Asymmetry in fatigue and recovery in ferroelectric Pb(Zr,Ti)O$_3$ thin-film capacitors

B. G. Chae, C. H. Park†, Y. S. Yang, and M. S. Jang

Research Center for Dielectric and Advanced Matter Physics, Pusan National University, Pusan 609-735, Korea

We investigate the fatigue and refreshment by dc-electrical field of the electrical properties of Pt/Pb(Ti,Zr)O$_3$/Pt ferroelectric capacitors. We find an asymmetry in the refreshment, that is, the fatigued state can be refreshed by application of negative high dc-voltage to the top electrode, but no refreshment is measured by positive dc-voltage application. We also find that the fatigue can be prevented by driving the capacitor asymmetrically.

Perovskite ferroelectrics are widely investigated since the perovskite compounds can be applied in developing low energy-consuming and high-speed semiconductor memories. A problem to be resolved for its application is fatigue. It has been recently extensively investigated. The fatigue can be prevented by the use of metal-oxide electrodes or layered perovskite ferroelectrics; however, the switchable polarization in these is small and the control of the electrical properties such as leakage current is not easy. Many kinds of explanations for the fatigue have been suggested such as large-scale defect migration, domain pinning by defects or grain boundary, and the screening at electrode interface; however the fatigue mechanism is not yet clearly understood.

An important property of the phenomena is that the fatigue polarization is refreshed by applying dc-electrical field, heat treatment, or UV-light illumination in finding the microscopic origin of the fatigue phenomena, the refreshment should be explained. However, the behavior of the refreshment is not frequently investigated. In this letter, we investigate the refreshment behaviors during applying dc electrical fields in the fatigued Pt/PZT/Pt capacitor.

The Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ films were grown on Pt/Ti/SiO$_2$/Si substrates by the sol-gel method. The ferroelectric films were deposited by a multilayer spin-coating technique and crystallized in air at 650°C for 30 min. The details were described in our recent articles. The perovskite ferroelectric films are measured to be oriented mainly along the [111] direction from X-ray diffraction patterns, and to be polycrystalline by scanning electron microscopy. The thickness of the PZT films is measured to be 300 nm. We fabricate the Pt top electrode with the area of 100×100 µm$^2$ by sputtering through the shadow mask at a temperature of around 500°C.

The polarizations of the PZT capacitor were repetitively switched by the square electrical pulses generated by a function generator connected to the RT66A ferroelectric tester. The measurement of the polarization was carried out by use of triangular shape of electrical pulse, whose peak voltage is ± 5 V which corresponds to the electrical field intensity of ± 167 kV/cm. For the refresh experiments, the bottom electrode of the thin film capacitor is grounded and the various voltages from 0 to ± 15 V were applied to the top electrode of the fatigued films.

Figures 1(a) and 1(b) describe the fatigue in the switchable polarization (P*-P$^*$) of a Pt/PZT/Pt capacitor. As shown in Fig. 1(a), as the peak voltage of the switching pulses increases from 3 V to 7 V, the switchable polarization is measured to fatigue faster. The fatigue starts around after 10$^4$ cyclings of switching, nearly independently to the peak voltages ranging from 3 V to 7 V. We also examined the fatigue as the variation of the frequency of the switching pulses. As described in Fig. 1(b), the development of the fatigue is dependent mainly on the number of the polarization switching. These indicate that the fatigue in the present Pt/PZT/Pt capacitor progresses mostly during the switching.

We measured the change of the remanent polarization during the application of the dc-field to the fatigued ferroelectric capacitors, as described in Fig. 2. When we applied the dc voltage of -10 V to the top electrode of the fatigued Pt/PZT/Pt capacitors, the remanent polarization is measured to be recovered very fast, up to 70 % of the initial value just after 1 s and nearly completely recovered after 100 s. By the application of the weaker electrical field, it is less rapidly recovered. After the application of the dc field for 100 s, the measured remanent polarization versus the applied voltage are shown in Fig. 3. We find that only if the dc voltage is larger than the coercive voltage, the polarization can be recovered eventually nearly to the initial value.

A surprising result is that the fatigue polarization is little refreshed by the application of positive dc voltage. In Fig. 2, the change of the polarization is described by the application of ±10 V. Only application of negative dc-voltage makes the polarization refreshed. The asymmetricity of the recovery should be related to the properties of the thin-film Pt/PZT/Pt capacitor, which will be discussed later.

We examined the re-fatigue of the recovered state. The recovered state is found to be still resistive to fatigue, however, the switchable polarization is a little more rapidly fatigued, ten times faster than the initial state, indicating that the recovered state is somewhat different from the initial as-grown state. But as the fatigue and refreshments are repeated twice and further, the behaviors of the further refatigues are found to be similar to
that of the first refatigue. We examined the recovery by the heat-treatment above Curie temperature. The re-fatigue behavior is similar to the above case. This indicates that there should be some redistribution of ions and defects during the fatigue that are not completely recovered by the dc field for a short time.

