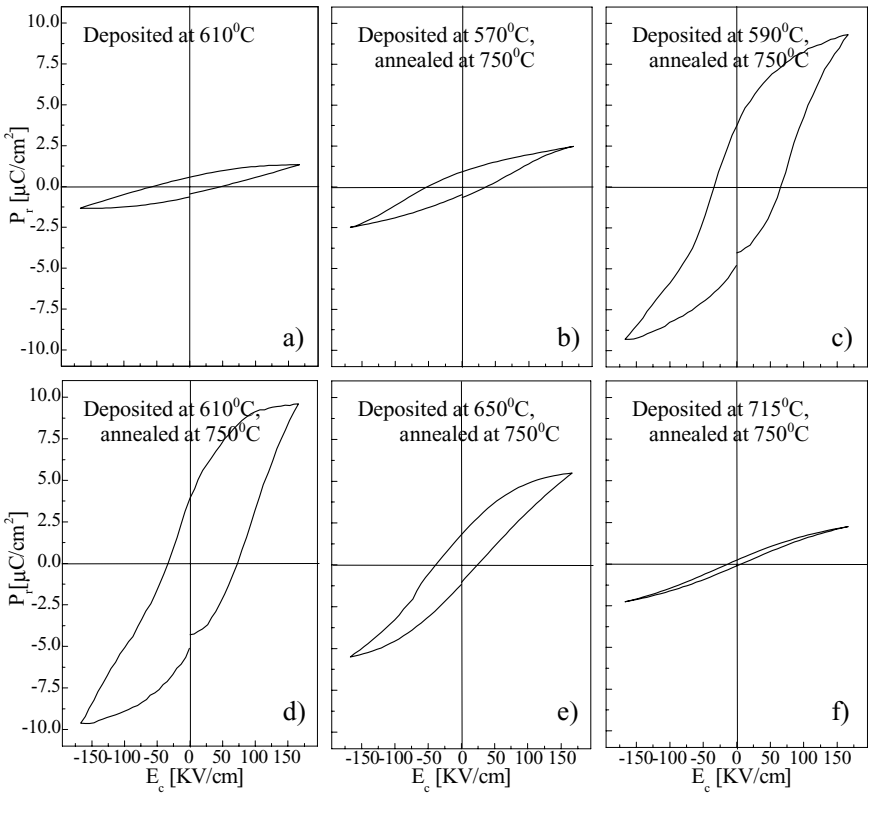

Figure 4 Hysteresis loops of the $SrBi_2Ta_2O_9$ films deposited on $Pt/TiO_2/SiO_2/Si$ substrates.

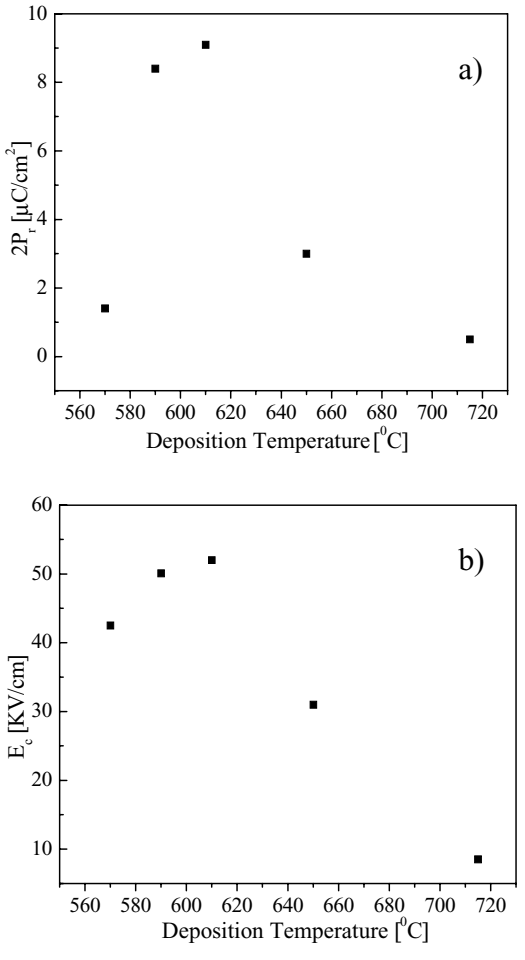

Figure 5 Dependence of (a) remnant polarization P_r and (b) coercive field, E_c, on the deposition temperature for $SrBi_2Ta_2O_9$ films annealed at 750 °C.

This work was partially supported by grants of DGAPA-UNAM, Proj. No. IN104000, and CoNaCyT Proj. No. 33586E Thanks are due to E. Aparicio, P. Casillas, J. Díaz, E. Flores and I. Gradilla for their technical help and to O. Raymond for fruitful discussions.

References

1. S. B. MAJUMDER, S. BHASKAR and R. S. KATIYAR, *Integr. Ferroelectr.* **42**(1–4) (2002) 245.
2. T. SCHNELLER and R. WASER, *Ferroelectrics.* **267** (2002) 293 .
3. H. N. LEE, D. N. ZAKHAROV, S. SENZ, A. PIGNOLET and D. HESSE, *Appl. Phys. Lett.* **79**(18) (2001) 2961.
4. H. N. LEE, A. VISINOIU, S. SENZ, C. HARNAGEA, A. PIGNOLET, D. HESSE and U. GOSELE, *J. Appl. Phys.* **88**(11) (2000) 6658.
5. S. E. MOO, T. K. SONG, S. B. BACK, S. I. KWUN, J. G. YOON and J. S LEE, *Appl. Phys. Lett.* **75** (1999) 2827.
6. J. LETTIERI, Y. JIA, M. URBANIK, C. I. WEBER, J. P. MARÍA, D. G. SCHLOM, H. LI, R. RAMESH, R. UECKER and P. REICHE, *ibid.* **73** (1998) 2923 .
7. M. P. CRUZ-JÁUREGUI, J. M. SIQUEIROS and J. PORTELLES, *J. Mater. Sci.: Mater. Electronics.* **12** (2001) 461.
8. R. E. NEWNHAM, R. W. WOLFE and J. F. DORRIAN, *Mater. Res. Bull.* **6** (1971) 1029.
9. Y. SHIMAKAWA, Y. KUBO, Y. NAKAGAWA, T. KAMIYAMA, H. ASANO and F. IZUMI, *Appl. Phys. Lett.* **74** (1999) 1904 .
10. B. AURIVULLIUS, *Arkiv för Kemi* **1** (1949) 463 .
11. A. D. RAE, J. G. THOMPSON and R. L. WITHERS, *Acta Crystall., Sect. B: Struct. Sci.* **48** (1992) 418 .
12. R. R. DAS, P. BHATTACHARYA, W. PÉREZ, A. MORALES CRUZ, R. S. KATIYAR and S. B. DESU, *Integr. Ferroelectr.* **42**(1–4) (2002) 305.
13. Y. P. WANG, T. ZHU and Z. G. LIU, *Appl. Phys.* A **74** (2002) 665.
14. G. A. SMOLENSKII, V. A. ISUPOV and A. I. AGRANOVSKAYA, *Soviet Phys.-Solid Stat* **3**(3) (1961) 651.

Received 2 September
and accepted 13 October 2003