Retention properties with high-temperature resistance in (Bi,Pr)(Fe,Mn)O3 thin film capacitor

Retention properties with high-temperature resistance in (Bi, Pr)(Fe, Mn)O_3 thin film capacitor

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$(Bi_{0.9}Pr_{0.1})(Fe_{0.97}Mn_{0.03})O_3$ (BPFM) thin film was deposited on Pt-coated Si(100) substrate by chemical solution deposition. Remnant polarization and coercive field in the BPFM film capacitor were 113 μC/cm^2 and 630 kV/cm at the maximum electric field of 1000 kV/cm, respectively. Switching charge measured by a rectangular pulse measurement was 118 μC/cm^2. Almost no polarization losses of BPFM film capacitor was observed even after retention time of 10^4 s at RT. Furthermore, the polarization loss at 450 °C was only 3.7 % even after 10^4 s. These results indicate that BPFM film capacitor is suitable for non-volatile memory applications at high temperature.

Ferroelectric random access memory (FeRAM) is one of the promising candidates for non-volatile memories because of its high speed, low power consumption and compatibility to current electrically erasable programmable read only memory (EEPROM) devices. Recently, FeRAM attempts to go to the medical field using the radiation hardness of the ferroelectric domain. The stability of remnant polarization over a wide temperature range is considered as one of the important factors for more expanded ferroelectric memory application areas. For instance, in a special memory application area, there are demands to storage archives for longer period over 100 years withstanding the temperature fluctuation. Besides, retention at higher temperatures for ID tag is required in heat treatment line at the factory of various products. Thus, superior data retention performance at higher temperature is required for more expanded application areas of FeRAM devices.

Generally, the amount of polarization charge decreases when the ferroelectric capacitor is kept for a long time after the polarization is completed. When the amount of polarization charge eventually decreases below a threshold level of FeRAM device, the memory of the bit is lost. Hence, polarization loss is considered to be an important issue for the expanded FeRAM application area over wide range of temperature.

As a ferroelectric material for FeRAM applications, $Pb(Zr,Ti)O_3$ (PZT) is well known because of its high remnant polarization, low coercive field and low processing temperature [1-3]. However, it is known that remnant polarization in PZT film capacitors shows serious polarization loss at high temperature [4-6]. Many researchers have focused on revealing the mechanism of polarization loss [4, 6-12]. It was explained that the internal field, which is formed by redistribution of defects charges near the interface between electrodes and ferroelectric layer, initiates the polarization back-switching during the retention time. Then, the amount of polarization charge decreased due to the polarization back-switching generated by the internal fields [4, 6, 13]. Furthermore, PZT thin films showed serious polarization losses at high temperature due to their weak heat-resistance [4-6]. Note that this polarization loss was also observed in other ferroelectric materials with high-T_c such as $SrBi_2Ta_2O_9$ (SBT) [9, 14].

Pb-free ferroelectric $BiFeO_3$ (BFO) has attracted much attention due to its high Curie temperature (830 °C) [15-19]. In addition, recent reports of a large spontaneous polarization (over 100 μC/cm^2), which enable to integrate

FeRAM, in thin films, bulk ceramic and single crystals of BFO have led to an interest in the BFO properties. A large coercive field is also a feature of the BFO films [19]. It was reported by Vopsaroiu *et al.* that the coercive field is well correlated to the barrier height of polarization loss on the basis of thermal dynamics [20]. Thus, BFO thin films may achieve the superior retention properties compared with other ferroelectric materials such as PZT and SBT thin films. In this paper, we investigate the retention properties at high-temperature in Pr, Mn co-doped BFO (BPFM) film capacitor. Here, the BPFM is a modified material for improving insulating properties of BFO [19, 21].

