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Preparation of $Ba(Pb_{1-x}Bi_x)O_3$ electrode thin films by rf magnetron sputtering

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Abstract

New electrode materials have been explored for $Pb(Zr,Ti)O_3$ (PZT) thin films in ferroelectric random access memory (FeRAM) devices. Among them, $Ba(Pb_{1-x}Bi_x)O_3$ (BPBO) is notable for its improved polarization and fatigue properties. Like PZT, the BPBO conductor contains lead (Pb) and oxygen (O). These structural similarities indicate that it has the same perovskite structure as PZT. BPBO thin films were prepared by rf magnetron sputtering, and the influence of growth conditions (sputtering gas, rf power, substrate temperature, Bi concentration and post-annealing) on crystallization and conductivity was investigated. A perovskite single phase was obtained above 400 °C at $x = 0$, when post-annealing after sputtering was conducted without substrate heating. In the absence of post-annealing, the perovskite single phase was obtained by sputtering on SiO_2/Si substrates heated to 350–500 °C. The crystallization temperature decreased with increasing Bi concentration (x), and $Ba(Pb_{0.8}Bi_{0.2})O_3$ films were prepared at 300 °C. Resistivity of the films also decreased with decreasing sputtering temperature and with increasing Bi concentration. Ferroelectric properties of PZT capacitors used for BPBO electrodes were also evaluated.

Keywords: A. Film; D. PZT; E. Electrode; BPO; BPBO; FeRAM; Magnetron sputtering

1. Introduction

$Pb(Zr,Ti)O_3$ (PZT) thin film capacitors have been extensively investigated due to their potential applications to FeRAM devices. In order to overcome fatigue and imprint-related problems, much research has been centered on the development of electrode materials for these capacitors. Several electrode materials that improve the properties at the interface between PZT and the electrode, such as Ir, IrO_2, RuO_2 and $SrRuO_3$, have been investigated [1–4]. Materials similar in crystal structure and composition to PZT have recently been used for electrodes. Perhaps most notable among these is the oxide conductor barium metaplumbate, $BaPbO_3$ (BPO) and $Ba(Pb_{1-x}Bi_x)O_3$ (BPBO). BPBO has a perovskite crystal structure with a (pseudo) cubic symmetry. The deleterious effects of lead defects in PZT capacitors with BPBO electrodes may be reduced due to the presence of lead in BPBO. BPBO bulk ceramics have previously been studied in connection with superconductors.

Sol–gel preparation of BPO thin films for FeRAM applications was first reported by Azuma et. al. [5,6] at the Kyushu Institute of Technology. BPO films have also been prepared by laser deposition [7] and rf sputtering [8]. An improvement in the electrical properties of PZT films with BPO electrodes was recently reported [9,10].

BPBO is a material in which the substitution of Pb to Bi in BPO occurs. Based on a report of bulk ceramics, BPBO may decrease the preparation temperature and sheet resistance [11]. The preparation of BPBO by laser deposition and the superconducting properties BPBO films have been reported [12], however BPBO have yet to be applied as electrodes for FeRAM capacitors.

The present study focuses on the fabrication of BPBO thin films by rf magnetron sputtering. The relationship between the properties of the films and the sputtering conditions is discussed, and the optimum processing conditions are identified. Results reveal that high quality BPBO films can be obtained by rf magnetron sputtering. PZT films are fabricated on a BPBO layer, and their electrical properties are reported.

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Table 1
Sputtering conditions

	BPBO	PZT
Temperature (°C)	RT −550	600
rf power (W)	50–150	100
Pressure (m torr)	5–80	10
Gas (sccm)	$Ar:O_2 = 1.0:1.0$	$Ar:O_2 = 1.8:0.4$
Time (min)	30	60
Thickness (nm)	300	200
Target	Pb + Bi:Ba = 1.5:1.0; Pb:Bi = 1:0–0:1	Pb:Zr:Ti = 120/50/50

2. Experimental

BPBO films on SiO_2/Si and Pt/Ti/SiO_2/Si substrates were deposited by rf magnetron sputtering (SPF-210H, Anelva) under the deposition conditions listed in Table 1. The films prepared without substrate heating were crystallized by furnace annealing (post-annealing) at temperatures ranging from 200 to 600 °C. The crystallinity for the obtained films and their temperature dependence were evaluated by XRD (X'Pert MRD, Phillips) with a heating stage (DHS-900, Phillips). The surface morphology and film thickness for the obtained films were measured by AFM (SPI3800N, SII) and surface profilometry, respectively.

