Transactions of the Materials Research Society of Japan 32[1] 91-94 (2007)

Influence of Degradation on Thermally Stimulated Current Measurements of Pb-rich Lead Zirconate Titanate Thin Films

Takashi Nishida, Masahiro Echizen, Takashi Takeda,

Kiyoshi Uchiyama, and Tadashi Shiosaki

Graduate School of Materials Science Nara Institute of Science and Technology (NAIST)

8916-5 TAKAYAMA-CHO, IKOMA, NARA 630-0101, JAPAN

Fax: 81-743-72-6069, e-mail: tnishida@ms.naist.jp

It is anticipated that $Pb(Zr_x,Ti_{1-x})O_3$ (PZT) films will be used in various next-generation high performance devices, such as ferroelectric memories and microelectromechanical systems (MEMS). However, PZT films show degradation problems due to the presence of crystal defects. In order to solve this problem, it is necessary to elucidate the degradation mechanisms. In this paper, PZT films containing excess lead content at the interface between the electrode and the PZT layer were evaluated by thermally stimulated current measurements, which is one of the evaluation methods for crystal defects. Although, defects at the interface increased with increasing excess lead content, fatigue performance was reduced. The number of defects in usual PZT films increase due to fatigue, and inversely, a decrease in defects with progress of fatigue was also observed in the excess-lead film. Based on these results, a very thin excess PbO_x layer containing crystal defects seems to exist at the interface, and compensates for the decrease in lead and oxygen content in the PZT layer by out-diffusion caused by fatigue.

Key words: PZT, TSC, thermally stimulated current, degradation, fatigue, thin films

1. INTRODUCTION

The preparation of PZT thin films has been widely investigated because of expectations of applications in ferroelectric random access memories (FeRAM) and microelectromechanical systems (MEMS). However, development has been restrained due to problems with degradation of electrical properties such as fatigue and imprint. Thus, work has been carried out on improving the properties, which has revealed that the interface between PZT and the electrode affects the degradation, and fatigue is reduced with new electrode materials such as Ir, Ru and oxide conductors. [1,2] On the other hand, investigations of the degradation mechanism are still in progress, and various models of the degradation have been proposed. However, details regarding the degradation phenomena have not been sufficiently clarified, since precise evaluation of the defects has been difficult.

Thermally stimulated current (TSC) measurement is one of the methods for the evaluation of crystal defects in organic materials, and defects in PZT can also be observed by TSC. An increase of defects by fatigue has been reported by several researchers. [3-5] However, precise measurement and identification of the defects has been difficult because of the complicated microstructures in PZT films as well as noise current. We have improved this measurement process, and have performed systematic evaluations of PZT film specimens prepared under various conditions, revealing that the defects observed can be identified successfully. [5] Recently, it was also revealed that defects of lead and oxygen at the interface are related to TSC observations and the degradation mechanisms. [6]

In this study, we prepared PZT film capacitor structures using a TiO_2 buffer layer with various thicknesses between the bottom electrode and the PZT layer, and evaluated their fatigue performance and TSC properties. From the results, the behavior of the PbO_x content and crystal defects at the interface was revealed.

Table I. Sputtering conditions for the TiO_2 buffer

Temperature	350°C
rf power	
TiO_2	400 W
Gas Ar:O_2(SCCM)	4.5:1.0
Gas Pressure	1.5 Pa
Time	1-10 min

Table II. Sputtering conditions for PZT

Temperature	350°C
rf power	
$Pb(Zr_{0.5}Ti_{0.5})O_3$	500 W
PbO	90 W
TiO_2	400 W
Gas Ar:O_2(SCCM)	4.5:1.0
Gas Pressure	1.5 Pa
Time	60 min
Thickness	170 nm

2. EXPERIMENTAL

The TiO_2 buffer layer and $Pb(Ti_{0.6}, Zr_{0.4})TiO_3$ thin films were deposited on $Pt/SiO_2/Si$ substrates by rf magnetron sputtering. The sputtering conditions used are summarized in Tables I and II. Film capacitors with the TiO_2 buffer layer with thickness ranging from 1nm to 5nm were prepared. The perovskite PZT(111) films were obtained by furnace annealing at 600°C for 1 hour and in air. The Pt top electrodes with 100 nm thickness were also deposited by rf sputtering at room temperature. The electrodes with 0.12 mm diameter were formed by a metal mask method. After the deposition of the top electrodes, annealing was performed at 600°C for 5 min in air. First, the specimens were evaluated by XRD and XRF. The ferroelectric properties of the capacitors were measured using a ferroelectric tester (TF2000, Aixacct Co.). TSC measurements were performed using the measurement conditions shown in Table III. The measurement process optimized for ferroelectric films was reported previously in detail. [3]

Table III. TSC measurement conditions

Temperature Range	R.T. – 290°C
Heating Rate	2 K/min
Trapping Voltage	1.0 V
Collection Voltage	5.0 mV

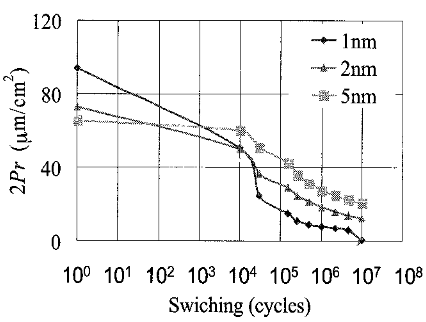

Fig. 1 The dependence of fatigue performance on thickness of the TiO_2 buffer layer at the bottom interface.

