

Fatigue Characteristics of $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ Thin Films by RF Magnetron Sputtering

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It is well known that Bi-layer compound, $\text{SrBi}_2\text{Ta}_2\text{O}_9$, shows good fatigue characteristic which is one of the important properties for FRAM applications. In this paper, we report on fatigue characteristics of $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ thin films on Pt(100)/MgO(100) and Pt(111)/glass substrates prepared by rf magnetron sputtering. The thin film on Pt(100)/MgO(100) substrate has comparatively good fatigue characteristics in the following; initial state, $P_r=7.5 \mu\text{C}/\text{cm}^2$, $E_c=174\text{kV}/\text{cm}$ and 10^9 pulsed state, $P_r=5.7 \mu\text{C}/\text{cm}^2$, $E_c=117\text{kV}/\text{cm}$.

1. INTRODUCTION

The interest in the use of the ferroelectric thin films for memory applications has increased in the recent years.¹⁾ If they will be used as a capacitor of DRAM, films with relatively small dielectric constants are required. On the other hand, films with relatively small dielectric constants are useful for application to non-volatile ferro-DRAM (FRAM). Therefore, precise control of the film composition is essential for both applications.

It is well known that among these ferroelectric materials, Bi-layer compound such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (Y-1) shows good fatigue characteristic which is one of the important properties for FRAM²⁾. In this paper, we report on fatigue properties of Bi-layer compound; $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ thin films prepared by rf magnetron sputtering for FRAM applications.

2. EXPERIMENTAL

$(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ (BTL) thin films were prepared using a conventional rf magnetron sputtering with ceramic powder target under the condition as listed in Table 1. The target powder was fired at 1023K for 2h. A gold film was sputtered for the top electrode.

The chemical composition of the films was determined by the inductively coupled plasma method (ICP). Thin-film crystallography was performed by X-ray diffraction (monochromatized $\text{CuK}\alpha$ radiation). The typical film thickness by the surface profilometer was about 400nm.

The dielectric constant was measured with a Hewlett-Packard (HP-4194A) impedance analyzer at 1kHz. Ferroelectric properties were measured using a Radiant Technology RT66A tester operating in the virtual ground mode. The period of measurement of the hysteresis loop was 9.6ms.

Table 1 Sputtering condition

Target	$\text{Bi}_2\text{O}_3 : \text{La}_2\text{O}_3 : \text{TiO}_2$ =2.065 : 0.25 : 3
Substrates	MgO(100),glass, Pt(100)/MgO(100), Pt(111)/glass
Substrate temp.	888 K
Sputtering gas	Ar : O_2 =9 : 1
Gas pressure	0.39 Pa
RF input power	100 W

3. RESULTS AND DISCUSSIONS

Figure 1 shows the crystal structures of the films. Only perovskite structure is found in these figures. The ICP analyses represent that this film has the composition of $(\text{Bi}_{1.56}\text{La}_{0.57})\text{Ti}_3\text{O}_{12}$. The orientations of the thin films are affected by the kinds of substrates. The films on MgO(100) and glass have good c-axis orientation. However, the films on Pt(100)/MgO(100) and Pt(111)/glass have the mixed (117) plan and c-axis orientation.

The dielectric constant (ϵ_r) for the BLT thin films on Pt(100)/MgO(100) and Pt(111)/glass were 112 and 161, respectively. It is noted that the films on Pt(100)/MgO(100) have lower ϵ_r compared to the films on Pt(111)/glass, which was attributed to the difference in the film orientation.

D-E hysteresis loops of the BLT thin films deposited on Pt(100)/MgO(100) and Pt(111)/glass before and after 10^9 switching cycles, are shown in Fig.2. Pr decreased and loop shifted to the right. Similar shifts were observed in the other films³⁾.