The asymmetry of the recovery indicates that there should be a similar asymmetric behavior of the fatigue. We examined the latter asymmetricity by applying asymmetrical sequence of electrical pulses to the capacitors in switching their polarizations, as described in the inset of Fig. 4, where $V_p^+$ is set to be different from $V_p^-$. The fatigue behaviors are described in Fig. 4, and Fig. 5 describes the measured switchable polarization after $4 \times 10^9$ cycles of switchings versus the asymmetry $A$. Here, we define the asymmetricity $A$ of the asymmetric switching pulses by $\Delta V/(V_p^+ + V_p^-)$ where $\Delta V = V_p^+ - V_p^-$. We fix the sum of $V_p^+$ and $V_p^-$ to be 10 V and the values of $V_p^+$ and $V_p^-$ were set to be at least greater than 2 V, which is larger than the coercive voltage of 1.5 V, so that the polarization can be switched. The negative $A$ means that $V_p^+$ is smaller than $V_p^-$. It is remarkable that in the case that $A$ is less than -0.3 the switchable polarization is found to be little fatigued, even after $4 \times 10^9$ cycles of polarization switching. In the inset of Fig. 5, the measured hysteresis loops of the polarizations before and after the $4 \times 10^9$ switching cycles are compared in the cases of $A = -0.4$. The hysteresis loop is only slightly right-shifted with an increase of the coercive field from the initial 52 kV/cm to 70 kV/cm. In the case of the positive asymmetricity $A$, the polarization fatigues more rapidly compared to the normal case of zero $A$.

We would note that recently a similar asymmetric behavior is reported in the direct observation of the pinned domain using atomic force microscopy (AFM) indicated that the pinned domain associated with the fatigue has a preferential orientation of polarization.

We suggest that these asymmetric behaviors in the fatigue and refresh are related to the asymmetric distribution of fatigue centers in the PZT thin film. Many experimental evidences indicate that the defects such as oxygen vacancies are a source of the fatigue phenomenon. It is well known that the concentration of defects such as oxygen deficiency and lead-vacancies in the ferroelectric films are more significant around the bottom electrode than around the top electrode, therefore, it is suggested that fatigue centers should be developed dominantly around the bottom electrode.

Electron paramagnetic resonance data indicated that the charge trappings at defects are accompanied with fatigue. Theoretical calculations indicated that oxygen vacancy induce tail-to-tail polarization around itself, and that the hole trap or electron ionization at oxygen vacancies can enhance the vacancy-induced polarization and indicated that their cooperative forces through their accumulation during the repetitive switching of the polarization can lead to strong domain pinning, becoming the fatigue center.

Since the oxygen vacancies are accumulated more around the bottom electrodes, the polarization direction of the pinned domain from these defects should preferably be from the bottom toward the top electrode.

In the refreshment by the application of the negative dc-voltage to top electrode, the positive carriers captured at the O vacancies around the interface of the bottom electrodes can migrate toward the top electrode, leading to the refreshment. Only if the polarization is inverted by a dc field larger than the coercive field, the region of the antiphase polarizations from the oxygen vacancies around interfaces, which leads to the capture of hole at the vacancies, is eliminated and the hole trapping at the defects should be reduced. However, by the positive voltage application, the migration of the captured holes can be prevented by the Schottky barrier between ferroelectrics and the bottom electrode. The PZT films are usually slightly p type doped due to the Pb-vacancies, which makes a Schottky barrier preventing hole diffusion to the bottom-electrode. Therefore only the negative voltage application can refresh the fatigue. For a similar reason, the negative $A$ asymmetric switching pulses can prevent the capture of holes at oxygen vacancies around the bottom electrode, which leads to the present fatigue-resistive behavior. On the other hand, the suggested accumulation of defects during fatigue can give an explanation to the re-fatigue behavior after the refreshment that is mentioned above. The accumulation of defects may not be eliminated by the application of short-time dc-electrical pulses, therefore the refatigue after the refreshment can proceed more rapidly, since the refatigue can be developed just by the capture of carriers at these accumulated defects.

It is recently reported that the ferroelectric capacitor by the use of n-type semiconductor at the top electrodes is more easily fatigued suggesting that electron captures at defects or interfaces are more effective in fatigue. We would suggest that the experimental data should be explained in the respect of the defect formations during the thin-film process rather than charge trapping, since the ferroelectrics/doped-semiconductor does not make the conventional p-n junction and the current density of injected carrier is not high, compared to the available leakage current.

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corresponding author, e-mail: chpark@phys.physics.pusan.ac.kr.

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FIG. 2. The change of the remanent polarization during the refreshment by the application of the dc electric field to the fatigued films. (solid circles for the application of +10 V to the top electrode and open circles for the application of -10 V). The inset describes the changes of the hysteresis loops before and after fatigue and after the refreshments.

FIG. 3. The measured remanent polarizations after the refreshments for 100 s vs the magnitude of the applied dc voltage. The values are divided by the initial value of the polarization before fatigue.

FIG. 4. Fatigue behaviors by the use of the asymmetric switching driving pulses which are described in the inset and whose frequency is 10 kHz. The asymmetry is described by $A = (V^p - V^-)/(V^p + V^-)$. The values of the switchable polarization $P_r$.

FIG. 5. The switchable polarizations after $4 \times 10^9$ cycles switching vs the asymmetry of the switching pulses. The inset shows the hysteresis loops before and after the switchings when the asymmetry $A$ is -0.4.