Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp606-607

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

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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 $Pb(Zr_xTi_{1-x})O_3$ films with Ti rich composition due to the large remanent polarization (*Pr*) and the good squareness 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 $Pb(Zr_xTi_{1-x})O_3$ films with Zr rich composition further enhance power consumption. Rhombohedral $Pb(Zr_xTi_{1-x})O_3$ 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 $Pb(Zr_xTi_{1-x})O_3$ 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 squareness of rhombohedral $Pb(Zr_xTi_{1-x})O_3$ is the key issues to reduce the power consumption of FeRAMs. However, the investigation of the squareness of rhombohedral $Pb(Zr,Ti)O_3$ films have been hardly reported.

In the present study, we tried to prepare epitaxial and fiber textured rhombohedral $Pb(Zr_{0.65}Ti_{0.35})O_3$ films by metalorganic chemical vapor deposition (MOCVD) and systematically investigated the change of the squerness in *P-E* hysteresis loops as a function of the measurement temperature. Based on these results, we discuss the determination factor of the P_r/P_{sat} ratio for rhombohedral $Pb(Zr,Ti)O_3$ films.

2. Experimental Procedure

$Pb(Zr_{0.65}Ti_{0.35})O_3$ [PZT] films with about 200 nm-thick were prepared at 540 °C by pulsed-MOCVD using $Pb(C_{11}H_{19}O_2)_2$, $Zr(O{\cdot}t\text{-}C_4H_9)_4$, $Ti(O{\cdot}i\text{-}C_3H_7)_4$ and O_2 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 O_2 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. $(100)SrRuO_3//(100)SrTiO_3$ and $(100)SrRuO_3//(100)LaNiO_3//(100)CeO_2//(100)YSZ//(100)Si$ were used for epitaxial film growth, while $(100)SrRuO_3/(100)LaNiO_3/(111)Pt/(100)SrTiO_3$ and $(100)SrRuO_3/(100)LaNiO_3/(111)Pt/TiO_2/(100)Si$ for the (100) fiber-textured ones [9, 10]. Psudocubic index was used for the description of crystal structure of $SrRuO_3$.

P-E hysteresis loops were measured at 1 kHz using a ferroelectric tester [FCE, TOYO Co.]. Temperature dependency of the electrical properties was measured using a proving system with temperature-controlled-stage. The squareness of the *P* - *E* hysteresis loops was estimated to be the ratio of the remanent polarization (P_r) to the saturation polarization (P_{sat}), the P_r/P_{sat} ratio.

3. Results and Discussion

Figure 1 shows the XRD θ-2θ patterns of films. All films shown (100) single orientation. X-ray pole figure measurement shows that the epitaxial films were obtained on $(100)SrRuO_3$ / $/(100)SrTiO_3$ and $(100)SrRuO_3//(100)LaNiO_3//(100)CeO_2//(100)YSZ//(100)Si$ substrates, while (100)-oriented fiber-textured films on $(100)SrRuO_3/(100)LaNiO_3/(111)Pt/(100)SrTiO_3$ and $(100)SrRuO_3/(100)LaNiO_3/(111)Pt/TiO_2/(100)Si$ substrates. It must be noted that the peak position mainly depend on kinds of substrates.

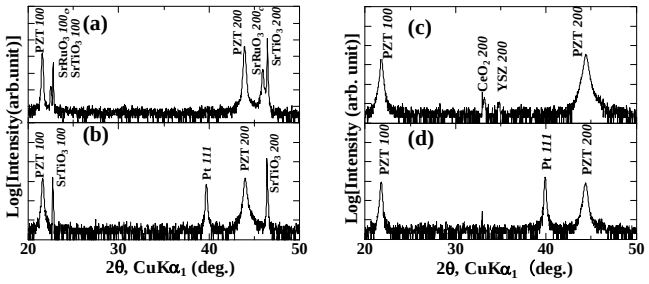

Fig. 1 XRD θ - 2θ patterns of films prepared on (a) $(100)SrRuO_3//(100)SrTiO_3$, (b), $(100)SrRuO_3/(100)LaNiO_3/(111)Pt/(100)SrTiO_3$ (c) $(100)SrRuO_3//(100)LaNiO_3//(100)CeO_2//(100)YSZ//(100)Si$ and (d) $(100)SrRuO_3/(100)LaNiO_3/(111)Pt/TiO_2/(100)Si$ substrates.

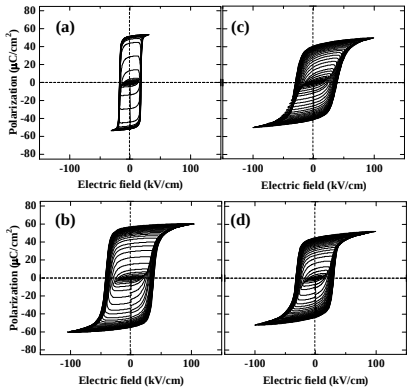

Fig. 2 Room temperature *P* - *E* hysteresis loops for the same films shown in Fig.1. (a) (100)$SrRuO_3$ //(100)$SrTiO_3$, (b) (100)$SrRuO_3$// (100)$LaNiO_3$ //(100)CeO_2 //(100)YSZ//(100)Si, (c) (100)$SrRuO_3$/(100)$LaNiO_3$/(111)Pt/ (100)$SrTiO_3$ and (d) (100)$SrRuO_3$ /(100)$LaNiO_3$/ (111)Pt/TiO_2/ (100)Si substrates.