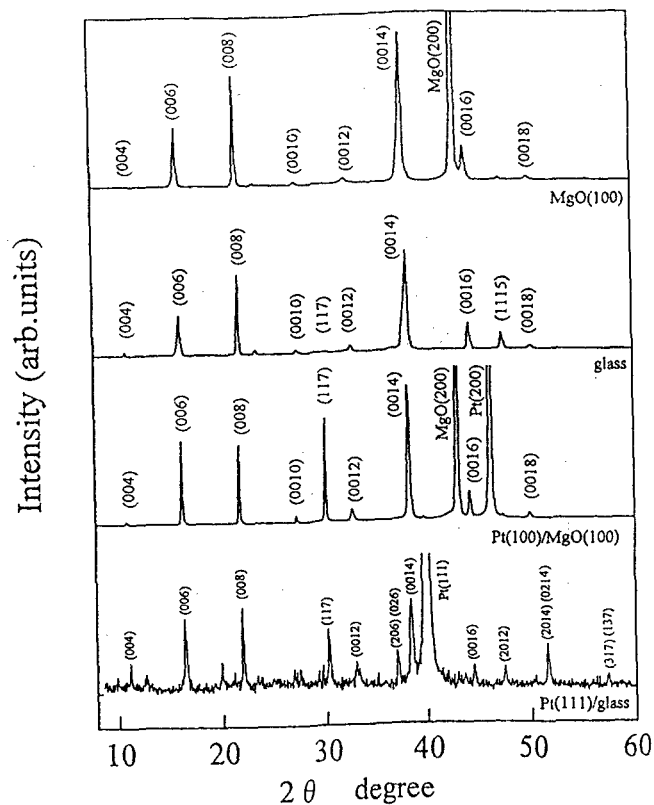


Fig. 1 X-ray diffraction patterns of $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ thin films on various substrates.

Figure 3 represents fatigue characteristics of the BLT thin films deposited on various substrates. Pr^* and Pr^- refer to switched and non-switched remanent polarization, respectively. The difference ($\text{Pr}^* - \text{Pr}^-$) is equivalent to 2Pr (assuming a symmetric loop). After 10^9 switching cycles, ($\text{Pr}^* - \text{Pr}^-$) of the films on these substrates decreased slightly due to fatigue. It is found from these figures that the thin film on Pt(100)/MgO(100) substrate has fairly good fatigue characteristics after application of 10^9 pulses.

The scheme for minimizing fatigue with ordinary metal electrode (for example Pt) is to modify the

