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Preparation of fatigue-free $SrBi_2Ta_2O_9$ thin films by r.f. magnetron sputtering and their ferroelectric properties

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Fatigue-free bismuth-layered $SrBi_2Ta_2O_9$ (SBT) films were deposited on $Pt/Ti/SiO_2/Si$ substrates by r.f. magnetron sputtering at room temperature. The variation of structure and electrical properties were studied as a function of annealing temperatures from 750–850 °C. The films annealed at 800 °C had a composition ratio of Sr : Br : Ta = 0.7 : 2.0 : 2.0. X-ray photoelectron spectroscopy signals of bismuth show an oxygen-deficient state within the SBT films. The films annealed at 800 °C have a thickness of 200 nm and a relatively dense microstructure. The remanent polarization ($2P_r$), and the coercive field ($2E_c$), obtained for the SBT films, were 9.1 $\mu C\,cm^{-2}$ and 85 $kV\,cm^{-1}$ at an applied voltage of 3 V, respectively. The films showed fatigue-free characteristics up to 10^{10} cycles under 5 V bipolar square pulses. The leakage current density was about 7×10^{-7} $A\,cm^{-2}$ at 150 $kV\,cm^{-1}$. The SBT films prepared by r.f. magnetron sputtering were attractive for application to non-volatile memories. © *1998 Kluwer Academic Publishers*

1. Introduction

Ferroelectric thin-film capacitors have been extensively investigated for non-volatile memory application [1–3]. The most popular ferroelectric materials under investigation for non-volatile memory applications are $PbZr_xTi_{1-x}O_3$ (PZT), because they have a high Curie temperature, and large remanent polarization. However, these ferroelectric materials have serious fatigue degradation problems after 10^7–10^8 cycles that are insufficient for intensive read/write application. For this reason, research has been conducted to improve the fatigue properties of PZT capacitors by using conductive oxide electrodes such as RuO_2, $LaSrCoO_3$, etc.; however, its disadvantage is that the resulting device is electrically leaky for some non-volatile memory devices [4, 5].

An alternative approach to control the fatigue problem in ferroelectric capacitors is to use other ferroelectric materials. In recent years, it has been reported [6, 7] that bismuth-based layered ferroelectrics are excellent for use in thin-film capacitors due to the absence of significant fatigue and good retention. The capacitors formed by bismuth layer ferroelectrics show no significant fatigue after 10^{12} switching cycles. A particularly successful approach has been developed, which involves the use of layered perovskite materials, such as $SrBi_2Ta_2O_9$ (SBT). SBT may more properly be written as $(Bi_2O_2)^{2+}$ and $(SrTa_2O_7)^{2-}$ layers and belongs to a large family of so-called multilayer interstitial compounds with $(Bi_2O_2)^{2+}$-$(A_{x-1}B_xO_{3x+1})^{2-}$ where, A is a twelve-coordination ion such as strontium, barium or calcium, and B is a six-coordinatioin ion such as tantalum, nickel or niobium and the values of x are 1, 2, 3, 4 and 5. Capacitors involving an SBT ferroelectric layer have been synthesized mainly by the sol–gel process [8–10], and pulsed laser ablation (PLD) [11, 12]; therefore, it is desirable to explore other technique such as the r.f. magnetron sputtering method. In this work, the dependency of annealing temperature on structure and electrical properties of the SBT film were studied.

2. Experimental procedure

The used target was a cold-pressed $SrBi_2Ta_2O_9$ ceramic with 30 mol % excess $SrCO_3$ and 20 mol % excess Bi_2O_3 to compensate the lack of strontium and bismuth in SBT films. The deposition of SBT films was performed with a sputtering pressure of 5×10^{-3} torr (1 torr = 133.322 Pa) at room temperature to minimize volatilization of strontium and bismuth. The typical deposition conditions of SBT thin films are summarized in Table I.

