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Polarization comparison of $Pb(Zr,Ti)O_3$ and $Bi_4Ti_3O_{12}$-based ferroelectrics

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Abstract

The spontaneous polarization (P_s) values of $Pb(Zr,Ti)O_3$ (PZT) and $Bi_4Ti_3O_{12}$-based ferroelectrics were compared based on data obtained from epitaxially-grown films. These two materials are the most promising candidates for use in ferroelectric random access memory (FeRAM). The P_s of tetragonal $Pb(Zr_{0.35}Ti_{0.65})O_3$ films was estimated to be about 90 μC/cm^2 based on data from perfectly (0 0 1)-oriented, polar-axis-oriented films. On the other hand, the P_s value of $(Bi_{3.5}Nd_{0.5})Ti_3O_{12}$ was estimated to be 56–58 μC/cm^2 based on data from (1 0 0)/(0 1 0)-, (1 1 0)-, and (1 0 4)/(0 1 4)-oriented epitaxial films. This value is the largest yet reported for bismuth layer-structured ferroelectrics. For both systems, the P_s value generally increased with increasing Curie temperature (T_c). However, it decreased when the T_c became very high and approached the values for $PbTiO_3$ and $Bi_4Ti_3O_{12}$. This decrease is attributed to pinning of the domain motion in the bulk. On the other hand, the obtained one-axis film, which is essential to diminish the cell-to-cell property distribution, had a (1 0 0)/(0 0 1) and (1 1 1) orientations for $Pb(Zr_{0.35}Ti_{0.65})O_3$ films, or a (0 0 1) orientation for $(Bi_{3.5}Nb_{0.5})Ti_3O_{12}$ films. Based on our findings, we expect the maximum remanent polarization (P_r) values to be almost the same for both materials.

Keywords: Spontaneous polarization; Remanent polarization; Epitaxial films; Ferroelectric random access memory; Piezoelectric material

1. Introduction

Ferroelectric random access memory (FeRAM) development is one of the most challenging current topics in materials science because it is difficult to use an integrated functional oxide capacitor without silicon oxide in the Si process [1]. In the case of two-transistor/two-capacitor and/or one-transistor/one-capacitor FeRAMs especially, the ferroelectric oxide material (together with the oxide electrodes) is the key material in achieving highly reliable capacitor formation [2].

Tetragonal $Pb(Zr,Ti)O_3$ (PZT)and $Bi_4Ti_3O_{12}$-based materials such as $(Bi,La)_4Ti_3O_{12}$ and $(Bi,Nd)_4Ti_3O_{12}$ are the leading candidates for use as ferroelectric materials. Table 1 summarizes the general characteristics of these two films. However, the basic properties of these materials have not yet been clarified because large-single crystals are hard to obtain. A large-single crystal without a 90° domain is difficult to grow above the Curie temperature (T_c) because the crystal structure symmetry changes at T_c. The spontaneous polarization (P_s) value, the most basic ferroelectric property, also corresponds to the maximum remanent polarization (P_r) of materials, suggesting its importance in the design of ferroelectric capacitors for FeRAMs.

One way to measure basic properties such as P_s is to use well-characterized high-quality epitaxial films. Since the ferroelectric property has polar characteristics, though orientation-controlled ferroelectric films are essential for such characterization.

In the present study, we compare $Pb(Zr,Ti)O_3$ and $Bi_4Ti_3O_{12}$-based films, especially with regard to their P_s and P_r values. For this purpose, we grew the epitaxial films on

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Table 1
Advantages and disadvantages of proposed ferroelectric materials for FeRAM

Lead-based perovskite $Pb(Zr,Ti)O_3$	Bismuth layer-structured ferroelectrics $SrBi_2Ta_2O_9(Bi,Ln)_4Ti_3O_{12}$
Advantage	Advantage
Large-switching charge (>70 μC/cm^2)	Lead-free
Self regulation of composition called “process window” for CVD-PZT	Fatigue-free
Low-process temperature (<600 °C)	
Accumulated knowledge	
Disadvantage	Disadvantage
Lead (excepted)	Small-switching charge (<40 μC/cm^2)
Fatigue (overcome by oxide electrodes)	High-process temperature (>600 °C)
	Complex structure (large anisotropy in the switching charge)

conductive substrates. Metal-organic chemical vapor deposition (MOCVD) was used as a growth method because it enables high-quality film growth as amply demonstrated in compound semiconductor growth. We used these films to characterize the P_s values of these materials. Moreover, taking account of the actually observed orientation on Si(1 0 0) substrates, we discuss the maximum switching charge, response to the two times of P_r, since an FeRAM is fabricated on Si(1 0 0) substrates in practice.