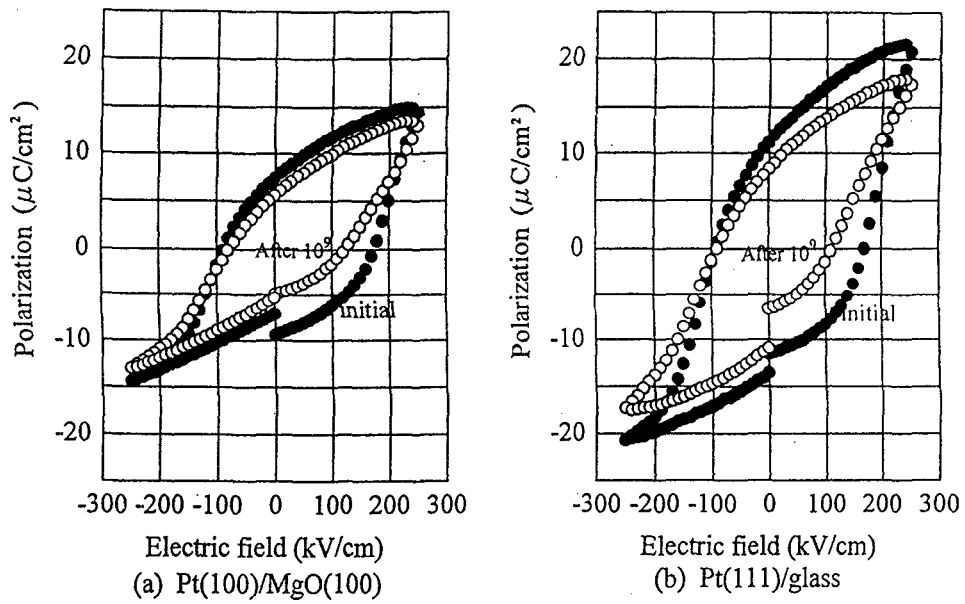


Fig. 2 D-E hysteresis loops of $(\text{Bi,La})_4\text{Ti}_3\text{O}_{12}$ thin films on (a) Pt(100)/MgO(100) and (b) Pt(111)/glass substrates before and after fatigue.

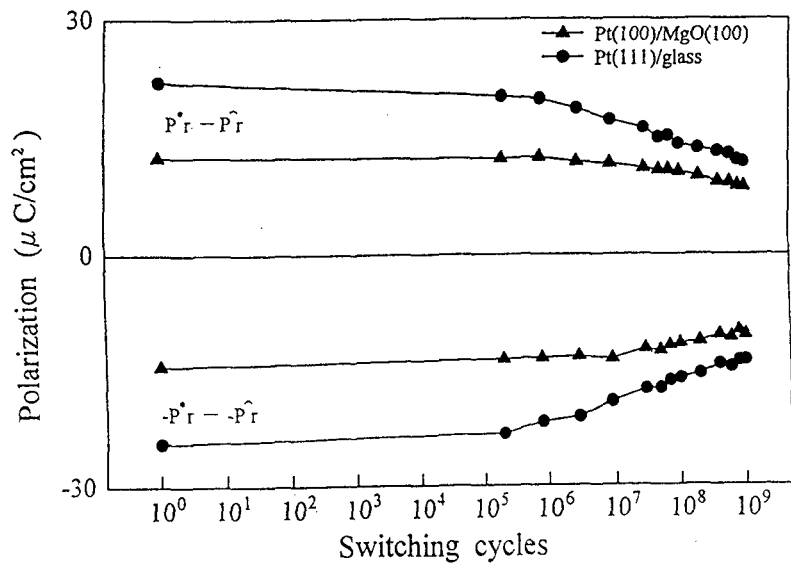


Fig. 3 Fatigue properties of $(\text{Bi,La})_4\text{Ti}_3\text{O}_{12}$ thin films on Pt(100)/MgO(100) and Pt(111)/glass substrates.

ferroelectrics. Such modification can be done by employing a more complicated ferroelectrics of the layered-structure perovskite oxide family epitomized by $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{NbTaO}_9$ ⁴⁾. $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ based thin films are also expected to be adequate materials for non-volatile RAM device applications because of lack of fatigue.

4. CONCLUSIONS

We will summarize our results as follows;

- 1) Single perovskite type compound of $(\text{Bi}_{3.56}\text{La}_{0.57})\text{Ti}_3\text{O}_{12}$ was prepared by rf sputtering method.
- 2) C-axis orientation was obtained for MgO(100) and glass substrates.

- 3) The thin film on Pt(100)/MgO(100) substrate showed fairly good fatigue properties in the following; initial state $P_r=7.5 \mu\text{C}/\text{cm}^2$, $E_c=174\text{kV}/\text{cm}$ and 10^9 pulsed state, $P_r=5.7 \mu\text{C}/\text{cm}^2$, $E_c=117\text{kV}/\text{cm}$.

REFERENCES

- 1) D. W. Bondurant and F. P. Gnadinger; IEEE Spectrum **26** (1989) 30
- 2) T. Mihara; Nikkei Electronics **581** (1993) 94
- 3) H. Maiwa, N. Ichinose and K. Okazaki; Jpn. J. Appl. Phys. **33** (1994) 5240
- 4) C. A-Paz de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott and J. F. Scott ;Nature, **374** (1995) 627