For electrical measurements, metal–insulator–metal (MIM) capacitors with $Pt/SBT/Pt/Ti/SiO_2/Si$ structure were fabricated and the top electrode (platinum) was deposited by d.c. sputtering using a shadow mask with a 100 μm diameter hole at room

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TABLE I Sputtering conditions of SBT film preparation

Target material	$Sr_{1.3}Bi_{2.2}Ta_{2.0}O_9$
Substrate	$Pt/Ti/SiO_2/Si$
Target diameter	5.08 cm
Base pressure of system	3×10^{-5} torr
Sputtering pressure	5 m torr
R.f. power	100 W
Sputtering gas ($Ar:O_2$)	1:3
Substrate temperature	Room temperature
Annealing temperature	750, 800, 850 °C

temperature. After deposition of the platinum top electrode, the films were annealed in an oxygen atmosphere at 750, 800 and 850 °C for 1 h.

The crystal structure of SBT films was characterized by X-ray diffraction (XRD) employing CuK_α radiation and a nickel filter. The morphology and the thickness of the deposited films were determined using a scanning electron microscope (SEM). The composition of the SBT films was determined by electron probe microanalysis (EPMA) and the depth profile of the SBT films was performed by secondary ion mass spectroscopy (SIMS, Cameca IMS 4f) using 5.5 keV O^{2+} and 200 nA. X-ray photoelectron spectroscopy (XPS, V.G. Scientific, Escalab-210) was used to analyse the secondary phases which are commonly incorporated in SBT films using, as source, MgK_α X-ray. The capacitance–voltage characteristic was measured by a Hewlett-Packard (4194A) impedance-gain phase analyser. Ferroelectric properties (polarization versus electric field and fatigue property) were measured using a RT66A ferroelectric tester (Radient Technology) operating in the virtual ground mode. The leakage current behaviour was measured by an electrometer (Keithley 617) with a voltage step of 0.1 V and a delay time of 20 s.

3. Results and discussion

Fig. 1 shows XRD patterns of SBT thin films annealed at various temperatures. The SBT films of the orthorhombic bismuth-layered structure were typically obtained under all conditions. As can be seen in Fig. 1, (1 1 5), (0 0 $\underline{1\,0}$), (2 2 0) and (3 0 4) peaks appear above the annealing temperature of 750 °C. The intensity of the (1 1 5) and (0 0 $\underline{1\,0}$) peaks gradually increase as the annealing temperature increases and the intensity of the (2 2 0) peak was strongest at 800 °C and decreased at 850 °C. The lattice constants calculated from (1 1 5), (2 0 0), (0 0 $\underline{1\,0}$) peaks for the SBT film annealed at 800 °C are $a = 0.5502$ nm, $b = 0.55902$ nm, and $c = 2.4852$ nm. These values are similar to those reported for bulk SBT [13]. However, the lattice constants of SBT films show a small difference with annealing temperature due to the different stress conditions of the films.

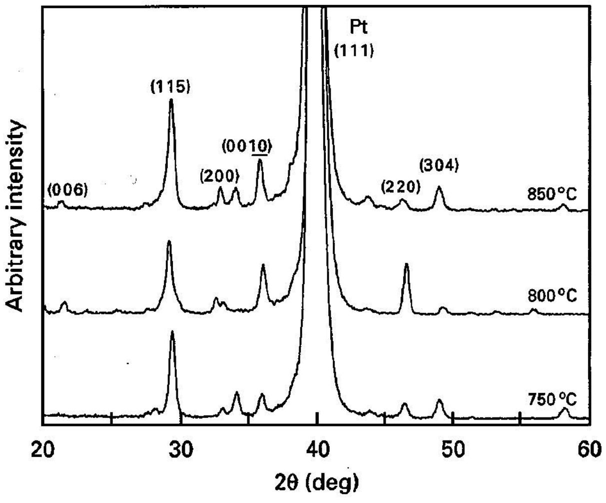

Figure 1 XRD patterns of SBT films annealed at various temperatures.