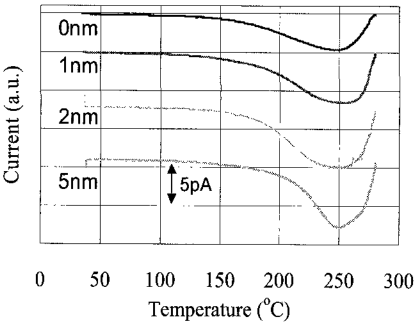

Fig. 2 The dependence of thermally stimulated current on thickness of the TiO_2 buffer layer at the bottom interface.

3. RESULTS AND DISCUSSION

The dependence of fatigue performance on the thickness of the TiO_2 buffer layer was evaluated, as shown in Fig.1. The remnant polarization of the as-grown films slightly decreased with increasing TiO_2 thickness; inversely, polarization above 10^5 cycles increased with increasing buffer thickness revealing that fatigue performance was improved. It has been revealed in our previous report that the TiO_2 buffer layer thickness affects not the orientation of PZT but lead composition at bottom interface because the buffer layer acts as a diffusion barrier, from XRD and SIMS depth profile measurements. [7] The lead content passes quickly through the grain boundary of the Pt bottom layer, and large quantity of lead is lost at the interface in PZT layer. The diffusion seems to be prevented by TiO_2 layer. Thus, in the case of a thick buffer, excess lead content exists at the interface, and the improvement in fatigue properties seems to be caused by the excess lead.

The dependence of TSC on the thickness was also evaluated, as shown in Fig. 2. A TSC peak was observed at 250°C. This peak relates to the crystal defects of PbO_x at the bottom interface. [6] From Fig. 2, the intensity of the TSC peaks, in other words, the defects increased with increasing TiO_2 thickness. In comparison with Fig. 1, although the defects increased with the buffer layer, fatigue was improved.

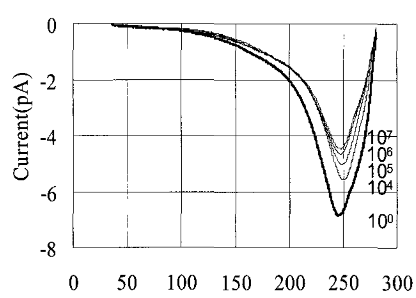

Fig. 3 The dependence of thermally stimulated current on fatigue.

Thus, the influence of fatigue treatment on TSC properties of the capacitor with a thick buffer layer of 5 nm was also evaluated. The specimen was applied continuous pulse for fatigue, and TSC measurements were carried out. The measurement cycles were repeated, and variations in the defects by fatigue degradation were investigated, as shown in Fig. 3. In past literature of TSC measurements on stoichiometric PZT films, the intensity of the TSC peak, that is, the density of defects, increased with fatigue degradation. [3-5] In contrast, in the present study, defects decreased with fatigue for the specimen with the thick buffer, as shown in Fig.3.

These interesting results, shown in Fig.2 and 3, revealed that a decrease in the defects was observed for the degraded sample in the Pb-rich PZT film. From these results, in the case of the Pb-rich specimen, the existence of a very thin layer of excess PbO_x at the surface of the PZT layer is expected. Such a thin layer contains a high density of defects, and appears to act as the source of the lead component. While elimination of the lead and oxygen content from the PZT grains is caused by degradation, an excess lead layer at the surface compensates for it, and the defects in the layer decrease.

4. CONCLUSIONS

The evaluation of fatigue performance and crystal defects in PZT film capacitors with excess lead composition was carried out. In contradiction to the usual results, a decrease in the defect density with degradation was found. By assuming that a thin excess-PbO_x layer exists at the interface, this phenomenon can be fully explained. Confirmation and investigation of such a layer will be part of future work.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. Yasuo Okajima for SIMS measurements, and Mr. Claus Schroeter for providing the Linux-GPIB package. We are also grateful to Dr. Yoichiro Masuda for his encouragement during this study. This work was partly supported by the Kinki Invention Center and Research Foundation for Materials Science.

REFERENCES

[1] T. Nakamura, Y. Nakao, A. Kamisawa and H. Takasu, Jpn. J. Appl. Phys., 33, 5207-5210 (1994).

[2] T. Nishida, I. Kawakami, M. Norimoto and T.

Shiosaki, Ceramics International, 30, 1089-1093 (2004).
[3] Z. Wu and M. Sayer, Proc. ISAF (IEEE, New York) 244-247 (1994).
[4] H. Okino, Y. Toyoda, M. Shimizu, T. Horiuchi, T. Shiosaki and K. Matsushige, Jpn. J. Appl. Phys., 37, 5137-5140 (1994) .
[5] T. Nishida, M. Matsuoka, S. Okamura and T. Shiosaki, Jpn. J. Appl. Phys., 42, 5947-5951 (2003).
[6] T. Nishida, Y. Nakayama, T. Takeda, K. Uchiyama and T. Shiosaki, Trans. of Mat. Res. Soc. Japan, 31, 169-171 (2006) .
[7] T. Nishida, T. Takeda, K. Uchiyama and T. Shiosaki, Ferroelectrics, in press.

(Received December 9, 2006;Accepted January 12, 2007)