Ferroelectric $Pb(Zr_{0.4}Ti_{0.6})O_3$ (PZT) films were also sputtered on BPBO/SiO_2/Si and Pt/Ti/SiO_2/Si substrates. The PZT sputtering conditions optimized for the Pt//Si substrate [13] were used, as shown in Table 1. In order to obtain film capacitors, top BPBO and Pt electrodes (∅ 0.2 mm) were formed with a metal mask. The electrical properties of the film capacitors, such as D–E hysteresis and fatigue performance, were evaluated using a ferroelectric tester (TF2000FE, aixACCT). The sheet resistance of the $Ba(Pb_{1-x}Bi_x)O_3$ films were also measured using the four probe method with 150 μm probe heads (K89PS150mR, Kyowa Riken).

3. Results and discussion

3.1. Deposition temperature of BPBO films

In order to investigate the crystallization temperature of $Ba(Pb_{1-x}Bi_x)O_3$, XRD measurements of BPBO were conducted at various temperatures. BPBO films (SiO_2/Si, thickness; 300 nm) sputtered without substrate heating, were used for the investigation. XRD patterns of the films set on the heating stage were measured with increasing stage temperature in air atmosphere. The temperature step and wait time for the measurements was 10 °C and 10 min, respectively. Fig. 1 shows the obtained XRD patterns for $BaPbO_3$ ($x = 0$). A perovskite BPO peaks appeared at 400 °C in the figure, indicating that crystallization temperature of this film was 400 °C.

Evaluations of other BPBO films with various compositions were also performed, and the dependence of the crystallization temperature on the Bi concentration (x) was evaluated, as shown in Fig. 2. Bi substitution to $BaPbO_3$ is thought to decrease deposition temperature because the temperature was observed to decrease as the Bi concentration increased. Furthermore, the results infer that the crystallization temperature decreases further under Bi rich conditions ($x > 40\%$), however, the temperature of Bi rich films could not be measured, because the substrate temperature was heated up to 200 °C during sputtering, and as-sputtered films of Bi-rich conditions ($x = 70$, 100%) contained perovskite crystals.

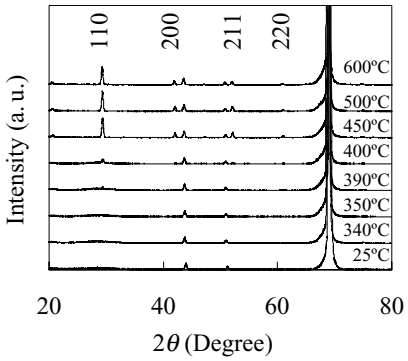

Fig. 1. Annealing temperature dependence of XRD patterns of $BaPbO_3/SiO_2/Si$.

Films prepared at various substrate temperatures were evaluated by XRD, and the influence of deposition temperature on the crystalline structure of the films was investigated. The XRD patterns for the $BaPbO_3$ ($x = 0$) films prepared

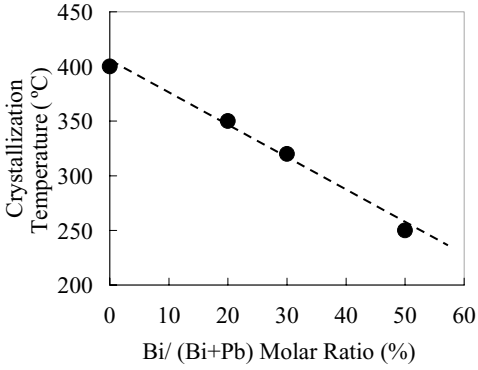

Fig. 2. Relationship between crystallization temperature and Bi concentration.

