Squarness Control in Polarization-electric filed Curves in Rhombohedral PZT Films

Hiroshi Funakubo, Akihiro Sumi, Hitoshi Morioka, Shoji Okamoto, Shintaro Yokoyama, Takahiro Oikawa, and Yoshitaka Ehara

Tokyo Institute of Technology,
J2-43, Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan
Phone: +81-45-924-5446, E-mail: funakubo.h.aa@m.titech.ac.jp

1. Introduction

Ferroelectric random access memories (FeRAMs) have been widely investigated due to their nonvolatile with low power consumption [1]. Present FeRAMs mainly use tetragonal Pb(Zr,Ti)O3 films with Ti rich composition due to the large remanant polarization (Pr) and the good squarness in polarization electric filed (P - E) curves. However, this composition has a fundamental problem of the large switching voltage originated to the large coercive field. To reduce the switching voltage for the power consumption, one way is reduce the film thickness because the switching voltage was reduced when the coercive field is not strongly depend on the film thickness [2]. In fact, we demonstrated 1 V saturation for 35 nm thick films using local epitaxial technique, in which each grains epitaxially grown from the bottom electrode layers [3].

Uses of the rhombohedral Pb(Zr,Ti,1-x)O3 films with Zr rich composition further enhance power consumption. Rhombohedral Pb(Zr,Ti,1-x)O3 film has various advantages for the requirements due to the lower coercive field ($E_c$) together with the low leakage current density [4]. However, the serious drawback of rhombohedral Pb(Zr,Ti,1-x)O3 films is the worse squarness in $P$ - $E$ hysteresis loops. This worse squarness is known to be improved by increasing the film thickness [5, 6] and for making epitaxial films [7]. Therefore, the control of squarness of rhombohedral Pb(Zr,Ti,1-x)O3 is the key issues to reduce the power consumption of FeRAMs. However, the investigation of the squarness of rhombohedral Pb(Zr,Ti)O3 films have been hardly reported.

In the present study, we tried to prepare epitaxial and fiber textured rhombohedral Pb(Zr0.65Ti0.35)O3 films by metalorganic chemical vapor deposition (MOCVD) and systematically investigated the change of the squarness in $P$ - $E$ hysteresis loops as a function of the measurement temperature. Based on these results, we discuss the determination factor of the $P_s/P_{sat}$ ratio for rhombohedral Pb(Zr,Ti)O3 films.

2. Experimental Procedure

Pb(Zr0.65Ti0.35)O3 (PZT) films with about 200 nm-thick were prepared at 540 °C by pulsed-MOCVD using Pb(C11H19O2)2, Zr(O·i-C3H7)4, TiO(i-C3H7)2, and O2 gas as the source materials. In pulsed-MOCVD, a mixture of the source gases was introduced in a pulse sequence for 10 seconds with a 5 seconds interval, while O2 gas was continuously introduced into the reaction chamber. The details of the pulse-MOCVD are already described elsewhere [8]. The composition of the films was adjusted by controlling the input gas flow rate of the source gases. (100)SrRuO3/|(100)SrTiO3 and (100)SrRuO3/|(100)LaNiO3/|(100)YSZ/|(100)Si were used for epitaxial film growth, while (100)SrRuO3/(100)LaNiO3/(111)Pt/(100)SrTiO3 and (100)SrRuO3/(111)Pt/TiO2/(100)Si for the (100) fiber-textured ones [9, 10].

3. Results and Discussion

Figure 1 shows the XRD $\theta$-$2\theta$ patterns of films. All films shown (100) single orientation. X-ray pole figure measurement shows that the epitaxial films were obtained on (100)SrRuO3 /|(100)SrTiO3 and (100)SrRuO3/|(100)LaNiO3/|(100)YSZ/|(100)Si substrates, while (100)-oriented fiber-textured films on (100)SrRuO3/(111)Pt/(100)SrTiO3 and (100)SrRuO3/(111)Pt/TiO2/(100)Si substrates. It must be noted that the peak position mainly depend on kinds of substrates.

![Fig. 1 XRD $\theta$ - $2\theta$ patterns of films prepared on (a) (100)SrRuO3/|(100)SrTiO3, (b) (100)SrRuO3/(100)LaNiO3/(111)Pt/(100)SrTiO3, (c) (100)SrRuO3/|(100)LaNiO3/(111)Pt/TiO2/|(100)Si, and (d) (100)SrRuO3/(100)LaNiO3/(111)Pt/TiO2/(100)Si substrates.](image)
Figure 2 show the room temperature $P - E$ hysteresis loops for the same films shown in Fig.1. Well saturation characteristics were observed for all films, but its $P/P_{sat}$ ratio was not the same. Figure 3 shows the change of $P - E$ hysteresis loops with temperature. High $P/P_{sat}$ ratio beyond 0.9 was observed at 10 K for all films, but was dropped with increasing temperature.

Figures 4 (a) and (b) respective show the $P/P_{sat}$ ratio at 10K and 300K as a function of two times of the two times of out-of-plane lattice spacing for PZT 200, $(2 \times d_{200})$ obtained from Fig.1. The $P/P_{sat}$ ratio increased with increasing $(2 \times d_{200})$. Fig.4(c) summarizes the temperature in which the $P/P_{sat}$ ratio became 95% of that at 10K as a function of $(2 \times d_{200})$. This value also increased with increasing $(2 \times d_{200})$. These data clearly show that strain in the films determine the $P/P_{sat}$ ratio of tetragonal PZT films.

4. Conclusions

$P/P_{sat}$ ratio in $P - E$ hysteresis loops of epitaxial and fiber-textured (100)-oriented rhombohedral PZT films were investigated as a function of temperature. It depended not only on the temperature but also on the out-of-plane $d_{200}$, indicating that the remained strain in the films affect to the $P/P_{sat}$ ratio. Present results induce the novel design concept for low voltage FeRAMs with good squareness of $P - E$ hysteresis loops.

Acknowledgement

This research is partially granted by the Japan Society for the Promotion of Science (JSPS) through the “Funding Program for World-Leading Innovative R&D on Science and Technology” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). This work was supported by the Japan Society for the Promotion of Science (JSPS) through the “Funding Program for World-Leading Innovative R&D on Science and Technology” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References