Fig. 2 shows typical SEM images obtained from SBT films annealed at various temperatures. From the

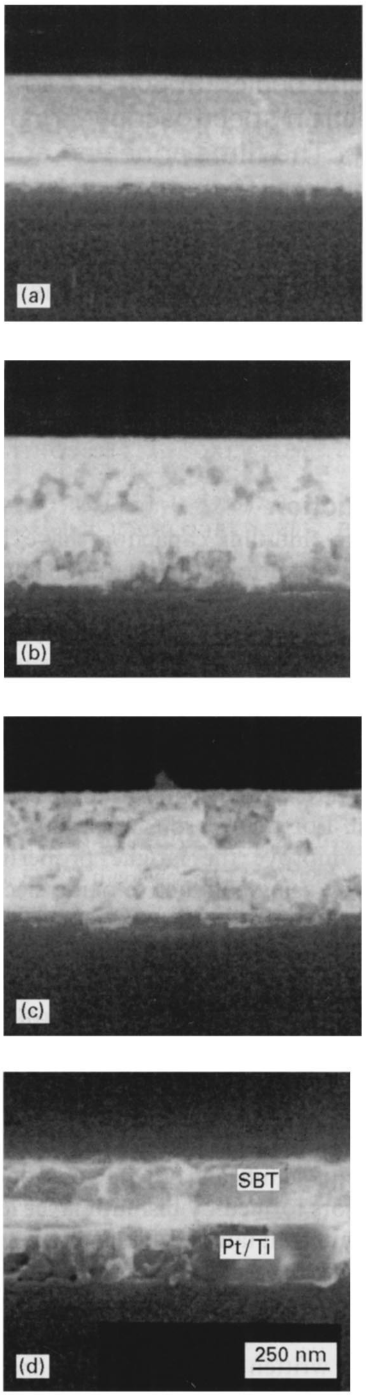

Figure 2 SEM cross-sectional images of SBT films annealed at various temperatures: (a) as-depo., (b) 750 °C, (c) 800 °C, (d) 850 °C.

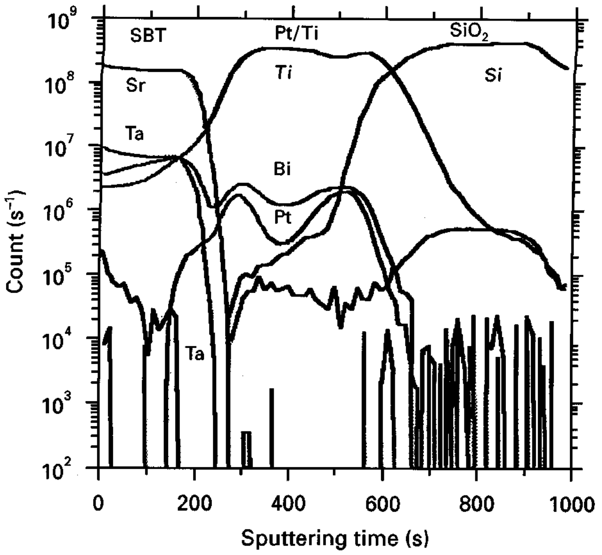

Figure 3 SIMS compositional depth profile of $Sr_{0.7}Bi_{2.0}Ta_{2.0}O_9$ thin film annealed at 800 °C.

images of the films annealed at 800 °C, the films are found to have a thickness of 200 nm and a dense microstructure. As the annealing temperature increases, the thickness of the SBT films decreases gradually due to densification and volatilization of bismuth in the films. However, films annealed at 850 °C have rough, large, grains due to merging of small grains during annealing. The composition of the films annealed at 800 °C was about Sr 0.7, Bi 2.0 and Ta 2.0 from measurement by EPMA.

Fig. 3 show the compositional depth profile of the SBT film annealed at 800 °C. From this figure, bismuth diffusion to the interface between the platinum and titanium layers of the bottom electrode was clearly observed. This bismuth diffusion was also observed in SBT films prepared by sol–gel [8] and pulsed laser ablation [11] methods and also a titanium buffer layer diffused into the SBT film through the platinum layer. The diffusion of titanium within the SBT film may form TiO_2 second phase. The influence of titanium on the electrical properties of SBT should be further studied. However, strontium and tantalum were not observed to diffuse into the bottom electrode.