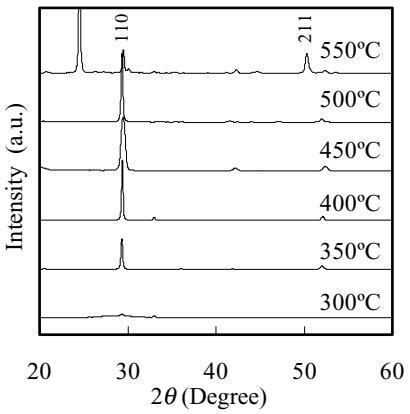

Fig. 3. Substrate temperature dependence of XRD patterns of $BaPbO_3$ films prepared on SiO_2/Si substrates.

are shown in Fig. 3. Films with a (1 1 0) preferred orientation were readily obtained, compared with those films obtained without heat. The results shown in Figs. 1 and 3 reveal that perovskite films were obtained by sputtering both with substrate heating at 350 °C and without substrate heating at 400 °C. Substrate heating while sputtering reduced the deposition temperature by about 50 °C. Fig. 4 shows the XRD pattern of a $Ba(Pb_{0.8}Bi_{0.2})O_3$ film prepared at a substrate temperature of 300 °C. Perovskite peaks can be clearly observed in the image. The process temperature was observed to further decrease with increasing Bi ($x > 0.2$), however BPBO changed from a metal to semiconductor at high Bi concentrations ($x > 0.4$) [14].

The crystallization temperature decreased upon addition of Bi to $BaPbO_3$ and substrate heating during sputtering, thus implying that the deposition temperature may be reduced. This finding is of particular importance in that the electrical properties of PZT films in a vacuum degrade at temperatures above 300 °C [13]. Thus, a reduction in the process temperature for the fabrication of electrode films is extremely desirable. Perovskite $Ba(Pb_{0.8}Bi_{0.2})O_3$ electrode films obtained at a substrate temperature of 300 °C may be utilized as top electrode in practice.

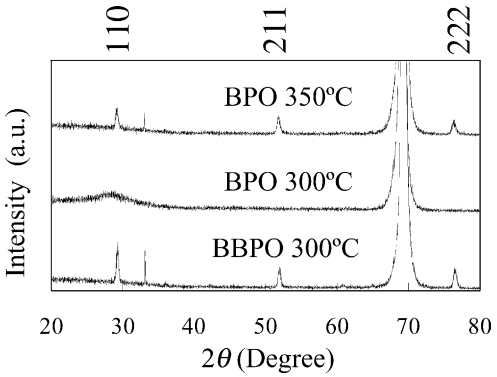

Fig. 4. XRD pattern of a $Ba(Pb_{0.8}Bi_{0.2})O_3/SiO_2/Si$ (substrate temperature; 300 °C).

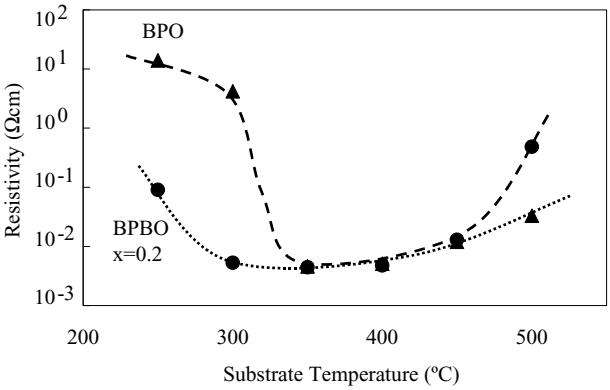

Fig. 5. Relationships between sheet resistance and preparation temperature of BPBO films.

3.2. Sheet resistance of BPBO films

Sheet resistance of the prepared BPBO films was also measured. The measurements were performed at 10 points on each film, and the dispersion of the resistivity within a film was found to be very small. Fig. 5 shows the resistivities of $BaPbO_3$ and $Ba(Pb_{0.8}Bi_{0.2})O_3$ films sputtered at various substrate temperatures. The resistivities of $BaPbO_3$ and $Ba(Pb_{0.8}Bi_{0.2})O_3$ were observed to increase below 300 and 350 °C, respectively, because perovskite BPBO films were not obtained at low substrate temperatures. In films prepared at low temperatures (around 300 °C), lower sheet resistance was obtained on $Ba(Pb_{0.8}Bi_{0.2})O_3$ films than on $BaPbO_3$ films.