BPFM thin film was deposited on Pt-coated Si (100) substrates by chemical solution deposition (CSD) method [21]. 150 nm-thick Pt bottom electrodes showed a preferential (111)-orientation. BPFM solution with the composition of $(B_{0.9}Pr_{0.1})(Fe_{0.97}Mn_{0.03})O_3$ was spin-coated at 3000 rpm for 30 s on the substrate, followed by a drying process at 240 °C for 10 min and a pyrolysis process at 350 °C for 10 min in atmosphere. These processes were repeated 10 times until the film thickness reached approximately 200 nm. Resultant films were then heat-treated for crystallization at 550 °C for 20 min in N_2 gas flow. The film thickness was measured by a spectroscopic ellipsometer (J. A. Woollam M-2000UI). For comparison, PZT thin film with a composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$ was fabricated by pulsed laser deposition (PLD) method. The PZT film of 200 nm thickness was deposited on $SrRuO_3$ (SRO)-coated $SrTiO_3$ (100) substrate. Pt top electrodes of 50 nm with an area of 2.5×10^{-5} cm^2 in square were deposited on the BPFM and PZT thin films by PLD method using a shadow mask, resulting in the metal-insulator-metal capacitor structure. Ferroelectric properties were measured by a ferroelectric test system (TOYO FCE-3).

The XRD measurement for BPFM film shows randomly-oriented polycrystalline perovskite phases without any impurity phases such as Bi_2O_3 and $Bi_2Fe_4O_9$ (Figure S1, supporting information). On the other hand, the PZT and SRO thin films shows (100)-orientation on the STO substrate without any pyrochlore phases (Figure S2, supporting information).

Figure 1 shows *P-E* curves for BPFM and PZT film capacitors measured with measurement frequency of 5 kHz at RT. As shown in the figure, well-saturated hysteresis loops are observed in the both films. The remnant polarization ($2P_r$) and the coercive field ($2E_c$) in the BPFM thin film was approximately 113 μC/cm^2 and 630 kV/cm at the maximum electric field of 1000 kV/cm, respectively. These values were close to those of BPFM thin films deposited on Pt-coated $SrTiO_3$ substrate [19]. On the other hand, $2P_r$ and $2E_c$ in the PZT film were approximately 123 μC/cm^2 and 160 kV/cm at the maximum electric field of 200 kV/cm, respectively. Measurement of retention properties was performed using the ferroelectric test system with conventional rectangular pulses [4, 6]. Pulse train for retention measurement is shown in Fig.2. After application of the write pulse with pulse width t_0 to the capacitor at RT, the capacitor was kept at retention temperatures from RT to 450 °C in N_2 gas flow. Then, retention times t_1 were varied from 10^{-3} to 10^4 s. As a read pulses, switching and non-switching pulses with pulse width t_0 were applied at RT, and the switching charges Q_{sw} were calculated by the difference of the obtained switching polarization and non-switching polarization. The pulse width t_0 and pulse interval t_2 were 5×10^{-5} and 10×10^{-5} s, respectively. Pulse amplitudes employed in the BPFM and PZT film capacitors were 1000 and 200 kV/cm, respectively, depending on the saturation properties of the polarization. Q_{sw} in BPFM and PZT films measured with a retention time t_1 of 10^{-3} s were approximately 118 and 98 μC/cm^2 at RT. The reduced Q_{sw} in PZT film compared with $2P_r$ shown in Fig.1 is attributed to a back-switching phenomena during the measurement. In addition, maximum applied electric field dependences of $2P_r$ and Q_{sw} in BPFM film capacitor shows almost same value (Figure S3, supporting information).

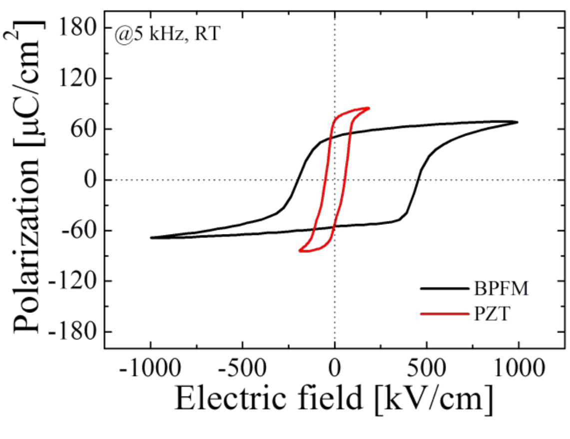

Figure 1 *P-E* curves of BPFM and PZT film capacitors with measurement frequency of 5 kHz at RT.