Fig. 4a and b show typical XPS surface survey scans and Bi 4f7/2 spectra of the SBT film annealed at 800 °C, respectively. From Fig. 4a, the films are seen to have excess bismuth and deficient strontium in surface before sputtering. The Pt 4f peak can result from sensing of the platinum top electrode due to the large area scan (3.2 mm × 3.2 mm). Sr 3d and Ta 4d spectra with sputtering time show that the films contain oxidation states of SrO and Ta_2O_5 which are similar to those of the bulk. However, as shown in Fig. 4b, Bi 4f spectra with sputtering time show a large difference between the surface and inside of the film. That is, the intensity of Bi_2O_3 is strong at the surface and the intensity of metallic bismuth gradually increases with sputtering time. This result suggests that oxidation of bismuth may be insufficient and the amount of $(Bi_2O_2)^{2+}$ ions in the SBT film may be deficient. Therefore, further study of the optimal condition for sufficient oxidation of SBT film should be undertaken.

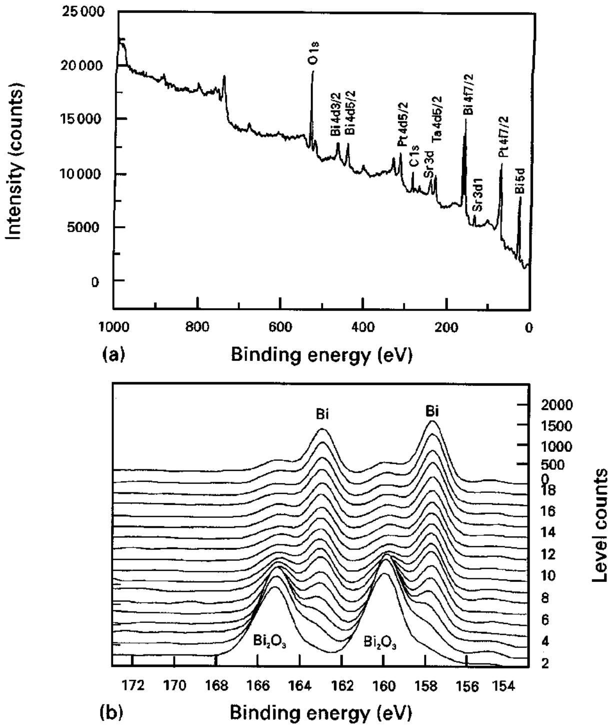

Figure 4 (a) XPS surface survey scan (Ar : O_2 = 1 : 3) and (b) Bi 4f spectra as a function of sputtering time, for the SBT film annealed at 800 °C.

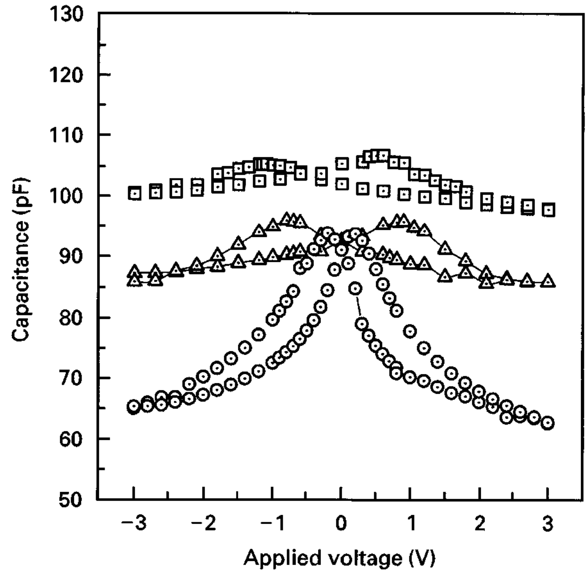

Figure 5 Capactitance–voltage characteristics of SBT films annealed at (△) 750 °C, (○) 800 °C, (□) 850 °C.

Fig. 5 shows capacitance versus voltage (C–V) characteristics of SBT films annealed at various temperatures. The small signal capacitance was measured at 100 kHz when the electric voltage was swept from a positive bias to a negative bias and back again. The capacitance shows hysteresis behaviour and this result indicates that the dielectric films have a ferroelectric property. The voltage showing the maximum capacitance decrease in the order of the annealing temperatures of 750, 850 and 800 °C. This tendency

