Evaluation of ferroelectric hysteresis loops of leaky multiferroic $BiFeO_3$ films using a system with a high driving frequency of 100 kHz system

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A measurement system with a high driving frequency of 100 kHz is effective for measuring the ferroelectricity of leaky ferroelectric materials such as multiferroic $BiFeO_3$ films. A high driving frequency reduces the measurement time, leading to a drastic reduction in the influence of the leakage current density on ferroelectric hysteresis loops. Phase-delay compensation is essential in a system with a driving frequency of 100 kHz; in this study a standard capacitor was used for phase-delay compensation. The value of remanent polarization of a $BiFeO_3$ film measured by the 100-kHz system was confirmed by a positive, up, negative and down measurement.

Key-words : Multiferroic $BiFeO_3$, Ferroelectricity, High frequency system, Leakage current, 100 kHz

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1. Introduction

Multiferroic $BiFeO_3$ is hypothesized to possess high remanent polarization because its remanent polarization has theoretically been calculated to be $\sim$100 $\mu C/cm^2$ (Ref. 1), and its has a high ferroelectric Curie temperature (T_C) of $\sim$1100 K.[2),3)] A high remanent polarization and high piezoresponse values were recently reported for $BiFeO_3$ films[4)–7)] and $BiFeO_3$ in bulk[8)] form. When focusing magneto-electric (ME) effect, the ferroelectric domain of 109 and 71° measured by piezo force microscopy (PFM) clearly switched together with antiferromagnetic domain of $BiFeO_3$ measured by X-ray photoemission electron microscopy (XPEM).[9)] This is because the polarization direction and antiferromagnetic plane has rectangular relationships, and the rectangular configuration is compensated by weak ferromagnetism of Dzyaloshinskii-Moriya (DM) interaction.[10),11)] In this system, theoretically, the ME effect can operate up to Néel temperature ($T_N = 653$ K). These findings have provided an impetus to studies on multiferroic property of the $BiFeO_3$ and have opened a new avenue for the development of new functional devices using host $BiFeO_3$ films. Polycrystalline $BiFeO_3$ films, however, have a high leakage current,[12)] therefore, the ferroelectric hysteresis loops show an unsaturated expanded shape at room temperature. The accurate evaluation of ferroelectricity without influence of leakage current is important subject to studies on multiferroic $BiFeO_3$ films. The influence of leakage current density can be reduced either by increasing the measurement frequency[13),14)] or by using positive-up-negative-down (PUND) measurements.[15)] In the present study, we have developed a measurement system that uses a high driving frequency of 100 kHz. We have evaluated the remanent polarization and the coercive field of the leaky polycrystalline $BiFeO_3$ films at room temperature using this system. We have also investigated the influence of phase-delay of polarization on the electric field, which strongly affects the shape of ferroelectric hysteresis loops.

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2. Experimental procedure

$BiFeO_3$ films were fabricated on $Pt/Ti/SiO_2/Si(100)$ substrates by chemical solution deposition (CSD) followed by post-deposition annealing at 723 K for 10 min in air. After annealing, a top Pt electrode was deposited by electron beam evaporation. The thickness of the $BiFeO_3$ film was approximately 180 nm. The formation of the single phase of polycrystalline $BiFeO_3$ film was identified by a conventional $\theta/2\theta$ X-ray diffraction pattern and a transmission electron microscopy (TEM) observation. The surface morphology of the fabricated $BiFeO_3$ film was observed by atomic force microscopy (AFM). The details of the film structural analyses are discussed elsewhere.[16)] The ferroelectric hysteresis loops of the leaky polycrystalline $BiFeO_3$ film at room temperature were obtained by using the high driving frequency of 100 kHz system (FCE-1A-type ferroelectric test system, TOYO Corporation). The leakage current properties at room temperature were measured by using a pA meter/voltage source (HP 4140B, Hewlett Packard).

3. Results and discussion

Figure 1 shows the leakage current density of the $BiFeO_3$ film (a) and the ferroelectric hysteresis (P–E) loop obtained by using a triangular pulse of 1 kHz (b). The leakage current density of the order of 1×10^{-5} A/cm^2 at 0.15 MV/cm at room temperature. As a low frequency of 1 kHz, the ferroelectric hysteresis loop of the polycrystalline $BiFeO_3$ film showed an expanded shape, which is attributable to the high leakage current density. This implies that the remanent polarization and coercive field of leaky ferroelectric materials such as $BiFeO_3$ films are over-estimated when a using low driving frequency of 1 kHz is used.

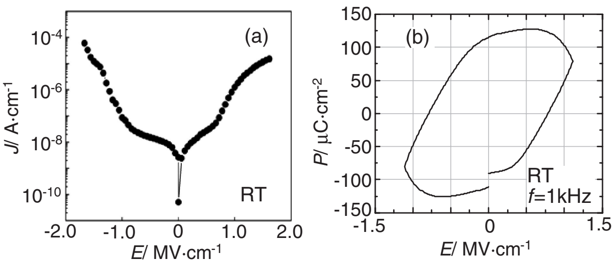

Fig. 1. The leakage current density of the $BiFeO_3$ film (a) and the ferroelectric hysteresis (*P–E*) loop obtained by using a triangular pulse of 1 kHz (b).

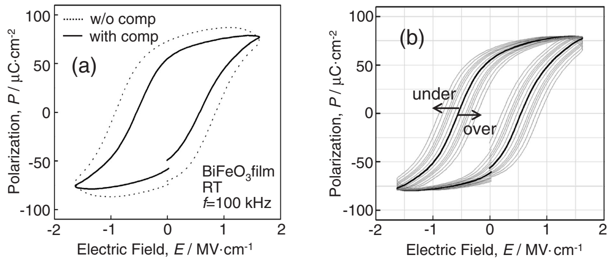

Fig. 2. The *P–E* loops measured using the high driving frequency of 100 kHz measurement systems. The figure indicates the *P–E* loops obtained 'with' and 'without' compensation of phase-delay.