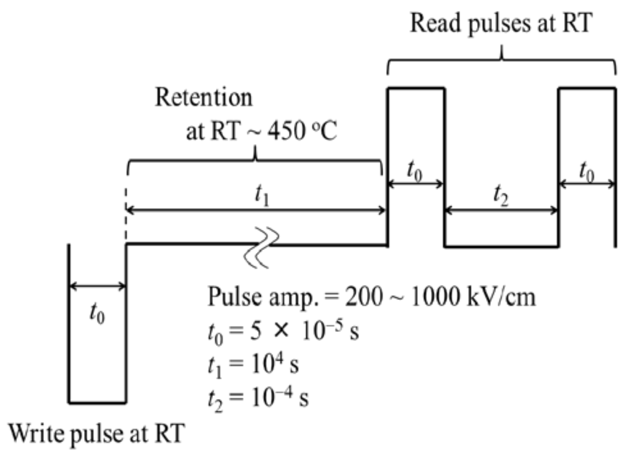

Figure 2 Pulse train employed for retention measurement with the downward polarization (-P_r state). Write pulse and read pulses were applied at RT and the retention temperature was varied from RT to 450 ºC. For the upward polarization (+P_r state), the polarities of three pulses were reversed.

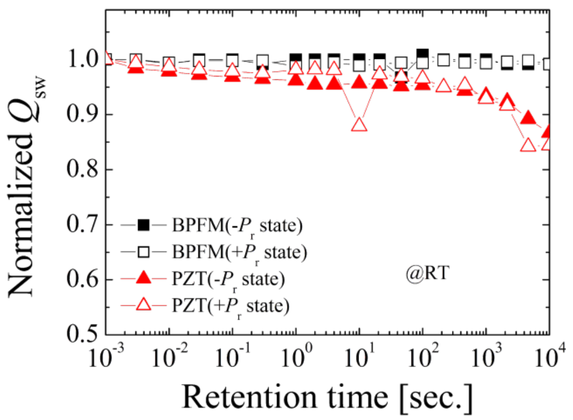

Figure 3 Retention properties of normalized Q_{sw} in BPFM and PZT film capacitors as a function of retention time t_1. Normalized Q_{sw} values in BPFM and PZT film capacitors were approximately 118 and 98 μC/cm^2 at RT, respectively. The retention temperature was RT. The upward and downward polarizations were denoted by +P_r and -P_r states, respectively.

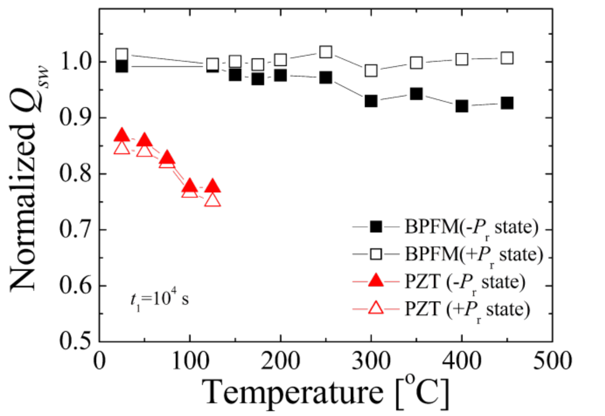

Figure 4 Retention temperature dependences of normalized Q_{sw} at t_1=10^4 second in BPFM and PZT film capacitors. The upward and downward polarizations were denoted by +P_r and –P_r states, respectively.