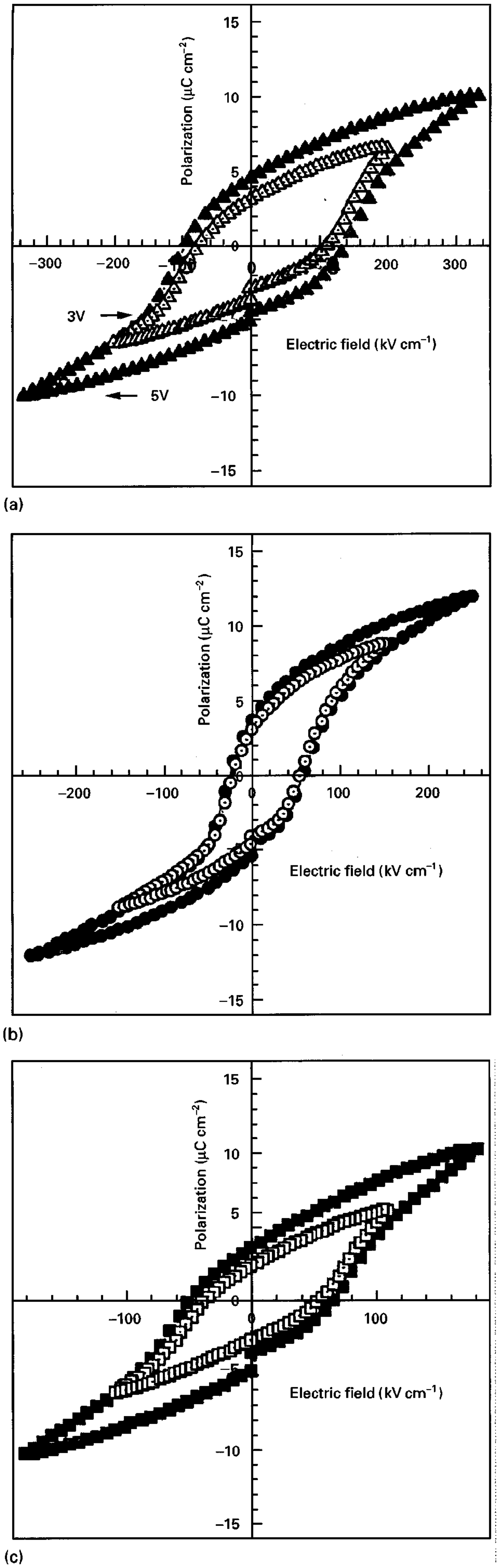

Figure 6 *P–E* hysteresis loops of annealed SBT films measured using excitation voltages of 3 and 5 V: (a) 750 °C, (b) 800 °C, (c) 850 °C.

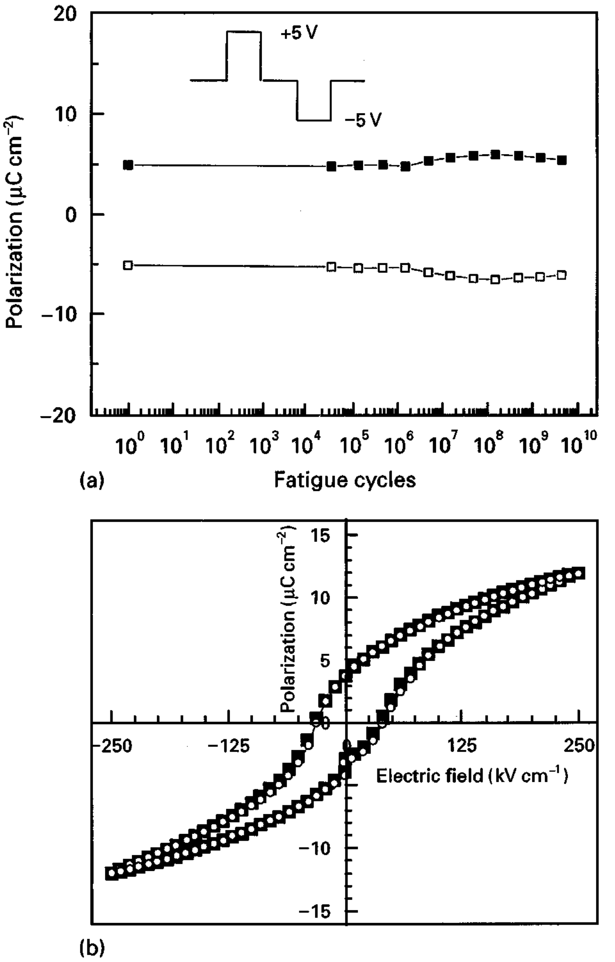

Figure 7 (a) Fatigue curves, (■) + ($P_r^* - P_r$); (□) − ($Pr^* - P_r$); and (b) *P–E* hysteresis loops (■) before and (○) after the fatigue test, of the SBT films annealed at 800 °C.

might influence the coercive field in the *P–E* curve. The applied field showing maximum capacitance was about 20 kV cm^{-1} for the SBT films annealed at 800 °C.