2. PZT films

PZT is widely used as a piezoelectric material and its *Ps* value has been estimated [3]. However, direct single-crystal measurement of the ferroelectric property has been limited [4,5]. For FeRAM applications, tetragonal PZT films have been used because they provide square-shaped hysteresis loops and high T_c [6]. We have succeeded in growing perfectly polar-axis-, *c*-axis-oriented PZT films on (1 0 0)$SrRuO_3$/(1 0 0)$SrTiO_3$ substrates by MOCVD [7,8]. This was done through high-temperature deposition of the PZT film on a substrate having a large-thermal expansion coefficient. Fig. 1 shows polarization–electric field (*P*–*E*) hysteresis loops for perfectly polar-axis-oriented 50-nm-thick films grown at 580 °C; the perfect polar-axis-orientation was confirmed by X-ray diffraction reciprocal mapping measurement [8]. Well-saturated hysteresis loops were obtained. Fig. 2 shows the Zr/(Zr + Ti) ratio dependence of the saturation polarization (P_{sat}), which corresponds to P_s [8]. It has already been ascertained through precise lattice parameter measurement using the X-ray reciprocal space mapping method that residual strain in the films has little effect on the polarization [8]. Fig. 3 shows the relationship between P_{sat} and the tetragonal distortion in the crystal structure, $((c/a) - 1)$. A linear relationship with a slope of 0.52 was observed between the logarithmic of P_s and $((c/a) - 1)$. This shows that the square of P_s is almost proportional to $((c/a) - 1)$, suggesting that P_s decreases with the decreasing *c*/*a* ratio that accompanies an increasing Zr/(Zr + Ti) ratio. The P_s value estimated from this equation is larger than that previously re-

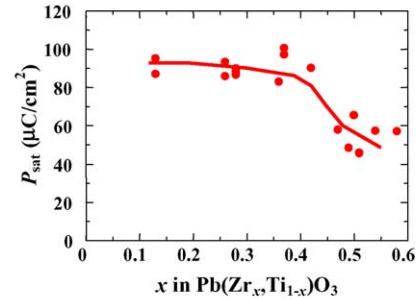

Fig. 2. P_{sat} as a function of x in $Pb(Zr_xTi_{1-x})O_3$ for perfectly polar-axis-, (0 0 1)-, *c*-axis, oriented tetragonal PZT films that were 50 nm thick.

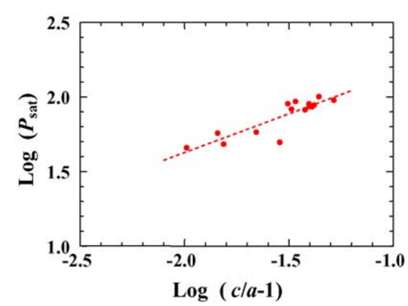

Fig. 3. Relationships between P_{sat} and tetragonal distortion $((c/a) - 1)$ for perfectly polar-axis-, *c*-axis, oriented tetragonal PZT films.

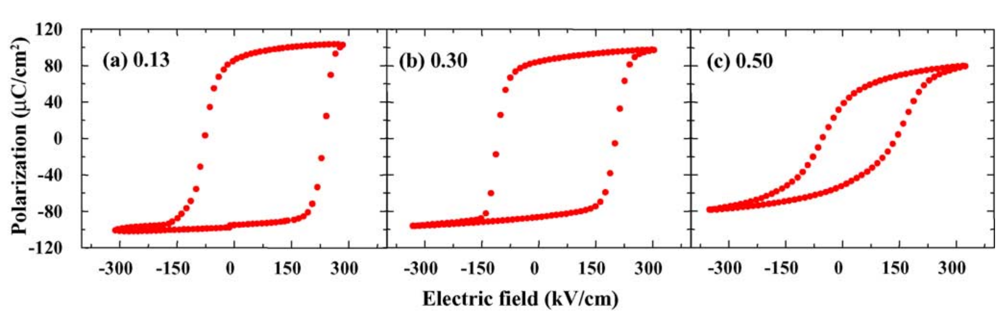

Fig. 1. *P*–*E* hysteresis loops of polar-axis-, (0 0 1), oriented tetragonal $Pb(Zr_xTi_{1-x})O_3$ films. Film thickness was 50 nm. (a) $x = 0.13$, (b) $x = 30$, (c) $x = 0.50$.