Figure 3 shows the normalized Q_{sw} in the BPFM and PZT film capacitors during the retention at RT as a function of the retention time t_1. Here, the value of Q_{sw} was normalized by that of Q_{sw} measured with a retention time t_1 of 10^{-3} s. As shown in the figure, the BPFM film capacitor showed good retention properties compared with that of PZT film, irrespective of the polarization direction (+P_r or -P_r state). The average polarization losses of BPFM and PZT film capacitors were about 0.9 and 14.5 % with retention time of 10^4 s at RT, respectively. In addition, results similar to our PZT film capacitor were reported in Pt/PZT/Pt structure by other group [4, 12].

In the case of PZT and SBT thin films, it is known that retention properties show rapid polarization losses even at 10^0 s due to their depolarization field [4, 6]. Furthermore, the long-time retention loss is attributed to the effect of redistribution of defect charges [4, 6, 10]. On the other hand, the retention properties of the BPFM film capacitor showed a constant retained polarization up to 10^4 s. Note that the coercive field of BPFM thin film was large in comparison with that of the SBT and PZT thin films as shown in Fig.1. Thus, it is indicated that the large coercive field in the BPFM suppresses the polarization losses. In other words, the polarization of BPFM is strong enough to withstand the depolarization phenomena at RT.

Figure 4 shows the normalized Q_{sw} as a function of retention temperature for BPFM and PZT film capacitors with retention time of t_1=10^4 s. As shown in Fig.4, Q_{sw} of –P_r state in BPFM film capacitor is gradually decreased with increasing the retention temperature while that of +P_r state is not decreased. Difference in the polarization loss between +P_r and –P_r was increased with increasing retention temperature. Average polarization loss of BPFM film capacitor measured with retention time of 10^4 s and at 450 °C was 3.7 % at most. On the other hand, as shown in the figure, Q_{sw} of PZT film capacitor was drastically decreased with increasing the retention temperature due to their weak heat-resistance [5]. Besides, above 125 °C, it was impossible to evaluate reliable Q_{sw} due to unstable retention behaviour. The average polarization loss in the PZT film measured at retention time of 10^4 s and at 125 °C was as large as 23.7 %. This polarization loss is almost close to the values reported previously [2, 4, 12], it is mainly caused by thermal depolarization effect due to the small coercive field or weak heat-resistance of PZT [4, 6]. The present BPFM film capacitor is found to have excellent retention properties at high temperature compared with PZT. Thus, it is indicated that the large coercive field in the BPFM also suppresses the polarization losses at high temperature.

About asymmetric switching behaviours, it has been often observed in many ferroelectric capacitors due to the presence of internal field [11]. Even when the same material is used for the top and bottom electrodes, effective work functions of the two electrodes might be different due to the different thermal conditions during the fabrication process. In fact, internal field $E_i = (|E_c^-| - |E_c^+|)/2$, which often causes imprint phenomenon, was observed in *P*-*E* curves of the present BPFM thin film as shown in Fig.1. E_i of the BPFM film was -120 kV/cm. During the fabrication process of ferroelectric thin film, it is known that atomic diffusion to bottom electrode through Pt grain boundary often occurs. To solve this problem, oxide electrodes were often used for suppression of interface defect [2, 12]. In current days, in order to obtain symmetric behaviours, we deposited SRO thin film with high work function and high electric conductivity film on Pt bottom electrode [21], resulting in Pt/BPFM/SRO/Pt structure. As a result, the average polarization loss measured with retention time of 10^4 s and at 400 °C was 6.4 % (Figure S4, supporting information). Besides, symmetric switching behaviour was observed in Pt/BPFM/SRO/Pt structure.

In summary, we have investigated the retention properties of BPFM film capacitor. The polarization loss of

BPFM capacitor was only 0.9 % at RT while that of PZT capacitor was as large as 14.5 % at RT. The average polarization loss of BPFM capacitor measured with retention time of 10^4 s and at 450 °C was 3.7 % at most. On the other hand, the average polarization loss in PZT capacitor measured at retention time of 10^4 s and at 125 °C was as large as 23.7 %. These results would lead to upgrading and expanding of data retention performance in FeRAM devices at high temperature operation, resulting in the long-term stability of remnant polarization over a wide temperature range.

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