The polarization versus electric field curves of SBT films using excitation voltages of 3 and 5 V are shown in Fig. 6. Upon comparing the shape of the curve and coercive field of each film, the films annealed at 800 °C have the sharpest shapes and low coercive field. However, for the films annealed at 750 and 850 °C, the end of the loops were rounded, indicating poorer saturation and higher coercive field than that annealed at 800 °C. Bernstein *et al.* [14] reported that the films having poor saturation showed a large leakage current. The change in coercive field identifies with the tendency of the applied field showing the maximum capacitance. The remanent polarization of the films was similar, irrespective of annealing temperature. The $2P_r$ and $2E_c$ values of the films annealed at 800 °C were 9.1 μC cm^{-2} and 85 kV cm^{-1} for an applied voltage of 3 V. These results are similar to results obtained by MOCVD [15].

Fatigue characteristics of the SBT films annealed at 800 °C are shown in Fig. 7. Fatigue testing was done using 5 V bipolar square pulses at 1 MHz produced by function generator. As shown in Fig. 7a, the SBT films show practically no polarization fatigue up to 10^{10}

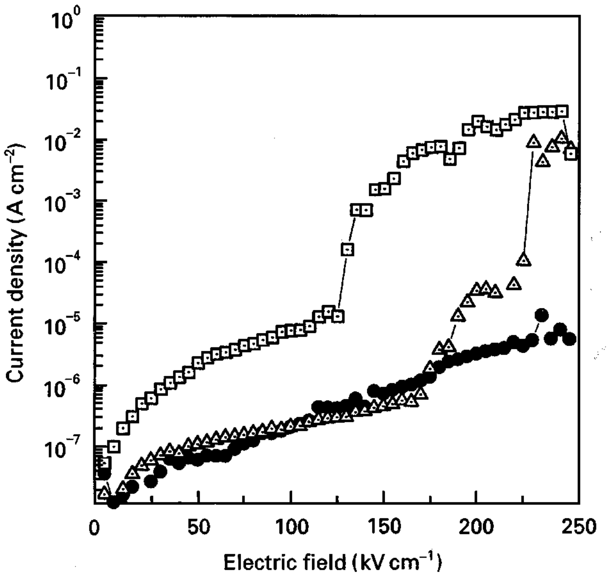

Figure 8 Leakage current of SBT films annealed at (△) 750 °C, (●) 800 °C, (□) 850 °C.

switching cycles. The *P–E* hysteresis loops of the SBT films before and after the fatigue test are shown in Fig. 7b. The hysteresis loops obtained after the fatigue tests were essentially identical to those observed before the fatigue test. Fig. 8 shows the leakage current characteristics of SBT films. It can be presumed from the shapes of the *P–E* curves that the leakage current density of the films annealed at 800 °C were the smallest. The leakage current density of the films was 7×10^{-7} A cm^{-2} at 150 kV cm^{-1}.

4. Conclusion

Fatigue-free bismuth-layered SBT films were successfully prepared on Pt/Ti/SiO_2/Si substrates by r.f. magnetron sputtering. The remanent polarization ($2P_r$) and the coercive field ($2E_c$) obtained for a 200 nm thick $Sr_{0.7}Bi_{2.0}Ta_{2.0}O_9$ film annealed 800 °C were 9.1 μC cm^{-2} and 85 kV cm^{-1} for an applied voltage of 3 V, respectively. The leakage current density was about 7×10^{-7} A cm^{-2} at 150 kV cm^{-1}. The films showed fatigue-free characteristics up to 1×10^{10} switching cycles under 5 V bipolar pulses. The SBT films prepared by r.f. magnetron sputtering are attractive for application to non-volatile memories.

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