The resistance also increased as the temperature increased above temperatures of 350 °C, as shown in Fig. 5. The influences of surface morphology and composition (Ba, Bi and Pb) on the resistance were also investigated. These conditions were found to have little effect on the resistance. However, the resistivity was considerably affected by gas pressure during deposition. The pressure dependence evaluated is shown in Fig. 6. It was also reported that the resistivity of $BaPbO_3$ prepared by laser deposition were previously reported to be influenced by the Ar/O_2 molar ratio in the deposition atmosphere [12]. Thus, the conductivity of the BPBO films may be related to the oxygen concentration in

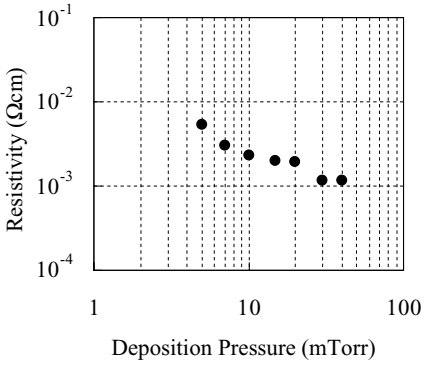

Fig. 6. Influence of gas pressure on resistivity of sputtered BPBO films.

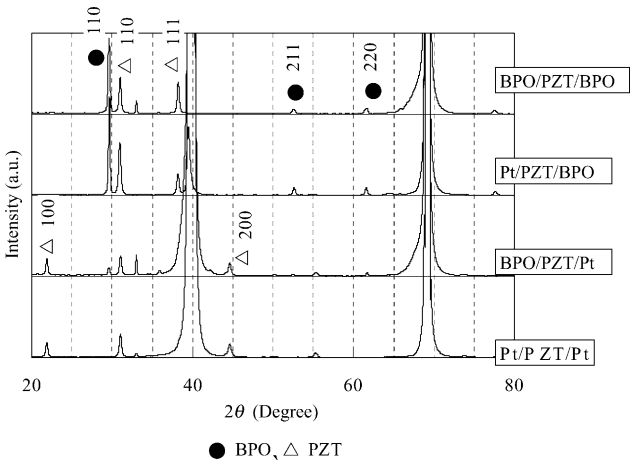

Fig. 7. XRD patterns of PZT film capacitors.

the films. This is further supported in that an oxygen deficiency and degradation of conductivity occurs at high deposition temperatures. The high preparation temperatures required to prepare PZT films (600 °C), may cause damage to the BPBO bottom electrodes during preparation of the PZT film. In order to assess the damage, BPO films sputtered at 350 °C were subjected to post-annealing at various temperatures up to 600 °C, however no obvious change in the resistivity was observed, revealing that post-treatments such as PZT preparation do not effect the electrodes. Thus, the temperature for the preparation of the BPO layer is thought to be important.

The resistivity can be decreased with Bi addition, optimum deposition temperature and an adequate oxygen atmosphere. The lowest resistivity value obtained, however, was above $1.0 \times 10^{-3}\ \Omega$ cm. Hence, in order to reduce sheet resistance, BPO/Pt double-layered electrodes are thought to be desirable for thin film device applications.

3.3. Fabrication of PZT film capacitors

Ferroelectric PZT films were also grown on BPO//Si and Pt//Si substrates, and various capacitor structures were prepared. The XRD patterns of capacitors obtained are shown in Fig. 7. Several BPO and PZT diffraction peaks exist in the patterns due to the polycrystallinity of the films. However, BPO/PZT/BPO films prepared on a SiO_2/Si substrate had a number of cracks, because the adhesion between the BPO film and SiO_2 layer was weak, and strong residual stress was caused by repetition of the heating process. The PZT layer prepared by post-annealing cystallization was exposed to a large amount of stress. In order to reduce the stress, the insertion a buffer layer and optimization of the preparation conditions for PZT may be required.

The electrical properties of the capacitors obtained were also measured. Fig. 8 shows D–E hysteresis properties for: (a) Pt/PZT/Pt/SiO_2/Si; (b) BPO/PZT/Pt/SiO_2/Si; and (c) Pt/PZT/BPO/SiO_2/Si structures. Remnant polarization 2Pr