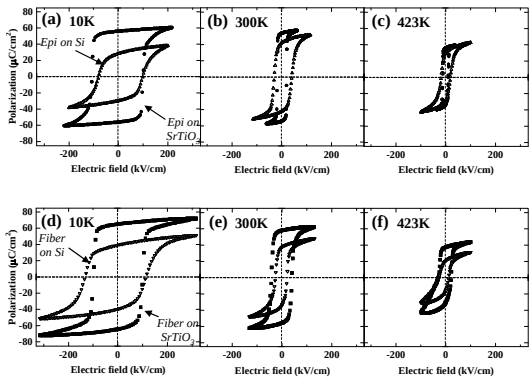

Fig. 3 Chang of *P* - *E* hysteresis loops with temperature for films [(a), (b) (c)] on (100)$SrRuO_3$ / /(100)$SrTiO_3$ and (100)$SrRuO_3$// (100)$LaNiO_3$ //(100)CeO_2 //(100)YSZ//(100)Si substrates and [(d), (e), (f)], on (100)$SrRuO_3$/ (100)$LaNiO_3$/ (111)Pt/ (100)$SrTiO_3$ and (100)$SrRuO_3$ /(100)$LaNiO_3$/ (111)Pt/TiO_2/ (100)Si substrates.

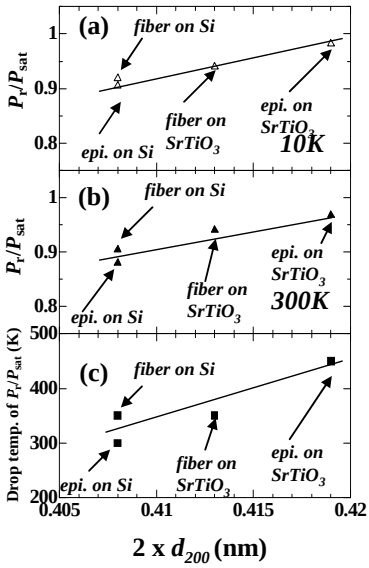

Fig.4 P_r/P_{sat} ratio at (a) 10K and (b) 300K and (c) drop temperature of P_r/P_{sat} as a function of two times of the out-of lattice spacing of PZT *200*, d_{200}.

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_r/P_{sat} ratio was not the same. Figure 3 shows the change of *P* – *E* hysteresis loops with temperature. High P_r/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_r/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 x d_{200}) obtained from Fig.1. The P_r/P_{sat} ratio increased with increasing (2 x d_{200}). Fig.4(c) summarizes the temperature in which the P_r/P_{sat} ratio became 95% of that at 10K as a function of (2 x d_{200}). This value also increased with increasing (2 x d_{200}). These data clearly show that strain in the films determine the P_r/P_{sat} ratio of tetragonal PZT films.

4. Conclusions

P_r/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_r/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

References

[1] K. Yakumar, K. Boku, K. Remack, J. Rodriguez, S. Summerfelt, F. Celli, S. Agawam, J. Martin, L. Hall, L. Matz, B. Rathsack, H. Mcadams, and T. Moise, Jpn. J. Appl. Phys. **45 (2006)** 3202.

[2] T. Oikawa, H. Morioka, A. Nagai, H. Funakubo and K. Saito, Appl. Phys. Lett. **85** (2004) 1754.

[3] H. Kuwabara, N. Menou, and H. Funakubo, Appl. Phys. Lett. **93** (2008) 152901.

[4] H. Funakubo, K. Tokita T. Oikawa, M. Aratani, and K. Saito, J. Appl. Phys. **92** (2002) 5448.

[5] S. Yokoyama, Y. Honda, H. Morioka, S. Okamoto, T. Iijima, H. Matsuda, K. Saito, and H. Funakubo, Integ. Ferro. **64** (2004) 217.

[6] H. Funakubo, A. Sumi, H. Morioka, S. Okamoto and S. Yokoyama, Mater. Res. Soc. Symp. Proc. **902E** (2006) 0902-T04-04.

[7] K. Nagashima, M. Aratani and H. Funakubo, J. Appl. Phys. **89** (2001) 4517.

[8] K. Nagashima, M. Aratani, and H. Funakubo, Jpn. J. Appl. Phys., **39** (2000) L996.

[9] S. Yokoyama, Y. Honda, H. Morioka, S. Okamoto, H. Funakubo, T. Iijima, H. Matsuda, K. Saito, T. Yamamoto, H. Okino, O. Sakata and S. Kimura, J. Appl. Phys., **98** (2005) 094106-1-8.

[10] S. Okamoto, S. Yokoyama, Y. Honda, G. Asano, and H. Funakubo, Jpn. J. Appl. Phys. **43** (2004) 6567.