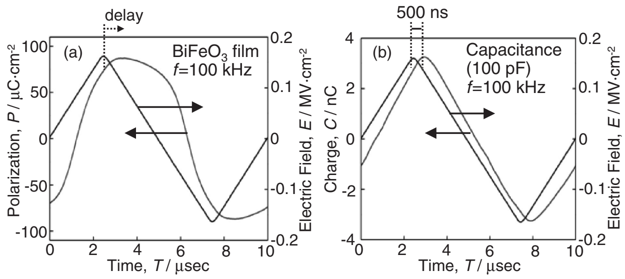

Fig. 3. Time dependence of the electric field and polarization for $BiFeO_3$ film (a), and capacitor of 100 pF (b).

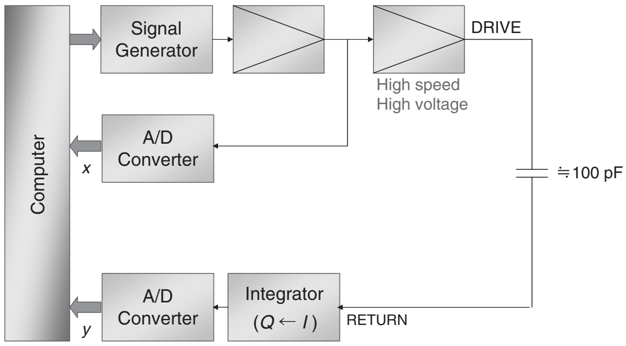

Fig. 4. Schematic illustration of high frequency measurement system.

Figure 2(a) shows the *P–E* loops measured using the high driving frequency of 100 kHz measurement systems. The figure indicates the *P–E* loops obtained 'with' and 'without' compensation of phase-delay. Without phase-delay compensation, the *P–E* loop shows an expanded shape. We checked for changes in the electric field and polarization against time [**Fig. 3**(a)]. Changes in polarization appear to be delayed with respect to the changes in the applied electric field; this can be deduced from the time difference between the occurrences of maximum polarization and maximum electric field. Therefore, this phase-delay needs to be compensated for. However, it was difficult to determine the phase-delay from Fig. 3(a) because of the difficulty in determining the position of maximum polarization. Hence, a standard 100-pF capacitor was used to evaluate the phase delay accurately [Fig. 3(b)], and the phase-delay was estimated to be approximately 500 nsec.

Figure 4 shows a schematic illustration of the high-frequency measurement system. In order to clarify the origin of the phase delay, we estimated the time constant of the 100-kHz system. The time constant of the circuit was estimated to be less than 10 ns, revealing that the phase-delay was mainly caused by the high-voltage amplifier and not by the reference capacitor. As a result, it was possible to compensate for the phase-delay by subtracting a constant time (500 ns) from the raw data. The *P–E* loop of the $BiFeO_3$ film after phase-delay compensation of 500 ns is indicated by the solid line in Fig. 2(a). We observed a ferroelectric hysteresis loop of high squareness with a twofold remanent polarization ($2P_r$) of 115 $\mu C/cm^2$ and a coercive field of 0.55 MV/cm. Incorrect estimation of the phase-delay led to a drastic change in the shape of the ferroelectric hysteresis loops. [Fig. 2(b)]; furthermore, it also led to an incorrect estimation of remanent polarizations and the coercive fields. Therefore, accurate estimation of phase delay is crucial.

In order to confirm the accuracy of the high-frequency system, we measured the remanent polarization of the $BiFeO_3$ film by positive, up, negative, down (PUND) measurements. The $2P_r$ was calculated to be 118 $\mu C/cm^2$; this value is almost equal to that estimated from the *P–E* loop with a phase-delay compensation of 500 ns. This result indicates that the phase compensation of 500 ns using a standard capacitor for the high-frequency system is correct. In addition, it should be noted that the phase delay depends on the arrangement of the probing and circuit systems; therefore, the phase-delay should be estimated for each high-frequency system.

As compared to low-frequency measurement, high-frequency measurement yields a ferroelectric hysteresis loop with high squareness even at room temperature; this is because of the drastic reduction in the influence of the leakage current density on the ferroelectric hysteresis loops. Furthermore, by using 100-kHz system, we were able to apply a high electric field to the $BiFeO_3$ film. This was possible because of the reduction in measurement time, which led to a reduction in the Joule heating damage. All the above-mentioned factors suggest that the 100-kHz system can potentially be an effective tool for finding new ferroelectric materials and/or for measuring the ferroelectricity of leaky ferroelectric materials.

4. Summary

A measurement system with a high driving frequency of 100 kHz was used to investigate the ferroelectric properties of leaky polycrystalline $BiFeO_3$ films. Using this system, it was possible to obtain ferroelectric hysteresis loops for leaky polycrystalline $BiFeO_3$ films even at room temperature because of the reduction in the influence of the leakage current. The phase delay due to a high-voltage amplifier was estimated to be 500 ns using a 100-pF capacitor. Phase compensation had a significant influence on the remanent polarization as well as the coercive field and polarization maximum. Therefore, accurate phase compensation is very important for estimating ferroelectricity using a high-frequency system. The accuracy of phase-delay compensation in the high-frequency system was confirmed by comparing the remanent polarization of a $BiFeO_3$ film measured by the system with the remanent polarization obtained by PUND measurements.

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