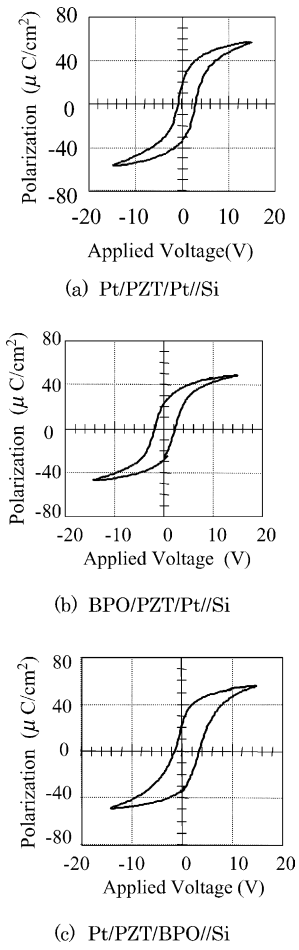

Fig. 8. Ferroelectric D–E properties of PZT film capacitors: (a) Pt/PZT/Pt/SiO_2/Si; (b) BPO/PZT/Pt/SiO_2/Si; and (c) Pt/PZT/BPO/SiO_2/Si.

of (a), (b) and (c) were 53.1, 55.7, and 74.7 μC/cm^2, and a large Pr was obtained with BPO electrodes. However, coercive voltage Vc was also increased by the BPO electrode. An especially large Vc was observed on the capacitor that used BPO for the bottom electrode, and a fat D–E loop was presented.

Fatigue performances of these capacitors are shown in Fig. 9. Polarization fatigue by reversal of polarization was caused in all samples, however slight improvement of the properties was observed in the capacitor with a BPO top electrode. Contrastingly, the Pr of the capacitor with a BPO bottom electrode was considerably decreased upon reversal of polarization due to the inadequate optimization of PZT preparation conditions for BPO substrates.

Capacitors utilizing with BPBO electrodes ($x = 0.2$) were also evaluated. Similar D–E and fatigue performances were observed.

For practical use of BPPO films as bottom electrodes, improvement in adhesion and crystallinity of PZT is essential. Thus, future work will be conducted in an effort to optimize the preparation conditions of PZT films on BPBO substrates.

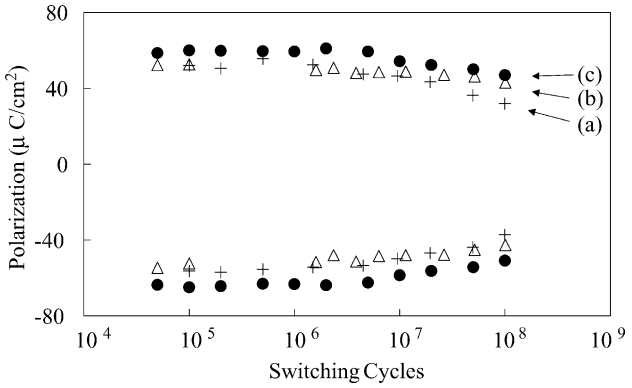

Fig. 9. Fatigue performance of PZT film capacitors: (a) Pt/PZT/Pt/SiO_2/Si; (b) BPO/PZT/Pt/SiO_2/Si; and (c) Pt/PZT/BPO/SiO_2/Si.

4. Conclusions

$Ba(Pb_{1-x}Bi_x)O_3$ (BPBO) films, novel electrode materials for FeRAM devices, were prepared by rf magnetron sputtering under various preparation conditions. The crystalization temperature of BPBO decreased with Bi substitution. $Ba(Pb_{0.8}Bi_{0.2})O_3$ films were obtained at 300 °C. Due to the lower deposition temperature required of these $Ba(Pb_{0.8}Bi_{0.2})O_3$ films, they may be suitable for use as top electrodes in order to reduce heating damage to the PZT layer. Furthermore, Bi rich BPBO films (above $x = 0.4$) can be obtained without substrate heating (200 °C).

The sheet resistance of prepared BPBO films also decreased upon addition of Bi at low preparation temperatures. Furthermore, in order to obtain low resistivity, it was necessary to prepare the films in an adequate oxygen atmosphere. Optimized BPBO electrode films can be obtained at a substrate temperature of 300 °C and at a Bi concentration of $x = 0.2$.

PZT film capacitors with BPBO electrodes were also evaluated. Slight improvement on remnant polarization and fatigue performance was obtained using a BPBO top electrode. However, when using a BPBO bottom electrode, cracks and degradation of electrical properties was observed, revealing that it is necessary to optimize the preparation conditions for PZT on BPBO substrates.

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